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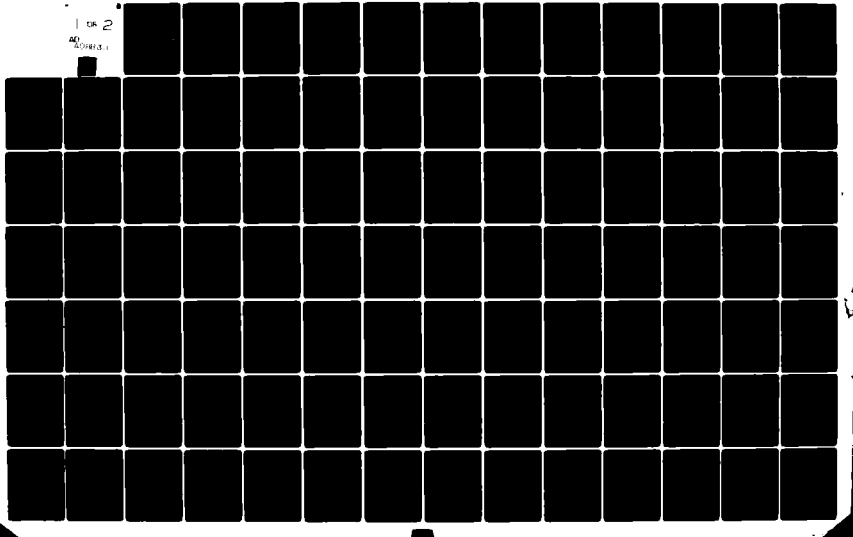

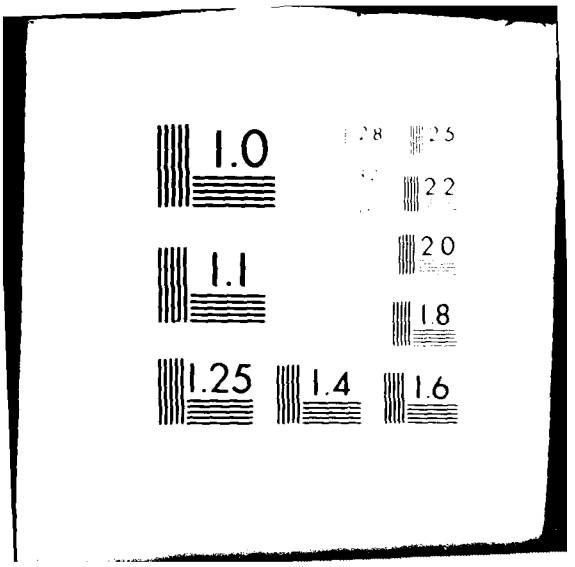
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ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY OF VANADIUM(IV) COMPLEXES AND RELATED SPECIES.

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The report details the successful application of e.p.r. spectroscopy to the study of vanadium(IV) oxohalide complexes. In particular, it has proven an invaluable structural tool for relating the structure of a complex in an amorphous or polycrystalline sample to that of the same complex in solution. Moreover, solution studies by e.p.r. have revealed previously unsuspected dissociation and displacement phenomena for complexes of the type $[VOX_2L_n]$ (X=Cl or Br, L=mono- or bi-dentate ligand), which means that many literature reports need to be reexamined. A comprehensive literature survey is included.

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CONTENTS

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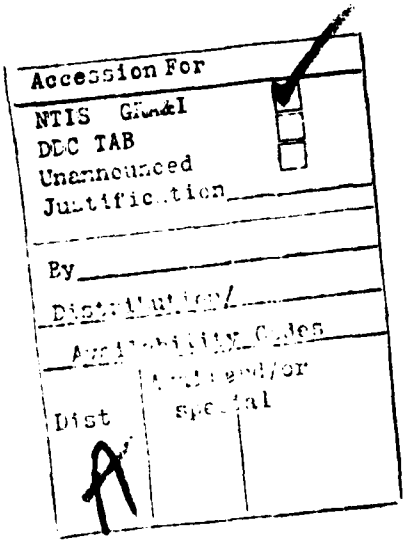


CONTENTS

LIGAND ABBREVIATIONS

acac	-	pentane-2,4-dione
acry	-	acrylonitrile
2-anis	-	2-methoxyaniline
3-anis	-	3-methoxyaniline
4-anis	-	4-methoxyaniline
2,2'-bipy	-	2,2'-bipyridine
4,4'-bipy	-	4,4'-bipyridine
Bu	-	butyl
clm	-	6-amino-hexanoic acid (ϵ-caprolactam)
cp	-	η^5-cyclopentadienyl
cy	-	cyclohexyl
diox	-	1,4-dioxan
dme	-	1,2-dimethoxyethane
dmp	-	2,6-dimethylpyrazine
2,2-dmp	-	2,2-dimethoxypropane
dmpo	-	2,6-dimethylpyridine-1-oxide
3,5-dmpy	-	3,5-dimethylpyridine (3,5-lutidine)
dmso	-	dimethylsulphoxide
dppe	-	1,2-bis(diphenylphosphinoethane)
$dppeO_2$	-	1,2-bis(diphenylphosphino)ethane dioxide
DPPH	-	1,1-diphenyl-2-picrylhydrazyl
dppm	-	bis(diphenylphosphino)methane
dpso	-	diphenylsulphoxide
Et	-	ethyl
hmpa	-	hexamethylphosphoramide
isoquin	-	isoquinoline
isoquinH	-	isoquinolinium
Me	-	methyl
Ph	-	phenyl
phen	-	1,10-phenanthroline
3-pic	-	3-picoline(β-picoline/3-methylpyridine)
4-pic	-	4-picoline(α-picoline/4-methylpyridine)
Pr	-	propyl
py	-	pyridine
pyH	-	pyridinium
qn	-	quinuclidine
quin	-	quinoline
quinH	-	quinolinium

o-tas	-	bis(*o*-dimethylarsinophenyl)methylarsine
v-tas	-	tris-1,1,1-(dimethylarsinomethyl)ethane
tclm	-	ε -thiocaprolactam
thf	-	tetrahydrofuran
thioph	-	thiophen
thiox	-	1,4-thioxan
thp	-	tetrahydropyran
tmu	-	tetramethylurea
tmtu	-	tetramethylthiourea
2-toluid	-	2-aminotoluene
3-toluid	-	3-aminotoluene
4-toluid	-	4-aminotoluene

SPECTROSCOPIC ABBREVIATIONS

e.p.r.	electron paramagnetic resonance
n.m.r.	nuclear magnetic resonance
i.r.	infrared
ν_{as}	asymmetric stretching frequency
vs	very strong
s	strong
m/s	medium strong
m	medium
w/m	weak/medium
w	weak
vw	very weak
sh	shoulder

DEFINITION OF SYMBOLS

A	-	hyperfine coupling constant
A_{iso}	-	isotropic hyperfine coupling constant
$A_{\parallel}$	-	'parallel' component of the anisotropic hyperfine tensor (axial symmetry)
$A_{\perp}$	-	'perpendicular' component of the anisotropic hyperfine tensor (axial symmetry)
β	-	Bohr magneton
β_N	-	nuclear Bohr magneton
c	-	velocity of light in vacuo
e	-	charge on the electron
g	-	electron g-factor
g_{iso}	-	isotropic g-factor
$g_{\parallel}$	-	'parallel' component of the anisotropic g-tensor for an axially symmetric system
$g_{\perp}$	-	'perpendicular' component of the anisotropic g-tensor for an axially symmetric system
g_N	-	nuclear g-factor
h	-	Planck's constant
H	-	magnetic flux density vector (the 'magnetic field')
I	-	value of the nuclear angular momentum (the 'nuclear spin')
$\bar{I}$	-	nuclear spin vector
m_I	-	quantum number charactertising the nuclear spin states of a system
m_N	-	nuclear mass
m_S	-	quantum number characterising the electron spin states of a system
S	-	value of the electronic angular momentum (the 'spin')
$\bar{S}$	-	electronic angular momentum vector

SECTION 1 : INTRODUCTION

1.1. VANADIUM CHEMISTRY

Vanadium is in group VA of the periodic table, and forms a wide variety of complexes in all oxidation states from +5 to -1, those in the +5, +4 and +3 states being the most common. In general, vanadium forms complexes readily with those ligands containing a donor atom such as nitrogen, oxygen or a halogen. Far fewer complexes are known with phosphorus or sulphur-donor ligands. The chemistry of vanadium is discussed in detail in many reviews [1-12] and, therefore, this section will concentrate on previous work relevant to the complexes studied in this project.

Vanadium(IV) chemistry is dominated by the numerous oxovanaidum complexes of the form $[VOX_n]$ or $[VOX_nY_m]$ where X is a negatively charged monodentate or bidentate ligand and Y is a neutral monodentate or bidentate ligand). Many interesting properties of vanadium(IV) complexes can be attributed to the d^1 electronic configuration. Most studies upon vanadium(IV) have concentrated on complexes of the type $[VO(L\text{-}L)_2]$ (where L-L is a bidentate oxygen ligand). Vanadium (IV)-oxygen bonds are usually very strong and these compounds are relatively stable under atmospheric conditions. Most other vanadium(IV) complexes, however, are difficult to prepare and are usually extremely moisture and oxygen sensitive. This is so, for instance, in the case of the halides and oxohalides and their complexes.

1.2. VANADIUM(IV) OXIDE DICHLORIDE AND ITS ADDUCTS

1.2.1 Vanadium(IV) Oxide Dichloride

Vanadium(IV) oxide dichloride was first reported in 1868 by Roscoe [13]. The preparation involved passing vanadium(V) oxide trichloride vapour and dihydrogen through a red-hot tube together. Other solid oxochlorides were formed as impurities, using this method. An alternative method, used by Roscoe, was the reduction of vanadium(V) oxide trichloride by metallic zinc in sealed tubes at 673 K [13].

A more recent and more efficient method involves the reaction of vanadium(V) oxide, vanadium(III) chloride and vanadium(V) oxide trichloride according to the equation[14]:

$$V_2O_5 + 3VCl_3 + VOCl_3 \longrightarrow 6VOCl_2$$

The reactants are sealed in a tube which is placed in a temperature gradient, the hot end being at 873 K. Vanadium(IV) oxide dichloride sublimes out of the hot reaction zone in 4-5 days [14,15]. The product forms green, deliqu escent plates which dissolve in water to give a blue solution.

Du Preez and Sadie [16] treated a concentrated aqueous solution of $VOCl_2$ with excess of thionyl chloride, heating under reflux for five hours. This is probably the simplest and most convenient, recent preparative method but impurities of sulphur were present in the product. Du Preez and Sadie, however, used this slightly impure product to form $VOCl_2.2.5CH_3CN$ [16], and impurities were removed during this next preparative stage.

Other recent methods include the interaction of vanadium(V) oxide trichloride with vanadium(III) oxide chloride [17] over the temperature gradient of 723-523 K, and the passage of hydrogen chloride gas over vanadium(III) chloride hexahydrate [18] at 433 K. High temperature preparative methods are, however, often avoided since vanadium(IV) oxide dichloride is thermally unstable above about 573 K, decomposing to vanadium(V) oxide trichloride and vanadium(III) oxide chloride [17,18,19]. The most recent method is the reduction of vanadium(V) oxide trichloride by sulphur. This involved heating under reflux under a dry nitrogen atmosphere [20].

A hydrate, $VOCl_2.xH_2O$, may be prepared as a syrupy liquid by evaporating a mixture of vanadium pentoxide, ethanol, hydrochloric acid and water until all the pentoxide has reacted [21]. Hydrates have been prepared with many values of x, the limits of x being 0-2.5 [12]. Many workers have used $VOCl_2.2H_2O$ as a starting material for their preparations of other oxodichlorovanadium(IV) complexes.

1.2.2. Adducts of Vanadium(IV) Oxide Dichloride

Many adducts of $VOCl_2$ have been prepared and studied: very few of these have been prepared by direct reaction with anhydrous $VOCl_2$. Many of the adducts were prepared by the partial hydrolysis of the corresponding VCl_4 complex, or by oxidation of a VCl_3 complex. The known complexes of $VOCl_2$ are listed in Tables 1.1-1.5. The overall impression given by these tables is of the many different methods used in the preparations.

The phosphine complexes have proved difficult to prepare. The first report of such a complex, $VOCl_2(Ph_3P)_2.2H_2O$ [22] has been discredited [23,24], the complex having been shown to be $[VOCl_2(Ph_3PO)_2]$. Many other workers have failed to prepare simple phosphine complexes [23,25], and the report of $VOCl_2(Ph_3P)_2.H_2O$ [26] in 1970 must be open to doubt, especially as the preparation *was under anhydrous conditions!* Recently, however, the preparation of $[VOCl_2(Ph_3P)_2]$ has been carried out [27]. The starting material used in this preparation was the same compound, $[VOCl_2(MeOH)_3]$, used in many other preparations [28] with basic nitrogen-donor ligands. With nitrogen-donor ligands, methanoloysis occurs and an intermediate is formed:

$$B + [VOCl_2(MeOH)_3] \longrightarrow [BH][VOCl_2(OMe)] + 2MeOH$$

The intermediate then reacts with excess ligand to give complexes of the type $VOCl_2L_n$. The complexes $[VOCl_2(PR_3)_2]$ (R = Et, Pr, Bu or Ph) and $[VOCl_2(PR_2Q)_2]$ (R = Me, Q = Ph; R = Ph, Q = Et) have been detected in toluene [29,30]. In fact, their presence was deduced from an e.p.r signal alone, recorded on a solution which was effectively a mixture of $VOCl_2$, phosphine and solvent. The phosphine complexes were not isolated. Similar interactions with tributylstibine in solution [31] have indicated the predominant species to be $[VOCl_2(SbR_3)]$. Again, these conclusions were drawn from an e.p.r solution spectrum.

The preparations carried out by Datta and Hamid [20] are interesting in that they involve ligand exchange. Firstly anhydrous $VOCl_2$ is reacted with tetrahydrofuran to give $[VOCl_2(thf)_2]$, and then this compound is reacted with the relevant methoxyaniline, aminotoluene or other ligand. The complexes $(C_6H_5N_2Cl).VOCl_2.H_2O$ and $(4\text{-}CH_3OC_6H_5N_2Cl)_2$ $VOCl_2.xH_2O$ have been reported [32] but their nature is not clear.

Complexes of the type $VOCl_2L_n$ are known with a wide range of stereochemistries. The most common coordination numbers are four, five and six. There have been many studies of the electronic structure of vanadium(IV) complexes containing a V=O double bond. Although most of these studies have concentrated on complexes such as $[VO(acac)_2]$, which has been subject to many detailed molecular orbital calaculations [33,34,35], some studies have been made of VOX_2L_n complexes.

Table 1.1 Complexes of $VOCl_2$ with Oxygen-Donor Ligands

ADDUCT	METHOD OF PREPARATION	SPECTRO-SCOPIC DATA	REF.
$[VOCl_2(diox)_2]$	$[VCl_4(diox)]$/diox/H_2O	a/d	39
	$[VOCl_2(CH_3OH)_3]$/diox	-	27
$[VOCl_2(diox)]$	Heat $[VOCl_2(diox)_2]$ at 348 K	a/d	39
$[VOCl_2(thf)_2]$	$[VCl_3(thf)_3]$/thf/O_2/hexane	a	43
	$VOCl_2$/thf	a/b	20
$[VOCl_2(thf)]$	$VOCl_2.2H_2O$/thf/pentane	a/d/e	51
$[VOCl_2(Et_2O)_2]$	$VOCl_2.2H_2O/CH_3OH/Et_2O$	a/d/e	51
$[VOCl_2(CH_3OH)_3]$	$VCl_4/CH_3OH/CCl_4$	-	52
$[VOCl_2(dmso)_3]$	$VCl_3.6H_2O$/dmso/EtOH-H_2O	a/e	53
	aq. $VOCl_2$/dmso/EtOH	a	21,45,47
$[VOCl_2(hmpa)_2]$	$VOCl_2$/HCl/hmpa/propanone-2,2-dmp	a/d/e	16
$[VOCl_2(tmu)_2]$	$VOCl_2$/HCl/tmu/propanone-2,2-dmp	a/d/e/g	16,38
	$VOCl_2$/MeCN/tmu/CH_2Cl_2	a/b/e	26
$[VOCl_2(clm)_2]$	$VOCl_2$/MeCN/clm/propanone/Et_2O	a/b/e	26
	$VCl_3.6H_2O/Ph_3PO$/EtOH	a/e	53
	$VOCl_2.2H_2O/Ph_3PO$/cyclohexanol	a	24
$[VOCl_2(Ph_3AsO)_4]$	$VCl_3.6H_2O/Ph_3AsO$/EtOH	a/e	53
$[VOCl_2(dmpo)_2]$	$VCl_3.6H_2O$/dmpo/propanone-2,2-dmp	a/e	54
$[VOCl_2(RC_5H_4NO)_2]$ {R=OCH_3,CH_3,Cl,Br or NO_2}	$VOCl_2/RC_5H_4NO$/propanone-2,2-dmp	a/e	54
$[VOCl_2(thp)_2]$	$[VOCl_2(thf)_2]$/thp/thf	a/b	20
$[VOCl_2(urea)_2]$	$VOCl_2.2H_2O$/urea	a/f	55
*$[VO(urea)_4]Cl_2$	$VOCl_2.2H_2O$/urea	a/f	55

* This compound was found to be ionic, rather like the compound $[VO(dmso)_4]Br_2$ [47]

Spectroscopic key: a-far i.r., b-Near i.r., c-e.p.r, d-diffuse reflectance, e-electronic absorption (solution), f-x-ray powder diffraction, g-x-ray crystal structure.

Table 1.2 Complexes of $VOCl_2$ with Nitrogen-Donor Ligands

ADDUCT	METHOD OF PREPARATION	SPECTRO-SCOPIC DATA	REF
$[VOCl_2(CH_3CN)_2]$	$VCl_4/CH_3CN/H_2O$	a/d	39
$VOCl_2(CH_3CN)_{2.5}$	$VOCl_2/CH_3CN$	a/d/e	16
$[VOCl_2(C_6H_5CN)_2]$	$[VOCl_2(CH_3CN)_2]/C_6H_5CN$	a/d/e	39
$[VOCl_2(py)_3]$	$[VOCl_2(CH_3OH)_3]/py/CCl_4$	-	52
	$VCl_3/py/O_2$	-	56
	$[VOCl_2(CH_3OH)_3]/py$	-	27,28
$[VOCl_2(py)_2]$	Heat $VOCl_2(py)_3(Et_2O)_{0.5}$	-	52
	Heat $[VOCl_2(py)_3]$ at 343 K	-	27,28
$[VOCl_2(3\text{-pic})_3]$	$[VOCl_2(CH_3OH)_3]/3\text{-pic}$	-	27,28
$[VOCl_2(3\text{-pic})_2]$	Heat $[VOCl_2(3\text{-pic})_3]$ at 343 K	-	27,28
$[VOCl_2(4\text{-pic})_3]$	$[VOCl_2(CH_3OH)_3]/4\text{-pic}$	-	27,28
$[VOCl_2(4\text{-pic})_2]$	Heat $[VOCl_2(4\text{-pic})_3]$ at 343 K	-	27,28
$[VOCl_2(iosquin)_3]$	$[VOCl_2(CH_3OH)_3]/isoquin$	-	27,28
$[VOCl_2(isoquin)_2]$	$[VOCl_2(isoquin)_3]/Et_2O$	-	27,28
	$[VOCl_2(thf)_2]/isoquin/thf$	a/b	20
$[VOCl_2(3,5\text{-dmpy})_2]$	$[VOCl_2(CH_3OH)_3]/3,5\text{-dmpy}/Et_2O$/Heat at 343 K	-	27,28
$VOCl_2.5NH_3$	$VOCl_3/NH_3$	a	57-63
$VOCl_2(NH_2Me)_4$	$VOCl_3/NH_2Me$	a/e	44
$VOCl_2(NHMe_2)_2$	$VOCl_3/NHMe_2$	a/e	44
$[VOCl_2(NMe_3)_2]$	$VOCl_3/NMe_3$	a/e/g	36,44
$VOCl_2(2,2'\text{-bipy})_2$	aq.$VOCl_2$/2,2'-bipy/propanone	a	21,45,47
$[VOCl_2(2,2'\text{-bipy})]$	$[VCl_4(2,2'\text{-bipy})]/CCl_4/H_2O$	a/b/d/e	64
	$[VOCl_2(CH_3OH)_3]/2,2'\text{-bipy}/Et_2O$	-	27,28
$VOCl_2(phen)_2$	aq.$VOCl_2$/phen/propanone	a	21,45,47
$[VOCl_2(phen)]$	$VCl_4(phen)/CCl_4/H_2O$	a/b/d/e	64
$(VOCl_2)_2(4,4'\text{-bipy})_3$	$VOCl_2(CH_3OH)_3/4,4'\text{-bipy}/Et_2O$	-	27,28
$[VOCl_2(2\text{-anis})_2]$	$VOCl_2(thf)_2/2\text{-anis/thf}$	a/b	20
$[VOCl_2(3\text{-anis})_2]$	$VOCl_2(thf)_2/3\text{-anis/thf}$	a/b	20
$[VOCl_2(4\text{-anis})_2]$	$VOCl_2(thf)_2/4\text{-anis/thf}$	a/b	20
$[VOCl_2(2\text{-toluid})_2]$	$VOCl_2(thf)_2/2\text{-toluid/thf}$	a/b	20
$[VOCl_2(3\text{-toluid})_2]$	$VOCl_2(thf)_2/3\text{-toluid/thf}$	a/b	20
$[VOCl_2(4\text{-toluid})_2]$	$VOCl_2(thf)_2/4\text{-toluid/thf}$	a/b	20
$[VOCl_2(quin)_2]$	$VOCl_2(thf)_2/quin/thf$	a/b	20

Spectroscopic key: a-far i.r., b-Near i.r., c-e.p.r., d-diffuse reflectance, e-electronic absorption(solution), f-x-ray powder diffraction, g-x-ray crystal structure.

Table 1.3 Complexes of $VOCl_2$ with Phosphorus and Arsenic Ligands

ADDUCT	METHOD OF PREPARATION	SPECTRO-SCOPIC DATA	REF
$[VOCl_2(Ph_3P)_2]$	$[VOCl_2(CH_3OH)_3]/Ph_3P/Et_2O$	-	27
$[VOCl_2(dppe)]$	$[VOCl_2(CH_3OH)_3]$/dppe/Et_2O	-	27
$[VOCl_2(o\text{-tas})]$	$[VCl_4(o\text{-tas})]/CCl_4/H_2O$	a/d/e	65
$[VOCl_2(v\text{-tas})]$	$[VCl_4(v\text{-tas})]/CCl_4/H_2O$	a/d/e	65

Spectroscopic key: a-far i.r., d-diffuse reflectance, e-electronic absorption (solution).

Table 1.4 Complexes of $VOCl_2$ with Sulphur-Donor Ligands

ADDUCT	METHOD OF PREPARATION	SPECTRO-SCOPIC DATA	REF
$[VOCl_2(Me_2S)_2]$	$VOCl_3/Me_2S$/2,2,4-triemthylpentane	-	27
$[VOCl_2(Et_2S)_2]$	$VOCl_3/Et_2S$/2,2,4-trimcthylpentane	-	27
$[VOCl_2(tclm)_2]$	$VOCl_2/CH_3CN$/ tclm/CH_2Cl_2	a/b/e	26
$[VOCl_2(tmtu)_2]$	$VOCl_2/CH_2CN$/tmtu/CH_2Cl_2	a/b/e	26
$[VOCl_2(thioph)_2]$	$[VOCl_2(thf)_2]$/thiophen/thf	a/b	20

Spectroscopic key: a-far i.r., b-near i.r., e-electronic absorption (solution).

Table 1.5 Complexes of $VOCl_2$ with Two Ligands

ADDUCT	METHOD OF PREPARATION	SPECTRO-SCOPIC DATA	REF
$VOCl_2(Ph_3P)_2.2H_2O$*	$VOCl_2.2H_2O/Ph_3P$/cyclohexanol	-	22
$VOCl_2(Ph_3P)_2.H_2O$**	$VOCl_2/CH_3CN/Ph_3P/CH_2Cl_2$	a/b/e	26
$VOCl_2(Et_2O)_2.2H_2O$	aq. $VOCl_2/Et_2O$	a/d/e	51
	$VCl_4/Et_2O/H_2O$	-	66
$VOCl_2(thf)_2.2H_2O$	$VOCl_2.2H_2O$/thf	a/d/e	51
$VOCl_2(diox)_3.2H_2O$	$VCl_3.6H_2O$/diox	-	52
$VOCl_2(diox).2H_2O$	Decomp. of $VOCl_2(diox)_3.2H_2O$	-	52
$VOCl_2(C_5H_5NO)_2.H_2O$	$VOCl_2/C_5H_5NO$/propanone-2,2-dmp	a/e	54
$VOCl_2(MeOC_5H_4NO)_4.2H_2O$	$VCl_3.6H_2O/MeOC_5H_4NO$/propanone-2,2-dmp	a/e	54
$VOCl_2(dppe).H_2O$	aq.$VOCl_2/CH_3OH$/dppe/CH_2Cl_2	a/e	23
$VOCl_2(dppeO_2).4H_2O$	aq. $VOCl_2/CH_3OH/dppeO_2/CH_2Cl_2$	a/e	23
$[VOCl_2(py)_2(CH_3OH)]$	$[VOCl_2(CH_3OH)_3]/py/CH_3OH$	-	52
$[VOCl_2(dme)(CH_3OH)]$	$[VOCl_2(CH_3OH)_3]$/dme	-	27
$[VOCl_2(dmp)(CH_3OH)]$	$[VOCl_2(CH_3OH)_3]$/dmp/Et_2O	-	27,28
$[VOCl_2(dmp)_2(CH_3OH)]$	$[VOCl_2(CH_3OH)_3]$/dmp/Et_2O	-	27,28
$[VOCl_2(dmp)(CH_3OH)_2]$	$[VOCl_2(dmp)_2(CH_3OH)]/Et_2O$	-	27,28
$VOCl_2(py)_3(Et_2O)_{0.5}$	$[VOCl_2(py)_2(CH_3OH)]/py/Et_2O$	-	52
$VOCl_2(CH_3CN)_2(diox)_{0.5}$	$VOCl_2(diox)_2/CH_3CN$	a/d	39
$VOCl_2(acry)_2(C_6H_6)_{0.4}$	$VCl_3(acry)_3/O_2/C_6H_6$	-	67

* existence disproved

** existence in doubt

Spectroscopic key a-far i.r., b-near i.r., d- diffuse reflectance, e-electronic absorption(solution).

The information available for such studies comes mainly from solid-state measurements. X-ray studies have been carried out on both $[VOCl_2(NMe_3)_2]$ [36,37] and $[VOCl_2(tmu)_2]$ [38]. Whereas all five-coordinate VOX_2L_2 species were thought to have structures based on a square pyramid (C_{2v}), the first of these compounds was shown to have a structure based on trigonal-bipyramid (C_{2v}) [36,37]. The tetramethylurea complex had the expected square-pyramidal geometry. Drake, Vekris and Wood [36,37] also used diffuse reflectance spectroscopy in their studies. Recently electronic spectra and molecular orbital calculations have been used in a bonding study on $[VOCl_2(tmu)_2]$ [50]. E.p.r spectra were also recorded.

Extensive near infrared (4000-650cm^{-1}) investigations on $VOCl_2$ complexes have been made by many workers [21,39,43-49]. However the far infrared region (650-200 cm^{-1}) has yet to be investigated in detail. Very few reports of V-Cl stretching frequencies exist. The stretching frequencies of the metal -oxygen double bond, $\nu(V=O)$, are found between 900 and 1100 cm^{-1}, depending on its environment.

Very little spectroscopic information is available from measurements in solution , and no unambiguous assignments have been made (due to the uncertainty in the ordering of the molecular orbitals, as a result of the presence of the V=O moiety). Many of the solvents used for solution studies of vanadium(IV) complexes show a tendency to displace other ligands from the complexes. This process will be commented on later in this report.

Very few e.p.r studies have been carried out on $VOCl_2$ complexes (those which have will be discussed in 1.6). This fact, along with the lack of i.r. data, the variety in preparative methods, the unreliability of solution measurements due to the ligand displacement effect mentioned above and the lack of solution data in general makes a study of the properties of $VOCl_2$ complexes worthwhile.

1.3 OXOTETRACHLOROVANADATE(IV) COMPLEXES

The known $[VOCl_4]^{2-}$ complexes are all extremely air and moisture sensitive. This is due to the ease with which V-Cl bonds are hydrolysed. Simple $[VOCl_4]^{2-}$ compounds are green in colour. Table 1.6 lists the known $[VOCl_4]^{2-}$ complexes and their methods of preparation. Table 1.7 contains a similar list for mixed ligand complexes, $[VOCl_4L_y]^{2-}$.

An X-ray study carried out by Haase and Hoppe [68] has indicated that the $[VOCl_4]^{2-}$ ion may have C_{4v} symmetry. Their study on $[Et_4N]_2$ $[TiOCl_4]$ showed titanium to have a slightly distorted tetragonal-pyramidal coordination with oxygen at the apex. Since $[VOCl_4]^{2-}$ is isomorphous with $[TiOCl_4]^{2-}$, Haase and Hoppe concluded that $[VOCl_4]^{2-}$ in $[Et_4N]_2[VOCl_4]$ would have the same symmetry. No single crystal X-ray studies have been carried out on complexes containing $[VOCl_4]^{2-}$ itself.

A comparative study of the e.p.r. spectra of the ions $[VOCl_4]^{2-}$ $[MoOCl_5]^{2-}$ and $[WOCl_5]^{2-}$ was reported in 1966 [69]. The value for $g_\perp$ was found to be greater than that for $g_\parallel$ for the $[VOCl_4]^{2-}$ ion. Studies were carried out using the compound $[Me_4N]_2[VOCl_4].EtOH$, prepared by Selbin and Holmes [21].

The electronic spectrum of the $[VOCl_4]^{2-}$ ion has been studied [70,71]. The first of these studies [70] was a study of the single-crystal absorption spectrum of $[Et_4N]_2[VOCl_4]$. Drake, Vekris and Wood [37] carried out a molecular orbital treatment for the ion, basing their calculations on the Ballhausen and Gray molecular orbital scheme for the $[VO(H_2O_5]^{2+}$ ion [33]. They used their result to assign bands in the charge-transfer spectra of vanadium(IV) and vanadium(V) species.

Kilty and Nicholls prepared many simple $[VOCl_4]^{2-}$ complexes, as well as some hydrates [72]. They carried out diffuse reflectance studies upon these compounds, and a study of the magnetic properties of these compounds was carried out at a later date by Machin and Murray [73]. $[pyH]_2[VOCl_4]$ and $[quinH]_2[VOCl_4]$ were found to have magnetic moments of 1.76 and 1.75 μ_B respectively at 300 K.

Infrared studies have concentrated on V=O stretching frequencies. There have been no V-Cl assignments reported. The strong band at 985±50 cm^{-1} observed in spectra of vanadyl complexes was first assigned to the V=O stretching frequency in 1959 [49]. Both Kilty and Nicholls [72] and Feltz [74,75] later confirmed this assignment. Kharitonov and Khalilova used i.r. spectroscopy to show that the vanadium-oxygen bond was indeed a multiple bond [76] and did not exist in vanadium-oxygen-vanadium chains.

Although all the simple $[VOCl_4]^{2-}$ complexes prepared have been green, the hydrates have been coloured differently [72]. $[pyH_2][VOCl_4].2H_2O$,

Table 1.6 Complexes of $[VOCl_4]^{2-}$

COMPLEX	METHOD OF PREPARATION	SPECTRO-SCOPIC DATA	REF
$K_2[VOCl_4]$	$[VOCl_2(diox)_2]$/liq.SO_2/KCl	a/d	74,75
	Heat monohydrate	a/f	77
$Rb_2[VOCl_4]$	$[VOCl_2(diox)_2]$/liq.SO_2/RbCl	a/d	74,75
	Heat monohydrate	a/f	77
$Cs_2[VOCl_4]$	$[VOCl_2(diox)_2]$/liq.SO_2/CsCl	a/d	74,75
	Heat $Cs_2[VOCl_5].H_2O$	a/f	77
$[NH_4]_2[VOCl_4]$	$VOCl_2(MeCN)_2(diox)_{0.5}$/MeCN/$NH_4Cl$	a/d	74,75
	Heat monohydrate	a/d/f	72,77
$[NH_3Me]_2[VOCl_4]$	Heat $[NH_3Me]_2[VOCl_4(MeCN)]$	a/d	74,75
$[NH_2Me_2]_2[VOCl_4]$	Heat $[NH_2Me_2]_2[VOCl_4(MeCN)]$	a/d	74,75
$[NHMe_3]_2[VOCl_4]$	Heat $[NHMe_3]_2[VOCl_4(MeCN)]$	a/d	74,75
$[NMe_4]_2[VOCl_4]$	Heat $[NMe_4]_2[VOCl_4(MeCN)]$	a/d	74,75
$[Et_2NH_2]_2[VOCl_4]$	$VOCl_2$/$[Et_2NH_2]Cl$/$CHCl_3$	d/e	37
$[Et_4N]_2[VOCl_4]$	$VOCl_2(MeCN)_2(diox)_{0.5}$/MeCN/$[Et_4N]Cl$	a/d	74,75
	$VOCl_2$/$[Et_4N]Cl$/$CHCl_3$	d/e	37
$[pyH]_2[VOCl_4]$	Dehydrate dihydrate over P_2O_5	a/d	72,73
	$VOCl_2$/[pyH]Cl/$CHCl_3$	d/e	37
$[quinH]_2[VOCl_4]$	Dehydrate dihydrate over P_2O_5	a/d	72,73
	$VOCl_2$/[quinH]Cl/$CHCl_3$	d/e	37
$[isoquinH]_2[VOCl_4]$	Dehydrate dihydrate over P_2O_5	a/d	72,73

Spectroscopic key : a-near i.r., d-diffuse reflectance, e-electronic absorption (solution), f-X-ray powder diffraction

Table 1.7 Complexes of $[VOCl_4L_y]^{2-}$

COMPLEX	METHOD OF PREPARATION	SPECTRO-SCOPIC DATA	REF
$K_2VOCl_4.2H_2O$	VCl_4/aq.HCl/KCl	a/f	76,78,79
$K_2[VOCl_4(H_2O)]$	$VOCl_3$/aq.HCl/KCl	a/f	77
$Rb_2VOCl_4.2H_2O$	VCl_4/aq.HCl/RbCl	a/f	76,78,79
$Rb_2[VOCl_4(H_2O)]$	$VOCl_3$/aq.HCl/RbCl	a/f	77
$Cs_2VOCl_4.2H_2O$	VCl_4/aq.HCl/CsCl	a/f	76,78,79
$Cs_2[VOCl_4(H_2O)]$	aq.$VOCl_2$/HCl/CsCl	a/d	72
	aq.$VOCl_2$/HCl/EtOH/CsCl	a/d	72
$[NH_4]_2VOCl_4.2H_2O$	VCl_4/aq.HCl/NH_4Cl	a/f	76,79
$[NH_4]_2[VOCl_4(H_2O)]$	NH_4VO_3/aq.HCl-EtOH	a/d	72
	$VOCl_3$/aq.HCl/NH_4Cl	a/f	77
$[NH_3Me]_2[VOCl_4(MeCN)]$	$[VOCl_2(diox)_2]$/MeCN/$[NH_3Me]Cl$	a/d	74,75
$[NH_2Me_2]_2[VOCl_4(MeCN)]$	$[VOCl_2(diox)_2]$/MeCN/$[NH_2Me_2]Cl$	a/d	74,75
$[NHMe_3]_2[VOCl_4(MeCN)]$	$[VOCl_2(diox)_2]$/MeCN/$[NHMe_3]Cl$	a/d	74,75
$[NMe_4]_2[VOCl_4(MeCN)]$	$[VOCl_2(diox)_2]$/MeCN/$[NMe_4]Cl$	a/d	74,75
$[NMe_4]_2[VOCl_4(EtOH)]$	aq.$VOCl_2$/EtOH/$[NMe_4]Cl$	a	21,45,47
$[pyH]_2VOCl_4.3H_2O$	aq.$VOCl_2$/EtOH/[pyH]Cl	-	80
$[pyH]_2VOCl_4.2H_2O$	V_2O_5/aq.HCl-EtOH/py	a/d	73,72
$[quinH]_2VOCl_4.5H_2O$	aq.$VOCl_2$/EtOH/[quinH]Cl	-	80
$[quinH]_2VOCl_4.2H_2O$	V_2O_5/aq.HCl-EtOH/quin	a/d	72
$[isoquinH]_2VOCl_4.2H_2O$	V_2O_5/aq.HCl-EtOH/isoquin	a/d	72

Spectroscopic data key as for Table 1.6

$[quinH]_2[VOCl_4].2H_2O$ and $[isoquinH]_2[VOCl_4].2H_2O$ were described as blue, $[NH_4]_2[VOCl_4(H_2O)]$ as light blue, and $Cs_2[VOCl_4(H_2O)]$ as either brown or green depending on the preparative details. The presence of coordinated water was deduced from the i.r. spectra of the hydrates. The i.r. data could also distinguish a dihydrate from a hydrate.

1.4 VANADIUM(IV) OXIDE DIBROMIDE AND ITS ADDUCTS

1.4.1 Vanadium(IV) Oxide Dibromide

Although first prepared by Šafařik [81] , the compound we now know to be $VOBr_2$ was first identified as $VOBr_2$ by Roscoe [13]. It was prepared by heating vanadium(V) oxide tribromide to 453 K, and was described as a very deliquescent yellow-brown solid. Later, $VOBr_2$ was prepared [82] by the action of bromine and sulphur monobromide on vanadium(V) oxide at 773-873 K, in the presence of sulphur. The product was collected at the cooler end of the sealed tube, in which the reactants were held, at a temperature of 533 K. A more recent preparation[2,11] involves the bromination of vanadium(III) oxide at 873 K in a flow system. Lappert and Prokai [83] reported that $VOBr_2$ could be prepared by heating BBr_3 and vanadium(V) oxide under reflux at 393-433 K but subsequent investigation has disproved this claim [25] . However, more recently, Druce and Lappert [84] have reported the preparation of $VOBr_2$ by the reaction of BBr_3 with vanadium(V) oxide trichloride. Savant and Patel [85] prepared $VOBr_2$ by the action of HBr upon $VO(OH)_2$, but did not quote analytical figures for their product. The most recent preparative route is by the action of HBr upon vanadium(V) oxide trichloride [86], the product being heated to 433 K. The initial product is vanadium(V) oxide triboromide, but this decomposes on heating to give vanadium(IV) oxide dibromide.

A hydrate, $VOBr_2.xH_2O$ has been prepared [21] in a manner analogous to that described for the corresponding vanadium(IV) oxide dichloride complex.

Few physical properties of vanadium(IV) oxide dibromide have been studied. It is partially decomposed at about 633 K to vanadium(III) oxide bromide [12], and at higher temperatures still, it is converted through to vanadium(II) oxide [40] , and not vanadium(V) oxide as reported by Clark [12] . The compound is yellow-brown and dissolves in water, giving a blue solution typical of the $[VO(H_2O)_5]^{2+}$ ion. The infrared spectrum of $VOBr_2$ has been reported [87] and was assigned upon C_s symmetry.

1.4.2 Adducts of Vanadium(IV) Oxide Dibromide

The adducts of vanadium(IV) oxide dibromide have received far less attention than those of vanadium(IV) oxide dichloride. The first systematic

study of these complexes appeared in 1973 [40-42]. The method used by Nicholls and Seddon for their preparations involved the reaction of the relevant ligand with vanadium(V) oxide tribromide, using cyclohexene as solvent. Reduction always occurred along with the coordination of the ligand. The use of a ligand exchange method, *via* oxodibromotris(ethanenitrile)vanadium(IV) as an intermediate, effected the preparation of a simple phosphine complex. This method has since been used in the preparation of $[VOBr_2(py)_3]$ and $[VOBr_2(4\text{-pic})_3]$ [88] , and should prove a general method for the preparation of other complexes in the future. All the known complexes of $VOBr_2$ are listed in Table 1.8 along with references to the spectroscopic data reported. Nicholls and Seddon [40-42] studied the far infrared region and reported V-Br stretching frequencies. This was shown to be particularly useful in assigning the symmetry of a complex. One class of spectra gives two strong ν(V-Br) stretches, the higher of the two being in the region 360-340 cm^{-1}; the other shows only one ν(V-Br) stretch, in the region 340-320 cm^{-1}. This is consistent with the latter class having a structure based on the square-pyramid, and the former class having a structure based on the trigonal-bipyramid. An examination of the oxovanadium(IV) stretching frequencies for the adducts revealed the following general trend:

$$\nu(V{=}O)_{anionic} > \nu(V{=}O)_{5\text{-coord}} > \nu(V{=}O)_{6\text{-coord}} > \nu(V{=}O)_{bidentate}.$$

The complex $[VO(dmso)_5]Br_2$ was shown to be ionic [40,42,45,47] by conductivity measurements.

Table 1.8 Complexes of Vanadium(IV) Oxide Dibromide

ADDUCT	METHOD OF PREPARATION	SPECTROSCOPIC DATA	REF
$[VO(dmso)_5]Br_2$	aq.$VOBr_2$/dmso	a	21,45,47
	$VOBr_3$/dmso/cyclohexene	a/b/e	40,42
$[VOBr_2(dpso)_3]$	$VOBr_3$/dpso/propanone	-	85
	$VOBr_3$/dpso/cyclohexene	a/b/e	40,42
$[VOBr_2(hmpa)_2]$	aq.$VOBr_2$/HBr/hmpa propanone-2, 2-dmp	a/d/e	16
	$VOBr_3$/dpso/cyclohexene	a/b/e	40,42
$[VOBr_2(tmu)_2]$	aq.$VOBr_2$/HBr/tmu/acetone-2,2-dmp	a/d/e	16
$[VOBr_2(qn)_2]$	$VBr_3(qn)_2/O_2$	a/b	90
$[VOBr_2(CH_3CN)_3]$	$VOBr_3/CH_3CN$/cyclohexene	a/b/e	40,41
$[VOBr_2(dme)]$	$VOBr_3$/dme/cyclohexene	a/b/e	40,42
$[VOBr_2(2,2'\text{-bipy})]$	$VOBr_3$/2,2'-bipy/cyclohexene	a/b/e	40,42
$[VOBr_2(thf)_2]$	$VOBr_3$/thf/cyclohexene	a/b/e	40,42
$[VOBr_2(diox)_2]$	$VOBr_3$/diox/cyclohexene	a/b/e	40,42
$[VOBr_2(thiox)_2]$	$VOBr_3$/thiox/cyclohexene	a/b/e	40,42
$[VOBr_2(py)_2]$	$VOBr_3$/py/cyclohexene	a/b/e	40,42
$[VOBr_2(quin)_2]$	$VOBr_3$/quin/cyclohexene	a/b/e	40,42
$[VOBr_2(tht)_2]$	$VOBr_3$/tht/cyclohexene	a/b/e	40,42
$[VOBr_2(Ph_3P)_2]$	$[VOBr_2(CH_3CN)_3]/Ph_3P$/thf	a/b/e	40,42
$[VOBr_2(py)_3]$	$VOBr_3$/py/cyclohexene	a/b/e	40,42
	$[VOBr_2(CH_3CN)_3]$/py/thf	-	88
$[VOBr_2(4\text{-pic})_3]$	$[VOBr_2(CH_3CN)_3]$/4-pic/thf	-	88
$VOBr_2.2H_2O$	V_2O_5/HBr/EtOH/H_2O	-	25
$VOBr_2.xH_2O$ (x~5)	V_2O_5/HBr/EtOH/H_2O	a	21,45,47
$VOBr_2.CH_3COOH$	V_2O_5/aq.HBr/CH_3COOH/CH_2Cl_2	-	25
$[VO(phen)_2]Br_2.H_2O$	aq.$VOBr_2$/phen/propanone	a	21,45,47
$[VO(2,2'\text{-bipy})_2]Br_2.H_2O$	aq. $VOBr_2$/2,2'-bipy/propanone	a	21,45,47
$[VO(dmpo)_4]Br_2.H_2O$	$VO(OH)_2$/HBr/dmpo/acetone-2,2-dmp	a/e	54
$VOBr_2(dppe).H_2O$	$VOBr_2.xH_2O/CH_3OH$/dppe/CH_2Cl_2	a/e	23
$VOBr_2(dppm).H_2O$	$VOBr_2.xH_2O/CH_3OH$/dppm/CH_2Cl_2	a/e	23
$(VOBr_2)_2(dppeO_2).H_2O$	$VOBr_2.xH_2O/CH_3OH/dppeO_2/CH_2Cl_2$	a/e	23
$[VO(NH_3)_5]Br_2$	$VOBr_2/NH_3$ at 240 K	a/b/d	86
$VOBr_2(NH_3)_2$	Heat $[VO(NH_3)_5]Br_2$ to 393 K	a/b/d	86
$VOBr_2(NH_3)_6$	$VOBr_3/NH_3$ at 240 K	a/b/d	86

ADDUCT	METHOD OF PREPARATION	SPECTRO-SCOPIC DATA	REF
$VOBr_2(CH_3OH)_3$	$VOBr_2/CH_3OH$	a/d	91
	$VOBr_3/CH_3OH$	a/d	91
$VOBr_2(EtOH)_2$	$VOBr_2/EtOH$	a/d	91
	$VOBr_3/EtOH$	a/d	91
$VOBr_2(NH_2Me)_5$	$VOBr_2/NH_2Me$	a/d	91
$VOBr_2(NHMe_2)_3$	$VOBr_2/NHMe_2$	a/d	91
$VOBr_2(NH_2Me)_6$	$VOBr_3/NH_2Me$	a/d	91
$VOBr_2(NHMe_2)_2$	$VOBr_3/NHMe_2$	a/d	91

Spectroscopic key: a-near i.r., b-far i.r., d-diffuse reflectance
e-electronic solution

1.5 OXOTETRABROMOVANADATE(IV) COMPLEXES

The $[VOBr_4]^{2-}$ ion was first detected as an ionic species in solution. Gutmann and Laussegger reported that the ion was formed when $VOBr_2$ was dissolved in ethanenitrile, trimethylphosphate and 1,2-propanediol carbonate [92] and in nitromethane [93]. These solutions were investigated by spectrophotometric, potentiometric and conductometric methods. Early attempts to isolate anionic oxo-bromo complexes from aqueous hydrogen bromide only resulted in reduction to vanadium(III), and the formation of aquabromovanadate(III) complexes [94].

More recently, however, some solid $[VOBr_4]^{2-}$ complexes have been prepared [40,41]. Two compounds, $[Et_4N]_2[VOBr_4]$ and $[pyH]_2[VOBr_4]$ were prepared by the reaction of vanadium(V) oxide tribromide with tetraethylammonium bromide and pyridinium bromide respectively, using nitromethane as solvent. $[Et_4N]_2[VOBr_4]$ could also be formed with ethanenitrile as solvent but when the pyridinium reaction was carried out in ethanenitrile, the complex $[pyH][VOBr_3(CH_3CN)_2]$ was formed.

The far i.r. spectrum of $[Et_4N]_2[VOBr_4]$ shows a complete and reversible transformation within the temperature range 293-308 K. Spectra were run on the same sample at 243 K, 308 K, and 243 K again, to study this transformation, and it was concluded [41] that the change was due to a reversible equilibrium between two different geometric forms of the $[VOBr_4]^{2-}$ ion: a C_{4v} form being stable at room temperature, a C_{2v} form being stable at lower temperatures. The C_{4v} species is stable at 308 K but only a very small percentage remains at 243 K. C_{4v} species are known to give only one strong band in this region. C_{2v} species show two strong bands in the region, as has been shown for $[VOCl_2(NMe_3)_2]$ [95].

In general the electronic spectra of the $[VOBr_4]^{2-}$ complexes were analogous to those of their chloro-counterparts [37,74,75].

1.6 E.P.R. STUDIES ON VANADIUM(IV) COMPLEXES

1.6.1 Introduction

The theory of electron paramagnetic resonance spectra can be found in standard texts [96-99] and will not be discussed in detail here. There have also been a number of books and reviews published, specifically

dealing with the e.p.r. spectra of transition metal ions [100-104] . There is however no single source which enables a simple interpretation of the e.p.r. spectra of vanadium(IV).

The computer simulation of vanadium(IV) e.p.r. spectra is an essential part of their interpretation. The only detailed publication upon computer simulation of vanadium(IV) e.p.r. spectra [105,106] has been shown to be in error [107]. Since then, however, programs have been developed [89] which should enable a far more accurate and detailed interpretation.

1.6.2 Isotropic Spectra of Vanadium(IV) Complexes

This section will concentrate on the room temperature solution spectra of vanadium(IV) complexes (i.e. a true isotropic situation). In the absence of a nuclear spin on vanadium, only a single resonance would be observed, due to the transition ($m_s = -\frac{1}{2}$) $\leftrightarrow$ ($m_s = +\frac{1}{2}$). However, ^{51}V (99.8% natural abundance) has a nuclear spin of 7/2, and so there is coupling between the nuclear spin, I, and the electron spin, S, in the absence of an external magnetic field. Thus, I and S are not "good" quantum numbers, and must be replaced by F such that:

$$\overline{F} = \overline{I} + \overline{S}$$

$$= {}^{7}/_{2} \pm {}^{1}/_{2} = 4,3$$

This coupling is broken down by a strong magnetic field, giving rise to eight possible electronic transitions governed by the selection rules:

$$\Delta m_I = 0, \ \Delta m_s = \pm 1.$$

Thus an e.p.r. spectrum containing eight lines would be expected, with seven equal hyperfine splittings.

1.6.3 Second-Order Correction and the Briet-Rabi Equation

As already stated, the ideal situation for vanadium(IV) complexes is that the hyperfine splitting between the eight lines is constant. However, in practice, this is not the case. The splittings increase going from low field to high field. This is due to a slight non-linearity of the m_I energy level splittings with magnetic field (originating with the weak coupling between I and S at low field strength). In order for g_{iso} and A_{iso} to be calculated from this spectrum, a correction must be applied. The Breit-Rabi equation [100,108] is an n^{th} -order expansion:

$$E_I = \frac{-\Delta W}{2(2I+1)} + g_N\beta_N m_F H \pm \frac{\Delta W}{2}\left\{\frac{1+4m_F x+x^2}{2I+1}\right\}^{\frac{1}{2}}$$

where

$$\Delta W = \frac{(2I+1)A}{2}$$

$$x = \frac{(g-g_N)\beta H}{\Delta W}$$

$$\simeq \frac{g\beta H}{\Delta W}$$

$$\beta_N = \frac{eh}{4\pi m_N c}$$

The second -order form of this equation is sufficient to explain the non-linearity of the vanadium spectra. The relationships between the experimental lines and the second-order correction lines are given by

$$H_1^{obs} = H_1 - \frac{7A^2}{4H_1}$$

$$H_2^{obs} = H_2 - \frac{19A^2}{4H_2}$$

$$H_3^{obs} = H_3 - \frac{27A^2}{4H_3}$$

$$H_4^{obs} = H_4 - \frac{31A^2}{4H_4}$$

$$H_5^{obs} = H_5 - \frac{31A^2}{4H_5}$$

$$H_6^{obs} = H_6 - \frac{27A^2}{4H_6}$$

$$H_7^{obs} = H_7 - \frac{19A^2}{4H_7}$$

$$H_8^{obs} = H_8 - \frac{7A^2}{4H_8}$$

where H_i^{obs} = experimental position of the i^{th} line

H_i = position after 2nd-order correction

As previously stated, a computer program can be used to apply this correction [89].

1.6.4 Anisotropic Spectra of Vanadium(IV) Complexes

If a solution of a complex is rapidly frozen to 77 K, a glass is formed. This glass gives rise to an anisotropic electron paramagnetic resonance spectrum of sixteen lines. This is a complex spectrum, consisting of two superimposed sets of eight lines (one due to species aligned parallel to the field, and the other due to species aligned perpendicular to the field). The major difficulty in interpreting these spectra is identifying which lines belong to which set. There are normally at least two equally likely assignments possible. When the assignment (or assignments) have been made, the second-order correction must be applied to these lines as follows.

For parallel species,

$$H_m^{obs} = H_m^{corr} - A_\perp \frac{[I(I+1)-m^2]}{2H_m^{corr}}$$

For perpendicular species

$$H_m^{obs} = H_m^{corr} - \frac{(A_\parallel^2 + A_\perp^2)\,[I(I+1)-m^2]}{4H_m^{corr}}$$

Thus, $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ can be calculated. An iterative computer program can again [89] be used to apply this second-order correction to the experimental results.

If only the parallel or perpendicular components can be identified, then the other can be calculated if the isotropic values are known. The isotropic and anisotropic parameters are related as follows:

$$g_{iso} = {}^{1}/_{3} (g_{\parallel} + 2g_{\perp})$$

$$A_{iso} = {}^{1}/_{3} (A_{\parallel} + 2A_{\perp})$$

1.6.5 Powder Spectra

In general, for solids, only a single broad absorption is observed. It is extremely rare to see hyperfine splitting from the nucleus. The three principal reasons for this are:

(a) Spin-lattice interactions
(b) Spin-spin interactions
(c) Broadening from (a) and (b) masks the hyperfine splitting

1.6.6. Vanadium(IV) e.p.r. literature

E.p.r. has been widely used as a technique to investigate the structure and bonding in many vanadium(IV) complexes. However, most of the work carried out has been concerned with oxovanadium(IV) chelates [109-112] , and the treatment of e.p.r. spectral parameters has, with some notable exceptions, been rather shallow. Where oxovanadium(IV) complexes containing monodentate ligands (of the type VOX_2L_n where X is a negatively-charged monodentate ligand and L a neutral monodentate ligand) are concerned, very little work has been done [29-31, 113,114] . The most thorough work has been published by Olivé and Henrici-Olivé [29-31] (on complexes $VOCl_2L_2$ produced in solution, but not isolated), and by Stewart and Porte [113] (on organometallic complexes). Two studies on the e.p.r. of the $[VOCl_4]^{2-}$ ion have been published [69,115] . Kon and Sharpless [69] studied the e.p.r. of the $[VOCl_4]^{2-}$ ion and compared it with the e.p.r. of both the $[CrOCl_5]^{2-}$ ion and the $[MoOCl_5]^{2-}$. Flowers *et al.* [115] carried out single crystal X-band e.p.r. studies of

oxovanadium(IV) in the matrix $[NH_4]_2[SbCl_5]$, which showed the impurity ions to substitute in an antimony site of approximately C_{4v} five-coordinate symmetry. Molecular orbital and ligand field calculations supported the assignment of the species responsible for the e.p.r. signal as $[VOCl_4]^{2-}$.

Olivé and Henrici-Olivé [29-31] studied a family of oxovanadium(IV)-phosphine complexes [29,30], $[VOCl_2(PR_3)_2]$, with varying bulkiness of the substituents R. Their e.p.r. spectra showed increasing linewidth with increasing molecular volume. The linewidth variation, they suggested, could be described by using an equation derived by Kivelson *et al.* [116-117] The spectrum of the compound $[VOCl_2(Et_3P)_2]$ was obtained both at room temperature in solution and in a rigid glass (2-methyltetrahydrofuran at -140 ^{o}C). At room temperature, the signal obtained was characteristic of the interaction of an unpaired electron of V(IV) with the ^{51}V nucleus ($I=^{7}/_{2}$) and with two equivalent ^{31}P nuclei ($I=\frac{1}{2}$), the latter interaction being responsible for the triplet splitting (1:2:1) of the eight vanadium lines. A study was then carried out [31] of the e.p.r. of a solution of $VOCl_2$ and tributylstibine in methylbenzene. The hyperfine lines of ^{121}Sb and ^{123}Sb were well resolved in the outer parts of the signal and values were obtained for the ligand hyperfine coupling constants. Henrici-Olivé and Olivé observed that a solution of $VOCl_2$ and excess Bu_3Sb in tetrahydrofuran gave a pure oxovanadium(IV) signal showing no interaction with the Sb nucleus. It was only when methylbenzene was used as solvent that fine structure was observed. The results obtained suggested that only one stibine molecule was coordinated to the vanadium.

SECTION 2 : EXPERIMENTAL METHODS

2.1. PREPARATION OF REAGENTS

2.1.1 Vanadium(IV) Oxide Dichloride

Anhydrous vanadium(IV) oxide dichloride was prepared by the method previously used by Du Preez and Sadie [16]. A mixture of vanadium(IV) oxide dichloride dihydrate (100 cm^3) and thionyl chloride (500 cm^3) was heated under reflux for six hours under dry nitrogen. A green solid was deposited and fumes of sulphur dioxide and hydrogen chloride were evolved during the reaction. When the reaction was complete, the evolution of gas ceased. After allowing the reaction flask to cool to room temperature, the supernatant liquid was decanted, and the green solid was dried *in vacuo* for twenty-four hours so that no thionyl chloride impurity remained. Analysis indicated a vanadium to chloride ratio of 1:2.02. (Found: V, 35.35; Cl, 49.68. Calc. for $VOCl_2$: V 36.96; Cl 51.44%).

12.1.2 Pyridinium Chloride

Hydrogen chloride was passed through a solution of pyridine (50 cm^3) in diethyl ether (500 cm^3). The white solid formed was collected by filtration, washed with diethyl ether (20 cm^3) and dried *in vacuo*.

2.2. PURIFICATION OF SOLIDS

2.2.1 Ionic Chlorides

Tetraphenylarsonium chloride (*ex* Cambrian) and tetramethylammonium chloride (*ex* BDH) were both dried *in vacuo* . Tetraethylammonium chloride monohydrate (*ex* BDH) was dried by heating at 353 K *in vacuo*. The water of hydration was lost and anhydrous tetraethylammonium chloride remained.

2.2.2 Other Solids

Triphenylarsine (*ex* Aldrich), triphenylstibine (*ex* Aldrich), triphenylamine (*ex* Aldrich), triphenylphosphine (*ex* BDH), triphenylphosphine oxide (*ex* Aldrich), tricyclohexylphosphine (*ex* Maybridge) bis(diphenylphsophino)methane (*ex* BDH), 1,2-bis(diphenylphosphino)ethane (*ex* BDH), diphenylsulphoxide (*ex* Fluorochem) and tetramethylthiourea (*ex* Aldrich) were used without purification. Tetramethylthiourea was stored in a refrigerator at 275 K.

2.3. PURIFICATION OF LIQUIDS

2.3.1 Vanadium(IV) Oxide Dichloride Dihydrate

Vanadium(IV) oxide dichloride dihydrate (*ex* BDH) was used without further purification.

2.3.2. Thionyl Chloride

Thionyl chloride (*ex* BDH) was used without further purification.

2.3.3. Nitrogen Donor Ligands

Pyridine (*ex* BDH) was dried over calcium hydride and purified by distillation *in vacuo*.

2.3.4. Oxygen Donor Ligands

Tetramethylurea (*ex* BDH), dimethylsulphoxide (*ex* Fisons) and hexamethylphosphoramide (*ex* Fisons) were all used without further purification.

2.3.5. Phosphorus Donor Ligands

Dimethylphenylphosphine (*ex* Maybridge) and methyldiphenylphosphine (*ex* Maybridge) were both used without further purification.

2.3.6. Solvents

Ethanenitrile (*ex* Fisons) was dried over phosphorus pentoxide and purified by distillation *in vacuo*.

Tetrahydrofuran (*ex* Fisons) and dichloromethane (*ex* Fisons) were dried by heating under reflux over calcium hydride and purified by distillation at atmospheric pressure.

Diethyl ether (*ex* Fisons) was used without further purification.

2.4. PURIFICATION OF GASES

"White spot" (< 1 ppm oxygen) nitrogen gas (*ex* B.O.C.) was dried by passage through columns of silica gel and phosphorus pentoxide suspended on glass wool.

Hydrogen chloride (*ex* Air Products) was dried by passage through concentrated sulphuric acid.

2.5. EXPERIMENTAL TECHNIQUES

2.5.1 Analytical Methods

Carbon, hydrogen, nitrogen and chlorine were determined by the microanalysis department of the Inorganic Chemistry Laboratory, Oxford and also by the Butterworth Microanalytical Consultancy Ltd., Middlesex. Vanadium and phosphorus (organic) were determined when necessary by The Butterworth Microanalytical Consultancy Ltd., Middlesex. Facilities in the Oxford department did not include the use of a dry box for air-sensitive compounds and this accounts for low analysis values occasionally obtained for halide.

2.5.2 Vacuum Line

Manipulations described as being performed *in vacuo* were carried out on a standard vacuum line. Techniques used included filtration and distillation. Descriptions of these vacuum techniques can be found in standard sources [118,119]. On one occasion filtration was carried out using standard Schlenk-line techniques. These too are described in detail in standard sources [119].

2.5.3. Dry Box

All of the vanadium(IV) complexes mentioned in this report are readily hydrolysed by moisture in the atmosphere. Manipulations of vanadium(IV) complexes were, therefore, carried out in a glove-box. The glove-box was flushed continuously with dry nitrogen, and contained an open bowl of phosphorus pentoxide.

Glassware and syringes were dried in an oven at 393 K and allowed to cool in a dessicator containing silica gel before introduction to the glove box. All common manipulations (e.g. mull and solution preparation, filling of analysis tubes or e.p.r. tubes etc.) were carried out in the dry box.

2.5.4. Infrared Spectroscopy

Infrared spectra were measured on a Perkin-Elmer 457 spectrometer (4000-250 cm^{-1}). Measurements were carried out using mulls of the various compounds in nujol. Spectra were calibrated by recording standard absorption frequencies for a thin polystyrene film (1601.5 cm^{-1} and 1028 cm^{-1}) and for indene (590.8 cm^{-1} and 381.4 cm^{-1}). Caesium iodide plates were used for all mull measurements, and for indene calibrations.

2.5.5. Electronic Spectroscopy

Electronic spectra were recorded on a Unicam SP700C spectrophotometer. Diffuse reflectance spectra were obtained using a standard attachment, with magnesium oxide as reference.

2.5.6. Electron Paramagnetic Resonance Spectroscopy

(i) The Spectrometer

E.p.r. spectra were recorded on a Jeol JES-3BX ESR spectrometer [120]. The important features of this instrument are illustrated schematically in Fig 2.1.

Traces of first derivative e.p.r. spectra were made using a servoscribe (Smith desk-type servoscribe potentiometric) chart recorder. A chart speed of no more than 1 cm min^{-1}, together with a scan time of at least 30 min were found necessary in order to obtain a well resolved spectrum.

A JES-VT-2 temperature controlling unit incorporated into the spectrometer enabled solution spectra to be recorded at temperatures in the region of 135 K. The unit operates by blowing cold nitrogen gas through the sample cavity and the cavity temperature is measured by means of a copper-constantan thermocouple probe.

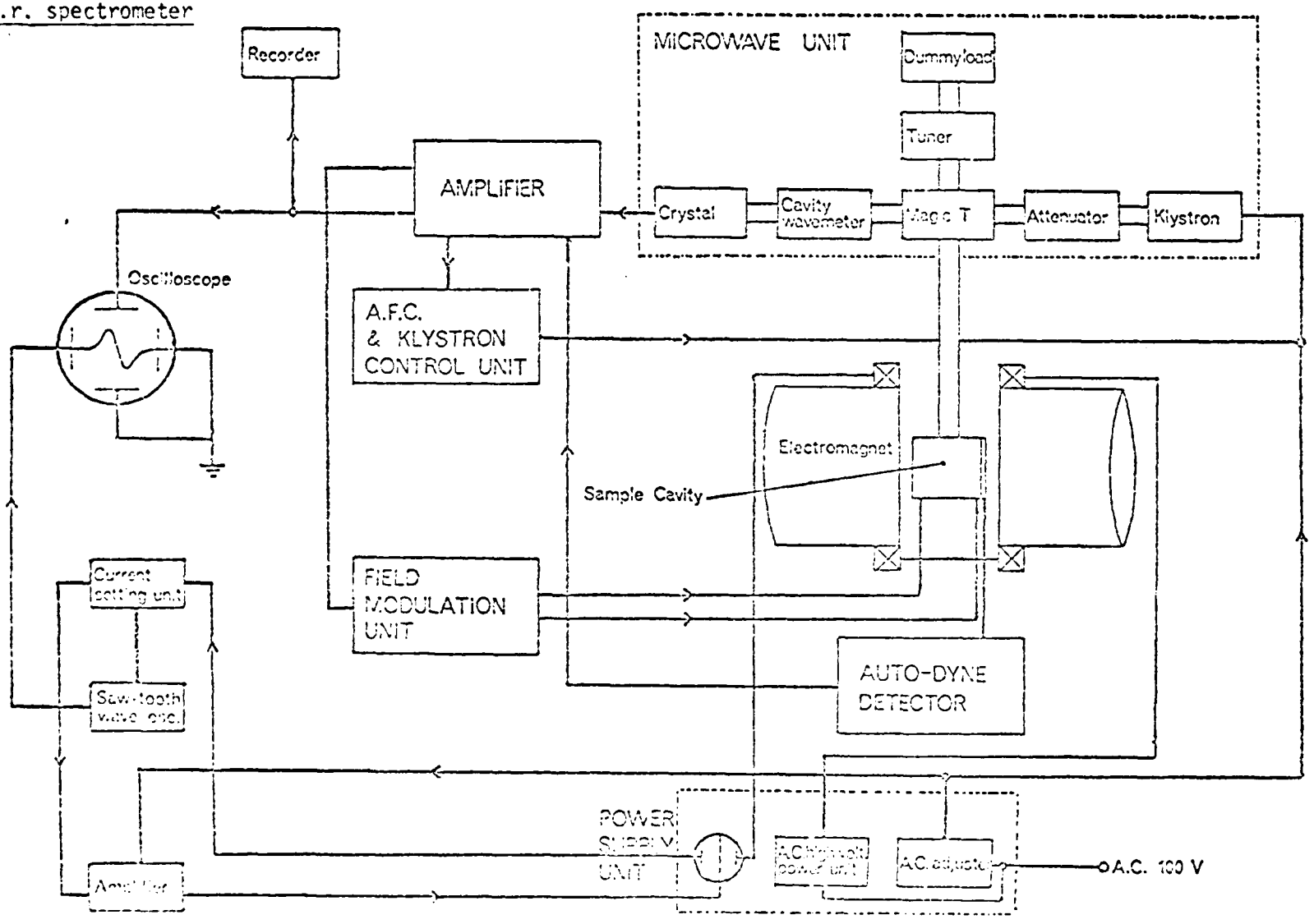
(ii) Sample Preparation

Solid samples were loaded into standard quartz e.p.r. tubes which were sealed with sealing wax and a sealing film to minimise the possibility of hydrolysis. For solutions of vanadium(IV) complexes in tetrahydrofuran standard e.p.r. tubes were again used. However, because ethanenitrile exhibits high dielectric loss, solutions of complexes in ethanenitrile were loaded into specially constructed liquid cells which allow a thin film of solution to be trapped between two flat walls of thin quartz glass. Concentrations of solutions of vanadium(IV) complexes used were in the range 10^{-3} *M* to 3.5×10^{-3} *M*. These concentrations enabled strong e.p.r. signals to be obtained, and yet were not sufficiently high for spin-spin broadening to occur to a significant extent [97].

(iii) Operation of the Spectrometer

For work on solid samples of vanadium(IV) complexes, the modulation amplitude used does not seem to be particularly important. Previous work was carried out with the modulation amplitude set at 18G [89], whereas work reported in this thesis was carried out with the amplitude set at 2 - 2.5G.

Fig 2.1 Structure of the JES-3BX e.p.r. spectrometer



(iv) Calibration of Spectra

The magnetic field per cm of chart paper was determined for each spectrum by calibration with a powdered sample of magnesium oxide containing manganese cations. The distance between the third and fourth lines corresponds to 86.7G.

It proved to be vital that calibrations were carried out under the same conditions (i.e. chart speed, scan time and sweep range) as the spectrum recorded for the sample concerned. To illustrate this, two manganese calibration spectra were recorded, under different conditions, for the same vanadium(IV) spectrum. The first calibration spectrum, run with a sweep range of ± 2000 G and a scan time of 60 min. gave a calibration of 39.25 G cm^{-1}. After suitable scaling down, the second calibration spectrum, run with a sweep range of ± 500G and a scan time of 30 min., gave a calibration of 41.65 G cm^{-1} for the same spectrum. These results show how an error of 5-6% could be introduced by recording calibration spectra under different conditions from those under which the original vanadium(IV) spectrum was recorded.

Positions of resonance, and hence g-factors, for each spectrum were determined by calibration with a powdered sample of 1,1-diphenyl-2-picrylhydrazyl (DPPH): g=2.0036. Further details concerning calibration and measurement of spectra can be obtained readily from standard texts [96-99].

2.5.7 Computer Programs

The two computer programs, ESRRT and ESRLT, used in this work are written in Algol 60 for use on the Oxford University Computing Laboratory 1906A computer. The programs [89] , were used to interpret and simulate e.p.r. spectra. Computer programs such as these are necessary in order to make unambiguous assignments of spectral lines in anisotropic and complex isotropic spectra of axially symmetric d^1 systems.

ESRRT simulates isotropic spectra. The input data contains approximate or accurate values of g_{iso}, A_{iso} and ligand hyperfine coupling constants (where appropriate). The data also specifies abundances and nuclear spins of the metal atom and coupled ligands and defines the experimental conditions. The program calculates the positions of the theoretical, high-field nuclear hyperfine spectral

lines by application of the Breit-Rabi second-order correction [108] to the input positions of experimentally observed lines. Values of g_{iso} and A_{iso} can then be extracted, and their reliability checked by comparing the final simulated spectrum (generated from these values) with the original experimental spectrum. The program then applies the second order correction in the reverse sense and simulates positions of resonance giving each line its correct relative intensity and a suitable lineshape. Finally the program differentiates the simulated e.p.r. absorption spectrum and an annotated, calibrated, first derivative spectrum is plotted.

ESRLT (recently renamed ESRLOWTEMP following minor alterations) deals fairly similarly with anisotropic e.p.r. spectra. Here the input data contains approximate values of $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ along with all the other input data mentioned for ESRRT. Experimentally obtained anisotropic spectra often show complex fine structure due to the superimposition of eight perpendicular nuclear hyperfine lines on eight parallel nuclear hyperfine lines. It is extremely difficult to unambiguously interpret such a spectrum. The input data for the first simulation of a spectrum includes measured distances of parallel and perpendicular lines from the DPPH calibration line, corresponding to a trial interpretation of the fine structure. The program will use this data to calculate the different g and A values and to simulate the spectrum. By comparing the simulated spectrum with the experimental, it is often possible to see where adjustments have to be made in the interpretation and measurement of the experimental spectrum. The experimental spectrum is then remeasured and the program used again with a new set of input data. A different set of g and A values, and a different, and hopefully improved, simulation will be obtained. This process may need to be repeated a number of times before the simulated spectrum obtained corresponds almost exactly to the original spectrum. In practice, this can involve up to ten iterations. The final set of g and A values are then considered to be the most accurate set.

SECTION 3 : EXPERIMENTAL

All the reactions described in this section were carried out under dry nitrogen unless otherwise stated.

3.1. REACTION $VOCl_2$ WITH ETHANENITRILE

Ethanenitrile (400 cm^3) was distilled *in vacuo* into a flask containing green vanadium(IV) oxide dichloride (60 g). An exothermic reaction took place immediately and the flask was cooled to prevent excess local heating. A blue solution was formed. After leaving the solution and any remaining solid to stand for twenty-four hours at room temperature, the flask was heated under reflux for two hours. The solution was then filtered *in vacuo* while still hot to remove impurities. The blue solution was then kept at 243 K for fiteen hours, during which time a blue solid formed. The flask was shaken vigorously to break up the solid, and the blue powder was then filtered off *in vacuo*, washed with ethanenitrile (20 cm^3), and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	21.9	2.95	12.4	32.1
Required for $VOCl_2(CH_3CN)_2$	21.84	2.75	12.74	32.24

The infrared spectrum confirmed the presence of coordinated ethanenitrile in the complex. The method used in this preparation is based on that used by Du Preez and Sadie [16]. They found, however, that their product was more consistent with the formulation $VOCl_2(CH_3CN)_{2.5}$. It is a well-known phenomenon that ethanenitrile complexes of vanadium have varying stoicheiometries depending upon the length of time for which they are evacuated[41].

3.2. REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH PYRIDINIUM CHLORIDE AND HEXAMETHYLPHOSPHORAMIDE

3.2.1 Mole Ratio 1:1.8:2.5 ($V:[pyH]^+:hmpa$)

Oxodichlorobis(ethanenitrile)vanadium(IV) (3.6 g) was dissolved in ethanenitrile (75 cm^3), giving a blue solution. Pyridinium chloride (2.35 g) was added to this, and the reaction flask was left to stand at room temperature until, after frequent, vigorous shaking, all the pyridinium chloride dissolved to give a green solution.

Hexamethylphosphoramide (8.1 cm^3) was added, finally, giving a blue-green solution. The solution was left to stand at 243 K for twenty-four hours, whence the blue-green crystals were formed. These were filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	29.3	8.12	16.9	14.4
Required for $VOCl_2(C_6H_{18}N_3OP)_2$	29.04	7.31	16.93	14.29

The infrared spectrum supports the identification of the product as oxodichlorobis(hexamethylphosphoramide)vanadium(IV).

3.2.2. Large Excess of [pyH]Cl and hmpa

Oxodichlorobis(ethanenitrile)vanadium(IV) (1 g) was dissolved in ethanenitrile (200 cm^3). Pyridinium chloride (5.5 g) was added to the solution followed by hexamethylphosphoramide (4.5 cm^3). When all the solid had dissolved, the blue-green solution was left to stand at 243 K for forty-eight hours, whence royal-blue microcrystals were formed. These were filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl	%P
Found	38.0	4.3	9.3	33.1	3.6

3.2.3 Mole Ratio 1:1:1.2 (V:[pyH]$^+$:hmpa)

The preparation was repeated as in 3.2.1 using oxochlorobis-(ethanenitrile) vanadium(IV) (1.8 g), pyridinium chloride (1.1 g), hexamethylphosphoramide (1.9 cm^3) and ethanenitrile (35 cm^3). After standing at 243 K for twenty-four hours, blue-green crystals were formed. Light-blue solid was also deposited on the sides of the flask. After vigorous shaking this solid broke away from the glass as thin "plates". All the solid was filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*. After drying for fifteen hours, some of the light-blue solid had undergone a colour change to light-green. The darker, blue-green crystals were separated from the rest of the solid and were identified by their infrared

spectrum as oxodichlorobis(hexamethylphosphoramide)vanadium(IV): no bands due to pyridinium cations were observed.

Analysis of the light-blue/light-green solid gave:

	%C	%H	%N	%Cl
Found	33.9	3.67	7.77	34.5
Required for $[C_5H_6N]_2[VOCl_4]$	32.55	3.28	7.59	38.43

The light-blue and light-green solids were separated to some extent in the dry box and infrared spectra were recorded for both the blue-rich and green-rich samples. Both were similar to those recorded at other times for $[pyH]_2[VOCl_4]$ samples. Both spectra confirmed the absence of coordinated hexamethylphosphoramide.

3.3. REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH TETRAETHYLAMMONIUM CHLORIDE AND HEXAMETHYLPHOSPHORAMIDE

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved in ethanenitrile (75 cm^3). Tetraethylammonium chloride (1.4 g) was added, giving a green solution. Finally, hexamethylphosphoramide (7.5 cm^3) was added and the solution became blue-green in colour. After allowing the flask to stand at 243 K for forty-eight hours, the solution was concentrated to 25 cm^3 by distilling off ethanenitrile *in vacuo*. Blue-green crystals were seen at this stage, and more of these crystals were formed when the flask was again left to stand at 243 K for forty-eight hours. The crystals were then filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	29.2	7.77	17.1	14.3
Required for $VOCl_2(C_6H_{18}N_3PO)_2$	29.04	7.31	16.93	14.29

The infrared spectrum confirmed the presence of coordinated hexamethylphosphoramide and the absence of tetraethylammonium cations.

3.4 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH PYRIDINIUM CHLORIDE AND TRIPHENYLPHOSPHINE OXIDE

3.4.1 Mole Ratio 1:1.2:2.2 ($V:[pyH]^+:Ph_3PO$)

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved

in ethanenitrile (75 cm^3). Pyridinium chloride (1.3 g) was added to the blue solution and a green colour resulted. Triphenylphosphine oxide (5.5 g) was added to the solution and almost immediately a pale-green powder was precipitated. The supernatant liquid remained green. The flask was allowed to stand at room temperature for several days and was vigorously shaken at regular intervals. The powder was then filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	62.2	4.56	0.00	10.4
Required for $VOCl_2(C_{18}H_{15}PO)_2$	62.27	4.35	0.00	10.21

The infrared spectrum confirmed the presence of coordinated triphenylphosphine oxide and the absence of pyridinium cations.

3.4.2 Mole Ratio 1:5:2 ($V:[pyH]^+:Ph_3PO$)

3.4.1 was repeated using oxodichlorobis(ethanenitrile)vanadium(IV) (2.2 g) in ethanenitrile (200 cm^3), pyridinium chloride (7 g) and triphenylphosphine oxide (5.5 g). Again some pale-green powder was precipitated on addition of the triphenylphosphine oxide, but the yield was small compared with that obtained in 3.4.1. Nevertheless the powder was filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*. The green filtrate was collected and left to stand at 275 K.

Analysis of the green powder gave:

	%C	%H	%N	%Cl
Found	61.7	4.38	0.00	10.4
Required for $VOCl_2(C_{18}H_{15}PO)_2$	62.27	4.35	0.00	10.21

Again the infrared spectrum confirmed the presence of coordinated triphenylphosphine oxide and the absence of pyridinium cations.

After several days standing at 275 K, blue-green crystals were precipitated from the green filtrate. These were filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*. The compound was identified by its infrared spectrum as being oxodichlorobis(triphenylphosphine oxide)vanadium(IV).

3.5 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH PYRIDINIUM CHLORIDE

3.5.1 Mole Ratio 1:3 (V:[pyH]Cl)

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved in ethanenitrile (80 cm^3). Pyridinium chloride (3.6 g) was added, giving a green solution. After standing for twenty-four hours at room temperature some light-coloured powder remained at the bottom of the flask. It was not clear whether this was a light-green product or simply white pyridinium chloride so ethanenitrile (60 cm^3) was added to redissolve the solid. The solution was left at 243 K for several days and a light-green solid precipitated out of the solution, which was then filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*. The green filtrate was collected and left to stand at 243 K.

Analysis of the green powder	%C	%H	%N	%Cl
Found	32.9	3.35	7.91	38.3
Required for $[C_5H_6N]_2[VOCl_4]$	32.55	3.28	7.59	38.43

The infrared spectrum confirmed the presence of pyridinium cations.

The green filtrate was left to stand at 243 K for a few days, whence both royal-blue and green solids were precipitated. The reaction flask was allowed to warm up to room temperature, and the solid became uniformly green. The flask was cooled again to 243 K and some blue colour returned. The flask was then left at 243 K for three months, during which time most of the originally green solid turned royal-blue. The solid was then filtered off *in vacuo* at 243 K using Schlenk-line techniques and was washed with cold ethanenitrile. The blue solid was maintained at 243 K, dried *in vacuo*, and then allowed to warm slowly to room temperature. Some of the blue solid underwent a colour change to green again. The blue and green solids were then separated from one another in the dry box.

Analysis for blue solid	%C	%H	%N	%Cl
Found	32.1	3.61	7.61	40.2
Required for $[C_5H_6N]_2[VOCl_4]$	32.55	3.28	7.59	38.43

Analysis for green solid	%C	%H	%N	%Cl
Found	34.3	4.52	8.65	35.3
Required for $[C_5H_6N]_2[VOCl_4]$	32.55	3.28	7.59	38.43

The infrared spectra of the two compounds were markedly different.

3.5.2 Mole Ratio (1:4) (V:[pyH]Cl)

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved in ethanenitrile (120 cm^3). Pyridinium chloride (4.3 g) was added, giving a green solution. After a few minutes a green precipitate was observed. After standing at room temperature for an hour, some of the solid had undergone a colour-change to royal blue. The percentage of solid which was blue in colour increased gradually. The flask was then left to stand at 275 K for two weeks. The solid, now predominantly blue in colour, was filtered off *in vacuo*, washed with ethanenitrile (10 cm^3), and dried *in vacuo*. When the solid had warmed to room temperature, it had become predominantly green. Attempts at separating the blue and green solids proved to be ineffective and so analysis was carried out on the mixture.

	%C	%H	%N	%Cl
Found	36.6	4.09	8.39	34.8
Required for $[C_6H_6N]_2[VOCl_4]$	32.55	3.28	7.59	38.43

The infrared spectrum confirmed the presence of pyridinium cations.

3.6 *REACTION OF* $[VOCl_2(CH_3CN)_2]$ *WITH TETRAETHYLAMMONIUM CHLORIDE*

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved in ethanenitrile (75 cm^3). Tetraethylammonium chloride (2.6 g) was added, giving a green solution. The solution was kept at 243 K for forty-eight hours but no precipitate was seen. After allowing the flask to warm to room temperature, the solution was concentrated to 30 cm^3 by distilling off ethanenitrile *in vacuo*. Green crystals were deposited at this stage. The flask was then left at 243 K for a further two days and more green crystals were formed. These were filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	40.9	9.05	6.00	30.5
Required for $[(C_2H_5)_4N]_2[VOCl_4]$	40.95	8.95	5.97	30.22

The infrared spectrum confirmed the presence of tetraethylammonium cations.

3.7 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH TETRAMETHYLAMMONIUM CHLORIDE

Oxodichlorobis(ethanenitrile)vanadium(IV) (3.3 g) was dissolved in ethanenitrile (140 cm^3). Tetramethylammonium chloride (4.9 g) was added, giving a blue-green solution. Both reagents took over twenty-four hours to dissolve completely and then a short while later a very pale-green solid was deposited. The solid was filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*. It was clear that the solid was not in fact a homogeneous pale-green solid but a mixture of pale-green and white solids.

Analysis	%C	%H	%N	%Cl
Found	29.7	8.33	8.98	32.9
Required for $[(CH_3)_4N]_2[VOCl_4]$	26.91	6.78	7.85	39.72

The product was a mixture of the green $[Me_4N]_2[VOCl_4]$ and the white starting material tetramethylammonium chloride. An attempt to repeat the preparation gave an even more heavily contaminated product.

3.8. REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH TETRAPHENYLARSONIUM CHLORIDE

(a) Oxodichlorobis(ethanenitrile)vanadium(IV) (1.1 g) was dissolved in ethanenitrile (90 cm^3). Tetraphenylarsonium chloride (4.4 g) was added, giving a green solution. After standing at 275 K for a few days, the only solid deposited was a small amount of white powder - presumably tetraphenylarsonium chloride. This white powder was filtered off *in vacuo*. The green filtrate was collected and left to stand at 243 K for forty-eight hours. The solution was then concentrated to 20 cm^3 by distilling off ethanenitrile *in vacuo*. The solution was kept at 275 K for twenty-four hours, by which time a green solid had formed. The solid was filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	59.8	4.16	0.00	14.6
Required for $[(C_6H_5)_4As]_2[VOCl_4]$	59.10	4.13	0.00	14.54

The infrared spectrum confirmed the presence of tetraphenylarsonium cations.

(b) A second preparation was carried out with a similar 1:2 mole ratio. Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved in ethanenitrile (100 cm^3). Tetraphenylarsonium chloride (7.7 g) was added to the blue solution. After frequent, vigorous shaking over a period of half an hour at room temperature all the solid dissolved to give a green solution. The solution was immediately concentrated to 20 cm^3 bydistilling off ethanenitrile *in vacuo*. The solution was then left to stand at room temperature for seventy-two hours and large green needle-like crystals were formed. These crystals were then filtered off *in vacuo*, washed with ethanenitrile (5 cm^3) and dried *in vacuo*.

The crystal form was lost during the evacuation and a light-green powder resulted.

Analysis	%C	%H	%N	%Cl
Found	58.7	3.92	0.00	14.6
Required for $[(C_6H_5)_4As]_2[VOCl_4]$	59.10	4.13	0.00	14.54

Again the infrared spectrum confirmed the presence of tetraphenylarsonium cations.

A small amount of the product was dissolved in dichloromethane and recrystallised. The product was crystalline.

3.9 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH PYRIDINE

3.9.1 In Tetrahydrofuran

3.9.1.1 Mole Ratio 1:3.5 (V:py)

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was added to tetrahydrofuran (75 cm^3), giving a dark-blue solution. When pyridine (2.6 cm^3) was added, the solution turned green. The solution was then left to stand at 243 K for forty-eight hours, whence a light-blue solid formed in very small yield. The solution also became a lighter blue in colour. The solid was filtered off *in vacuo*, washed with tetrahydrofuran (5 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	38.1	3.99	8.58	23.0
Required for $VOCl_2(C_5H_5N)_2$	40.57	3.40	9.46	23.95

The infrared spectrum for the product confirmed the presence of coordinated pyridine.

3.9.1.2 Mole Ratio 1:6 (V:py)

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved in tetrahydrofuran (125 cm^3). Pyridine (4.5 cm^3) was added, giving a turquoise solution. The solution was left to stand for twenty-four hours at 433 K and a blue solid was formed. The blue solid was filtered off *in vacuo*, washed with tetrahydrofuran (5 cm^3) and dried *in vacuo*. The yield of the solid was again very small. An infrared spectrum was recorded and this confirmed the presence of coordinated pyridine. The spectrum was different from that obtained in 3.9.1.1. There was insufficient product for analysis to be carried out.

3.9.2 In Ethanenitrile

Oxodichlorobis(ethanenitrile)vanadium(IV) (1.2 g) was dissolved in ethanenitrile (50 cm^3). Pyridine (2.7 cm^3) was added, giving a blue-green solution. After standing at 243 K for a week, the solution was concentrated to 15 cm^3 by distilling off ethanenitrile *in vacuo*. A pale blue-green solid was precipitated and the solution darkened in colour. The solution was evacuated to dryness giving a pale blue-green solid.

Analysis	%C	%H	%N	%Cl
Found	44.2	4.31	10.3	20.6
Required for $VOCl_2(C_5H_5N)_2$	40.57	3.40	9.46	23.95
" " $VOCl_2(C_5H_5N)_3$	48.02	4.03	11.20	18.90
" " $VOCl_2(C_5H_5N)_{2.5}$	44.78	3.76	10.45	21.16

Two infrared spectra were recorded for the product, the first soon after preparation and the second after two months, by which time the compound had undergone a colour change to green. Both spectra confirmed the presence of coordinated pyridine, but the two spectra were different from each other.

3.10 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH TRIPHENYLPHOSPHINE

3.10.1 In Tetrahydrofuran

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved in tetrahydrofuran (125 cm^3). Triphenylphosphine (7.2 g) was added, giving a royal-blue solution. After standing at 243 K for a few days, the solution was concentrated to 25 cm^3 by distilling off tetrahydrofuran *in vacuo*. A dark-green solid was deposited at this stage. The solid was filtered off *in vacuo*, washed with tetrahydrofuran (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	65.7	4.89	0.00	10.8
Required for $VOCl_2(C_{18}H_{15}P)_2$	65.27	4.56	0.00	10.85

The infrared spectrum confirmed the presence of coordinated triphenylphosphine.

3.10.2 In Ethanenitrile

Oxodichlorobis(ethanenitrile)vanadium(IV) (2.2 g) was dissolved in ethanenitrile (80 cm^3). Triphenylphosphine (8 g) was added, giving a blue-green solution. After standing at room temperature for a few minutes, a dark green powder was precipitated in large quantity. The solid was filtered off *in vacuo*, washed in ethanenitrile (20 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	65.8	4.59	0.00	10.9
Required for $VOCl_2(C_{18}H_{15}P)_2$	65.27	4.56	0.00	10.85

The infrared spectrum again confirmed the presence of coordinated triphenylphosphine.

3.11 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH TRICYCLOHEXYLPHOSPHINE

(a) Oxodichlorobis(ethanenitrile)vanadium(IV) (2.8 g) was dissolved in tetrahydrofuran (90 cm^3). Tricyclohexylphosphine (7.7 g) was added, giving a blue-green solution. After standing at room temperature for a few minutes, a light-green powder was precipitated in large quantity. The solid was filtered off *in vacuo*, washed with tetrahydrofuran (20 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl	%P
Found	51.5	7.36	0.00	17.0	7.23
Required for $VOCl_2(C_{18}H_{33}P)$	51.69	7.45	0.00	17.9	7.41

The infrared spectrum confirmed the presence of tricyclohexylphosphine.

(b) The preparation was repeated for the same mole ratio, but with different quantities, namely oxodichlorobis(ethanenitrile)vanadium(IV) (2.5 g), tetrahydrofuran (80 cm^3) and tricyclohexylphosphine (6.8 g). A similar light-green powder was precipitated.

Analysis	%C	%H	%N	%Cl
Found	52.0	7.53	0.00	17.1
Required for $VOCl_2(C_{18}H_{33}P)$	51.69	7.45	0.00	17.19

Again the infrared spectrum confirmed the presence of tricyclohexylphosphine.

3.12 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH DIPHENYLSULPHOXIDE

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved in tetrahydrofuran (75 cm^3). Diphenylsulphoxide (5.4 g) was added, giving a royal-blue solution. The solution was left to stand for a week at 243 K. A small amount of light-blue solid was deposited. The solution was concentrated to 20 cm^3 by distilling off tetrahydrofuran *in vacuo*. The solution was left to stand at 243 K for a further two days and a larger quantity of the blue solid was precipitated, which was filtered *in vacuo*, washed with tetrahydrofuran (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	58.4	4.60	0.00	9.47
Required for $VOCl_2(C_{12}H_{10}SO)_3$	58.07	4.06	0.00	9.66

The infrared spectrum confirmed the presence of coordinated diphenylsulphoxide.

3.13 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH DIMETHYLSULPHOXIDE

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved in tetrahydrofuran (75 cm^3). Dimethylsulphoxide (4 cm^3) was added, giving a green solution. After a few minutes there appeared to be a fine suspension of light blue-green solid in the solution. After vigorous shaking, a turquoise oil separated from the green solution. After further vigorous shaking, the oil became a light blue-green solid and the solution darkened slightly. The solution was left to stand for a week at 275 K, by which time more solid had been deposited, and the solution had turned pale-green. The solid was then filtered off *in vacuo* , washed with tetrahydrofuran (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	19.1	5.27	0.00	19.0
Required for $VOCl_2(C_2H_6SO)_3$	19.36	4.87	0.00	19.32

The infrared spectrum recorded for the compound confirmed the presence of coordinated dimethylsulphoxide.

3.14 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH TRIPHENYLSTIBINE

3.14.1. In Ethanenitrile

3.14.1.1 Mole Ratio 1:3 (V:Ph_3Sb)

Oxodichlorobis(ethanenitrile)vanadium(IV) (1.8 g) was dissolved in ethanenitrile (90 cm^3). Triphenylstibine (8.8 g) was added to the blue solution. The solution, which did not change colour appreciably on addition of the triphenylstibine, was left to stand for twelve hours at room temperature, and then for a further three days at 243 K. A pale solid was deposited. This solid was filtered *in vacuo*, and the white needle-like crystals were washed with ethanenitrile (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N
Found	61.3	4.50	0.00
Required for $C_{18}H_{15}Sb$	61.23	4.28	0.00

The infrared spectrum confirmed that the white compound was triphenylstibine.

3.14.1.2 Mole Ratio 1:1 ($V:Ph_3Sb$)

The reaction was repeated with oxodichlorobis(ethanenitrile)vanadium(IV) (2.6 g), ethanenitrile (60 cm^3) and triphenylstibine (4.2 g). The reactants did not dissolve readily, even after frequent, vigorous shaking. More ethanenitrile (30 cm^3) was added. The reactants still did not dissolve, but the solution darkened, gradually, to a fairly dark blue, and some heat was evolved. After leaving to stand for forty-eight hours at room temperature both the solution and the remaining solid had become black in colour, suggesting reduction had occurred.

3.14.2 In Tetrahydrofuran

Oxodichlorobis(ethanenitrile)vanadium(IV) (1.5 g) was dissolved in tetrahydrofuran (80 cm^3). Triphenylstibine (7.2 g) was added, giving a royal-blue solution. The solution was left to stand at 275 K for twenty-four hours, during which time a white precipitate formed. The solution was allowed to warm to room temperature and it became dark-blue in colour very rapidly. The solution was then left to stand for twenty-four hours in a dark place but the colour continued to darken and a blue-black solid was deposited. The dark solid was filtered off *in vacuo*, washed with tetrahydrofuran (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	9.32	2.39	0.44	2.95

The infrared spectrum recorded for the dark solid was similar to those of vanadium oxides.

3.15 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH TRIPHENYLARSINE

Oxodichlorobis(ethanenitrile)vanadium(IV) (2 g) was dissolved in ethanenitrile (100 cm^3). Triphenylarsine (2.8 g) was added to the solution but the royal-blue colour remained unchanged. Some heat was evolved as the solids dissolved. The solution was left to stand at

room temperature for six weeks, by which time only a small amount of white solid remained undissolved. This solid was filtered off *in vacuo*. The royal-blue filtrate was collected, and left to stand at room temperature for a further two days. The solution was then concentrated to 20 cm^3 by distilling off ethanenitrile *in vacuo*. Blue crystals and a light-grey powder were both deposited at this stage. All the solid was filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*. The blue crystals were then separated from the grey solid in the dry box, and were identified by their infrared spectrum which was identical to that obtained for the oxodichlorobis(ethanenitrile)vanadium(IV) starting material.

Analysis was carried out for the grey solid.

	%C	%H	%N
Found	68.2	5.07	0.00
Required for $C_{18}H_{15}As$	70.60	4.94	0.00

The infrared spectrum for the grey solid was identical to the spectrum of triphenylarsine.

3.16 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH TRIPHENYLAMINE

Oxodichlorobis(ethanenitrile)vanadium(IV) (2.4 g) was added to ethanenitrile (125 cm^3). Triphenylamine (4.8 g) was added to the solution and a turquoise colour resulted. Large proportions of both reactants remained undissolved despite vigorous shaking and the solution was left standing at room temperature for eighteen hours. The solution turned green-brown in colour and a white solid formed in large quantity. After standing at room temperature for a few days, the white solid was filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*. The green-brown filtrate was collected and left to stand for a few days at 275 K, by which time both blue crystals and more white solid had formed. After a further week at 275 K the blue crystals became contaminated with black impurity and the solution was discarded.

Analysis of the white solid	%C	%H	%N
Found	88.8	6.40	5.92
Required for $C_{18}H_{15}N$	88.13	6.16	5.71

The infrared spectrum for the white product was identical to that of triphenylamine.

3.17 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH TETRAMETHYLUREA

Oxodichlorobis(ethanenitrile)vanadium(IV) (2.8 g) was added to ethanenitrile (65 cm^3). Tetramethylurea (3.5 cm^3) was added, giving a turquoise solution. Despite frequent, vigorous shaking, a little vanadium salt remained undissolved and so the solution was left to stand at room temperature. After a few days, not only had all the oxodichlorobis(ethanenitrile)vanadium(IV) dissolved, but turquoise crystals had been precipitated. These crystals were filtered off *in vacuo*, washed with ethanenitrile (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	32.1	6.70	15.0	18.8
Required for $VOCl_2(C_5H_{12}N_2O)_2$	32.45	6.54	15.14	19.15

The infrared spectrum for the compound confirmed the presence of coordinated tetramethylurea.

3.18 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH TETRAMETHYLTHIOUREA

3.18.1 In Ethanenitrile

Oxodichlorobis(ethanenitrile)vanadium(IV) (2.7 g) was added to ethanenitrile (80 cm^3). Tetramethylthiourea (3.6 g) was added, giving a turquoise solution. Despite vigorous shaking, not all the oxodichlorobis(ethanenitrile)vanadium(IV) dissolved and, within a few minutes, a light green powder had formed as well. The solution was left to stand at room temperature for twenty-four hours and all the starting material dissolved, leaving only the light-green powder. The powder was filtered off *in vacuo*, washed with ethanenitrile (20 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	29.3	6.03	13.7	17.2
Required for $VOCl_2(C_5H_{12}N_2S)_2$	29.86	6.01	13.93	17.62

The infrared spectrum for the light-green product confirmed the presence of coordinated tetramethylthiourea.

3.18.2 In Tetrahydrofuran

Oxodichlorobis(ethanenitrile)vanadium(IV) (1 g) was dissolved in tetrahydrofuran (65 cm^3). Tetramethylthiourea (1.3 g) was added, giving a royal-blue solution. After a few minutes a light-green powder was precipitated but only in small quantity. The solution was then left to stand at 275 K for a week but no extra precipitate was deposited. The solution was then concentrated to 15 cm^3 by distilling off tetrahydrofuran *in vacuo*. More light-green precipitate was deposited which was then filtered off *in vacuo*, washed with tetrahydrofuran (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	28.5	5.82	13.3	16.7
Required for $VOCl_2(C_5H_{12}N_2S)_2$	29.86	6.01	13.93	17.62

Again the infrared spectrum confirmed the presence of coordinated tetramethylthiourea.

3.19 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH METHYLDIPHENYLPHOSPHINE

Oxodichlorobis(ethanenitrile)vanadium(IV) (2.8g) was dissolved in tetrahydrofuran (125 cm^3). Methyldiphenylphosphine (6.7 cm^3) was added giving a dark blue-green solution. The solution was left to stand at 243 K for twenty-four hours. Since only a little green solid had precipitated, the solution was concentrated to 20 cm^3 by distilling off tetrahydrofuran *in vacuo*. Dark-green, plate-like crystals were precipitated in a large quantity and these were left to stand at room temperature for twenty-four hours with frequent, vigorous shaking. They were then filtered *in vacuo*, washed with tetrahydrofuran (10 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	58.3	5.40	0.00	13.0
Required for $VOCl_2(C_{13}H_{13}P)_2$	58.01	4.87	0.00	13.17

3.20 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH DIMETHYLPHENYLPHOSPHINE

Oxodichlorobis(ethanenitrile)(IV) (2 g) was dissolved in tetrahydrofuran (50 cm^3). Dimethylphenylphosphine (2.8 cm^3) was added, giving a dark-green solution. The solution was left to stand at 243 K for twenty-four hours. Since only a little green solid had

precipitated, the solution was concentrated to 10 cm^3 by distilling off tetrahydrofuran *in vacuo*. There was still no solid present so the solution was left to stand at 243 K for a further week. The supersaturated solution solidified completely at 243 K, but when it was allowed to warm to room temperature, it became an oil, leaving no solid. Eventually, after a further period at 243 K, the compound was filtered *in vacuo* as it was warming to room temperature and a very small yield was obtained. The dark-green solid was washed with tetrahydrofuran (2 cm^3) and dried *in vacuo*. The solid obtained was extremely oily in nature and a satisfactory infrared spectrum could not be obtained.

Analysis	%C	%H	%N	%Cl
Found	44.2	5.73	0.00	15.9
Required for $VOCl_2(C_8H_{11}P)_2$	46.40	5.35	0.00	17.12

3.21 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH BIS(DIPHENYLPHOSPHINO)METHANE

Oxodichlorobis(ethanenitrile)vanadium(IV) (1.1 g) was dissolved in tetrahydrofuran (50 cm^3). Bis(diphenylphosphino)methane (2 g) was added, giving a royal-blue solution. The solution was left to stand at 243 K for twenty-four hours and, since no solid had formed, it was then concentrated to 20 cm^3 by distilling off tetrahydrofuran *in vacuo*. Royal-blue crystals were deposited from the blue solution. The solution was left to stand for a week at 275 K, and was shaken at regular intervals. The crystals were then filtered off *in vacuo*, washed with tetrahydrofuran (10 cm^3) and dried *in vacuo*.

Analysis for the blue crystals	%C	%H	%N	%Cl
Found	57.3	6.11	0.00	10.5
Required for $VOCl_2(C_{25}H_{22}P_2)$	57.50	4.25	0.00	13.58

The infrared spectrum, as well as suggesting that slight hydrolysis had occurred, confirmed that bis(diphenylphosphino)methane was present.

3.22 REACTION OF $[VOCl_2(CH_3CN)_2]$ WITH 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE

Oxodichlorobis(ethanenitrile)vanadium(IV) (1.7 g) was dissolved in tetrahydrofuran (100 cm^3). 1,2-bis(diphenylphosphino)ethane (3.5 g) was added, giving a blue solution. The solution was left to stand at 243 K for three days and, since no precipitate resulted, the

solution was concentrated to 20 cm^3 by distilling of tetrahydrofuran *in vacuo*. After standing for a further day at 243 K a green solid was precipitated. The green powder was shaken vigorously at regular intervals and was then filtered off *in vacuo*, washed with tetrahydrofuran (20 cm^3) and dried *in vacuo*.

Analysis	%C	%H	%N	%Cl
Found	57.4	4.62	0.00	12.9
Required for $VOCl_2(C_{26}H_{24}P_2)$	58.23	4.51	0.00	13.22

The infrared spectrum confirmed that 1,2-bis(diphenylphosphine)ethane was present.

SECTION 4: RESULTS AND DISCUSSION

4.1. DISCUSSION OF EXPERIMENTAL RESULTS

4.1.1 Introduction

The aim of this project was to prepare various complexes, either of the form $[VOCl_2L_n]$ (where L is a neutral ligand) or containing $[VOCl_4]^{2-}$, characterise them, and to carry out e.p.r. studies on them. Past e.p.r. studies on complexes of the type $VOBr_2L_n$ had suggested that the amount of hyperfine structure seen in the e.p.r. spectrum of the solid sample depended on the size of the ligand L [89]. Similarly with $[VOBr_4]^{2-}$ complexes, the amount of hyperfine structure depended on the size of the cation present. The complexes prepared and studied in this project were chosen so as to have a wide range of ligand and cation sizes.

The preparations, which are described in Section 3, all involved ligand exchange except for the initial preparation of oxodichlorobis-(ethanenitrile)vanadium(IV) (Section 3.1). Ethanenitrile reacted with vanadium(IV) oxide dichloride to give $[VOCl_2(CH_3CN)_2]$, a blue powder. This compound was prepared as a starting material for the preparation of the desired complexes by ligand exchange reactions with other ligands. Oxodibromotris(ethanenitrile)vanadium(IV) had previously been used successfully in the preparation of $[VOBr_2(Ph_3P)_2]$, $[VOBr_2(py)_3]$ and $[VOBr_2(4\text{-pic})_3]$ [40,88]. The blue powder described in Section 3.1 analysed as $[VOCl_2(CH_3CN)_2]$ and not $VOCl_2(CH_3CN)_{2.5}$ as reported by du Preez and Sadie [16]. This difference is due to the weakenss of ethanenitrile as a ligand, which frequently leads to non-stoichciometry in complexes, owing to the ready evolution of ethanenitrile at room temperature *in vacuo*. For example, Clark *et al.*[121] found that when they reacted anhydrous vanadium(III) chloride with ethanenitrile, the product obtained varied in composition between $[VCl_3(CH_3CN)_3]$ and $VCl_3(CH_3CN)_4$. Nicholls *et al.* have also reported this problem, both in the preparation of $[VCl_3(CH_3CN)_3]$ by reacting $[PCl_4][VCl_5]$ with ethanenitrile [122], and in the preparation of $[VOBr_2(CH_3CN)_3]$ from $VOBr_3$ and ethanenitrile [40,41].

Ligand-exchange methods have been widely used for the preparation of many transition metal complexes, but, surprisingly, have been almost ignored for the preparation of oxovanadium(IV) complexes (see Tables 1.1-1.6). $[VOCl_2(thf)_2]$ has been used by Datta and Hamid [20], but the starting

material $[VOCl_2(CH_3CN)_2]$ is particularly suitable in that its preparation on a large scale is extremely facile, and ethanenitrile is so readily displaced as a ligand. It dissolves readily in ethanenitrile (to give a royal-blue solution) and in tetrahydrofuran (to give a dark-blue solution). The difference in colours suggested that tetrahydrofuran had replaced ethanenitrile, forming the complex $[VOCl_2(thf)_2]$ *in situ*. This complex, was, however, not isolated. The only ligands investigated which did not replace ethanenitrile readily were triphenylstibine, triphenylarsine and triphenylamine (Sections 3.14-3.16), all of which are themselves only weakly basic. The types of ligand replacement reactions observed are illustrated by the following equations:

$$[VOCl_2(CH_3CN)_2] + 2ACl \longrightarrow A_2[VOCl_4] + 2CH_3CN$$

$$[VOCl_2(CH_3CN)_2] + nL \longrightarrow [VOCl_2L_n] + 2CH_3CN$$

In these equations A is a ction, L is a neutral monodentate or bidentate ligand and n = 1, 2 or 3.

4.1.2 Anionic Complexes

The $[VOCl_4]^{2-}$ ion itself has never been the subject of a single-crystal X-ray structure investigation. A study has been carried out on the $[TiOCl_4]^{2-}$ ion [68] showing it to have C_{4v} symmetry and $[VOCl_4]^{2-}$ has been assumed [68] to have the same symmetry, although no molecular parameters are known. Spectroscopic data for $[VOCl_4]^{2-}$ complexes has rarely been reported in great detail (see Table 1.6) and these complexes were prepared, not only to study their e.p.r. spectra, but also to investigate their infrared and diffuse reflectance spectra, and hopefully to prepare a crystalline sample suitable for X-ray studies.

$[Et_4N]_2[VOBr_4]$ has been the most studied $[VOBr_4]^{2-}$ complex, and there have been very interesting observations in both the infrared spectrum of the compound [40,41] and the e.p.r. spectrum [89]. The e.p.r. spectrum of a solid sample showed hyperfine structure due

to interactions of the unpaired d^1 electron with the ^{51}V ($I=^{7}/_{2}$) nucleus. In contrast the e.p.r. spectrum for $[pyH]_2[VOBr_4]$ gave a simple first-derivative curve. This difference was attributed to the difference in cation size and it was this observation thatinfluenced the choice of $[VOCl_4]^{2-}$ complexes studied in this project. The four $[VOCl_4]^{2-}$ complexes prepared were, in order of increasing cation size, $[pyH]_2[VOCl_4]$, $[Me_4N]_2[VOCl_4]$, $[Et_4N]_2[VOCl_4]$ and $[Ph_4As]_2[VOCl_4]$. The tetramethylammonium cation is of a similar size to the pyridinium cation but because the pyridinium cation is planar, the tetramethylammonium cation can be considered to be stereochemically more bulky.

All four preparations were carried out in ethanenitrile. $[Et_4N]_2[VOCl_4]$ was isolated as green crystals but these were, unfortunately, not suitable for single-crystal X-ray studies [123]. The crystals were twinned (*i.e.* two different orientations of a lattice existed in what was apparently one crystal), which made the crystals unsuitable for X-ray structural analysis [124]. $[Et_4N]_2[VOBr_4]$ has also been shown to be twinned and hence, single-crystal X-ray structure studies were not possible for this complex either [123a].

$[pyH]_2[VOCl_4]$ was prepared as described in Section 3.5. It had previously been reported as a green solid [72] but at 243 K the product obtained in the reactions described in section 3.5 was predominantly royal-blue. At room temperature (295 K) the product became green in colour. At first this was interpreted in terms of a solvation effect, since compounds like $[pyH]_2[VOCl_4].2H_2O$ and $[quinH]_2[VOCl_4].2H_2O$ had been previously prepared as blue solids [72]. However, the blue solid was isolated and its infrared spectrum revealed the absence of ethanenitrile. Analysis figures and the infrared spectrum for the compound suggested that the product was $[pyH]_2[VOCl_4]$. The different colours were interpreted as being due to an equilibrium between two geometrical isomers, namely the $[VOCl_4]^{2-}$ species in C_{4v} (square pyramidal) and C_{2v} (trigonal bipyramidal) symmetry states. This type of equilibrium has been observed previously for the $[VOF_4]^-$ ion in solution, where n.m.r was used to show the existence of an equilibrium [125], and for $[VOBr_4]^{2-}$ where the far-infrared spectrum of $[Et_4N]_2[VOBr_4]$ showed there to be a temperature-dependent equilibrium [40,41]. In the latter case, the C_{4v} state was stable at

308 K, and the C_{2v} state stable at 243 K.

As well as being temperature-dependent, the colour of $[pyH]_2[VOCl_4]$ appeared to depend on the chloride ion concentration in the mother liquor. In Section 3.5.2 when the mole ratio (V:pyHCl) was 1:4, a blue colour was observed at room temperature, whereas, in Section 3.5.1 when the mole ratio (V:pyHCl) was 1:3, the blue colour did not appear until the reaction flask had been cooled at 243 K for some time. In Section 3.2.2 the reaction between pyridinium chloride, hexamethylphosphoramide and oxodichlorobis-(ethanenitrile)vanadium(IV) is described. Both pyridinium chloride and hexamethylphosphoramide were in large excess and the product was a royal-blue solid. Analysis figures suggested that there was hexamethylphosphoramide present in the product, and that the product was probably a complex, $[pyH]_2[VOCl_4].xhmpa$, where x was approximately 0.7. The infrared spectrum for the product, reported in Section 4.2, shows that very little hexamethylphosphoramide is present. The absence of a strong band in the 960-990 cm^{-1} region is particularly striking. It is possible, therefore, that the sample analysed was not completely dry. The hexamethylphosphoramide present does however appear to stablilise the blue form of $[VOCl_4]^{2-}$ at room temperature and the infrared spectrum for the product is very similar to that of the blue $[pyH]_2[VOCl_4]$ sample obtained in the absence of hexamethylphosphoramide.

The analysis figures quoted for the various samples of green and blue $[pyH]_2[VOCl_4]$ often seem to be particularly low for chlorine. The two higher chlorine analysis figures of 38.3 and 40.2 quoted in Section 3.5.1 were both obtained by sending samples to the Butterworth Microanalytical Company (see Section 2.5.1) for analysis, which was carried out under an inert nitrogen atmosphere. The remainder of the analyses, however, were obtained under conditions where hydrolysis of the V-Cl bonds occurred to some extent. Although this resulted in low chlorine analysis figures, the figures were still in the range which might be expected for the product being $[pyH]_2[VOCl_4]$.

The preparation of $[Me_4N]_2[VOCl_4]$ by the method described in Section 3.7 was on the whole unsatisfactory. The product obtained was predominantly white tetramethylammonium chloride, but the green solid present was shown to be $[Me_4N]_2[VOCl_4]$ by its infrared spectrum. It is interesting that, whereas, on addition of the chloride in the other

preparations, the blue solution turned green, on addition of tetramethylammonium chloride, a blue-green colour was seen. This suggested that only partial reaction had occurred, a fact confirmed by the impure product. The main reason for wishing to prepare $[Me_4N]_2[VOCl_4]$ was to study its e.p.r. spectrum. Since $[Me_4N]Cl$ does not give any e.p.r. signal, an e.p.r. spectrum could still be recorded for the impure product and results interpreted in terms of a signal due to $[Me_4N]_2[VOCl_4]$. These results are discussed in Section 4.4.

The reaction giving rise to $[Ph_4As]_2[VOCl_4]$ is described in Section 3.8. The tetraphenylarsonium cation was chosen as a large cation because single-crystal X-ray studies of the compound $[Ph_4As][CrOCl_4]$ had already been reported [126]. The $[CrOCl_4]^-$ ion is isoelectronic with the $[VOCl_4]^{2-}$ ion and it was hoped that crystals of $[Ph_4As]_2[VOCl_4]$ would be prepared. Although most samples of this compound prepared were light-green powders, as in the cases of most $[pyH]_2[VOCl_4]$ samples, green needle-like crystals were formed at one stage (section 3.8(b)) and a small sample of $[Ph_4As]_2[VOCl_4]$ was later recrystallised from dichloromethane. However, no crystals suitable for crystallographic study were obtained.

4.1.3 Neutral Complexes

A series of $[VOCl_2L_n]$ adducts were prepared using the same ligand exchange method. Ethanenitrile and tetrahydrofuran were employed as solvents. They are coordinating solvents, and it is possible that some of the colours seen in the reactions were due, not to the product eventually isolated as a solid, but to a different species of the form $VOCl_2L_nX_m$ (where X is CH_3CN or thf) and where n may in some cases be zero. This phenomenon has been observed in the equilibrium

$$[VOBr_2(Ph_3P)_2] \underset{Ph_3P}{\overset{thf}{\rightleftharpoons}} [VOBr_2(Ph_3P)(thf)] \underset{Ph_3P}{\overset{thf}{\rightleftharpoons}} [VOBr_2(thf)_2]$$

which has been investigated using e.p.r. [89]. If dissociation of this form is shown to be a regular occurrence, then many results reported previously, discussing electronic spectral studies and e.p.r. studies on solutions of oxodihalovanadium(IV) complexes in coordinating solvents, must be open to doubt [*e.g.* 26,51,64].

The reaction of oxodichlorobis(ethanenitrile)vanadium(IV) with pyridine is described in Section 3.9. The products isolated gave analysis

figures and infrared spectra which suggested that the products were mixtures of $[VOCl_2(py)_2]$ and $[VOCl_2(py)_3]$, the former being the major constituent in 3.9.1.1 and the latter being the major constituent in 3.9.1.2. In 3.9.2, the two infrared spectra recorded suggest that although the initial product was a mixture, after two months the product was mainly $[VOCl_2(py)_2]$. On heating *in vacuo*, $[VOBr_2(py)_3]$ is known to lose a mole of pyridine [127] and it has also been suggested that e.p.r. studies show the dissociation of $[VOBr_2(py)_3]$ in methylbenzene to yield $[VOBr_2(py)_2]$[89].

$$[VOBr_2(py)_3] \underset{py}{\overset{PhCH_3}{\rightleftharpoons}} [VOBr_2(py)_2] + py$$

In pyridine solution the equilibrium shifts to the left. This is therefore in accord with $[VOCl_2(py)_3]$ being unstable at room temperature.

Of the oxygen-donor ligands studied, dimethylsulphoxide and diphenylsulphoxide yielded light-blue powders (sections 3.13 and 3.12) of the form $[VOCl_2L_3]$. This is particularly interesting in the dimethylsulphoxide case, since, in the $VOBr_2$ system the ionic $[VO(dmso)_5]Br_2$ is formed. Here, however, even with a 1:6(V:dmso) mole ratio, only the 3:1 adduct was formed. Although this complex had already been reported [53], it was thought that a 5:1 adduct might be formed with a large excess of dimethylsulphoxide. The complexes $[VOCl_2(tmu)_2]$ and $[VOCl_2(tmtu)_2]$ were isolated as turquoise crystals and a light-green powder respectively, tetramethylthiourea being the only sulphur-donor ligand studied.

By far the most interesting set of adducts formed were those with phosphine ligands. As mentioned in Sections 1.2 and 1.4, very few oxovanadium(IV)-phosphine complexes are known. The ligand-exchange method using $[VOCl_2(CH_3CN)_2]$ seems to provide a relatively straightforward synthetic route to phosphine complexes. With $[VOBr_2(CH_3CN)_3]$ as starting material, $[VOBr_2(Ph_3P)_2]$ had previously been prepared [40] as a green solid. The first phosphine complex studied was the chloro-analogue, $[VOCl_2(Ph_3P)_2]$. The preparation is described in Section 3.10. The complex precipitated as a green powder from both tetrahydrofuran and ethanenitrile as solvents. $[VOBr_2(Ph_3P)_2]$ was shown to have a trigonal bipyramidal structure by i.r. studies [40,42] and similar studies on $[VOCl_2(Ph_3P)_2]$ are discussed in Section 4.2. The reaction of oxodichlorobis(ethanenitrile)vanadium(IV) with tricyclohexylphosphine is

described in Section 3.11. The light-green powder obtained was analysed as $[VOCl_2(cy_3P)]$. This was only the 1:1 adduct formed with a monodentate ligand. Tricyclohexylphosphine is a bulkier ligand than triphenylphosphine. Sections 3.19 and 3.20 describe the reactions of $[VOCl_2(CH_3CN)_2]$ with two other monodentate phosphine ligands, namely methyldiphenylphosphine and dimethylphenylphosphine. Whereas in the other two phosphine reactions a green solid was precipitated almost immediately, $[VOCl_2(Ph_2MeP)_2]$, a dark green solid, took many hours to form and in the latter reaction a dark green oily solid was obtained. Although the analysis figures for this solid suggest the formulation $[VOCl_2(PhMe_2P)_2]$, it was impossible to prepare a reasonable nujol mull of the complex and hence the infrared spectrum for the compound was difficult to interpret. Two bidentate phosphine ligands, bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane, were studied. As described in Section 3.21, with bis(diphenylphosphino)methane, royal-blue crystals were formed but these were partially hydrolysed during evacuation to dryness, which accounts for the low analysis figure for chlorine. The analysis figures are, despite this, reasonable enough to confirm the presence of a 1:1 adduct $[VOCl_2(dppm)]$. Considering the similarity of the other bidentate ligand, it was surprising that the product, $[VOCl_2(dppe)]$ described in section 3.22, should be a green powder. This may be due to a difference in structure between the two products. Four of the oxodichlorovanadium(IV)-phosphine complexes prepared have not previously been reported. Olivé and Henrici-Olivé [29-31] carried out e.p.r. studies on oxovanadium(IV)-phosphine complexes in solution. These studies are discussed in greater detail in Section 1.6. They observed ligand hyperfine structure in their spectra due to $^{31}P(I=\frac{1}{2})$ atoms. E.p.r. studies on both solid samples and solutions of phosphine complexes mentioned in this discussion are described in Section 4.4. Olivé and Henrici-Olivé [31] also went on to study a solution containing $VOCl_2$ and Bu_3Sb. Since they observed ligand hyperfine structure due to ^{122}Sb, they concluded that they had formed an oxodichlorovanadium(IV)-stibine complex. The e.p.r. spectrum obtained suggested that the species was the four-coordinate $[VOCl_2(Bu_3Sb)]$. This complex would be four-coordinate due to the large size of the stibine ligand. The complex was never isolated as a solid from the methylbenzene solution. Attempts to form

stibine and arsine adducts in ethanenitrile and tetrahydrofuran as described in Sections 3.14 and 3.15, always resulted in reduction to vanadium(III) (hence the black solids formed) or in no reaction at all. In Section 3.15 both starting materials were recovered from the reaction solution, unchanged.

4.1.4 Mixed Complexes

Since complexes of the form $[VOCl_2L_n]$ and $[VOCl_4]^{2-}$ have been readily prepared, it was hoped that complexes of the form $[VOCl_3L_2]^-$ might be formed. If chloride ion is in excess in a reaction mixture, then $[VOCl_4]^{2-}$ complexes are likely to be formed. By choosing the ratios of reactants carefully it was hoped to stop the process shown in the equation below at the $[VOCl_3L_2]^-$ complex. L here is a neutral monodentate ligand, and A a cation.

$$[VOCl_2(CH_3CN)_2] \xrightarrow[ACl]{L} [VOCl_2L_2] \xrightarrow{ACl} A[VOCl_3L_2] \xrightarrow{ACl} [A]_2[VOCl_4] \text{ or } [A]_2[VOCl_4]$$

Garner *et al.* [128] reported the preparation of the complexes $[MoOCl_3(Ph_3PO)_2]$ and $[MoOCl_3(hmpa)_2]$ which would have similar electronic configurations, for the valence electrons, to the vanadium compounds. The electronic structure of $[MoOCl_3(hmpa)_2]$ was investigated using polarised single crystal, nujol mull, and solution electronic spectroscopic and single crystal e.p.r. techniques. Attempts to form the complexes $[pyH][VOCl_3(Ph_3PO)_2]$ and $[pyH][VOCl_3(hmpa)_2]$ are described in Sections 3.2 and 3.4. These attempts have always resulted in the formation of $[VOCl_2(hmpa)_2]$, $[VOCl_2(Ph_3PO)_2]$ or $[pyH]_2[VOCl_4]$ depending on the relative amounts of the various reagents. In 3.2.3, both $[VOCl_2(hmpa)_2]$ and $[pyH]_2[VOCl_4]$ were isolated from the same reaction mixture. In 3.4.2, $[VOCl_2(Ph_3PO)_2]$ was isolated, both as a light-green powder and as blue-green crystals. Under these conditions then, it was not possible to form the $[VOCl_3L_2]^-$ ions required. In Section 3.3., tetraethylammonium chloride was used instead of pyridinium chloride but this made no difference, and the $[VOCl_2(hmpa)_2]$ complex was again formed. Although it may have been expected that $[VOCl_3L_2]^-$ would not form, it is somewhat surprising that complexes of the type $[VOCl_3L]^-$ or $[VOCl_4L]^{2-}$ were not observed.

4.2. INFRARED STUDIES

4.2.1 Introduction

4.2.1.1 Far Infrared Spectroscopy

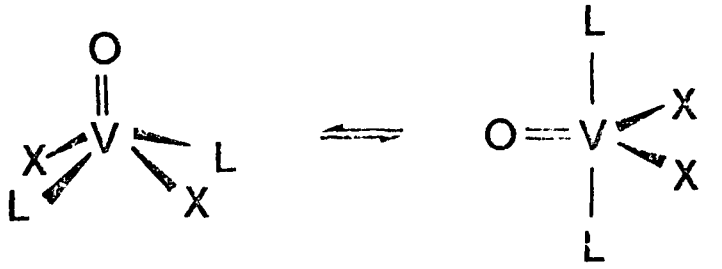
Despite the extensive literature upon $VOCl_2$ complexes (both anionic and neutral), it is surprising to find that the far infrared spectra of only three of these complexes have been reported. The ν(V-Cl) assignments are given in Table 4.1, along with the ν(V-Br) assignments reported for $VOBr_2$ complexes.

Recently Datta and Hamid [20] made some very tentative assignments of ν(V-Cl) frequencies, but they quote a number of possible frequencies for some complexes, and have clearly made no attempts to study related complexes, and hence eliminate ligand bands in the region. Similarly du Preez and Gibson [26] have tentatively assigned the band at 372 cm^{-1} in the infrared spectrum of $[VOCl_2(tmtu)_2]$ as being due to a ν(V-Cl) stretching frequency.

Of the complexes mentioned in Table 4.1, only the structure of $[VOCl_2(NMe_3)_2]$ is known. Single-crystal X-ray studies have shown [36] it to have a trigonal bipyramidal structure. The data in the literature does not form a firm foundation for the assignment of the far infrared spectra of vanadium(IV) oxide dichloride complexes. However, the work carried out by Nicholls and Seddon [40-42] has shown that there are certain trends which apply to the far infrared spectra of vanadium(IV) oxide dibromide complexes. In Table 4.1 the letters a-d are used to classify the complexes in terms of the structures they are likely to have, according to the infrared bands observed. In general, it is well established [129] that ν(M-X), where X is a halide, increased as coordination number decreases. Thus,

$$\nu_{MX}(4\text{-coord}) > \nu_{MX}(5\text{-coord}) > \nu_{MX}(6\text{-coord})$$

Nicholls and Seddon [40-42] showed how infrared spectra can be used to distinguish between trigonal bipyramidal and square pyramidal five-coordinate complexes. Considering complexes of the general type VOX_2L_2, the two most likely five-coordinate structures, both having C_{2v} symmetry are:

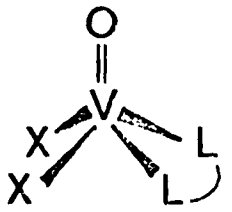


(I) (II)

Structure (I) will have only one strong infrared absorption due to ν_{as}(M-X) (as the symmetrical band will be virtually infrared inactive), whereas structure (II) will have two strong infrared active bands due to ν(M-X).

There is evidence to confirm this in that trigonal bipyramidal $[VOCl_2(NMe_3)_2]$ shows two ν(V-Cl) stretching frequencies [95]. Both $[TiOCl_4]^{2-}$ [68,130] and $[InCl_5]^{2-}$ [131] have been shown to have C_{4v} symmetry by X-ray structural analysis. The infrared spectrum of $[TiOCl_4]^{2-}$ [95] showed only one ν(Ti-Cl) band, and a full vibrational analysis of $[InCl_5]^{2-}$ [132] revealed one very strong band and only a very weak shoulder due to the symmetrical mode.

For complexes with a bidentate ligand, L-L, of the type VOX_2(L-L), the only likely five-coordinate structure is:



This should also have two infrared ac ν(M-X) bands.

Table 4.1 Metal-Halide Stretching Frequencies for VOX_2 Complexes (units of cm^{-1})

COMPLEX	ν(v-X)	REF	COMPLEX	ν(V-X)	REF
$[VOCl_2(NMe_3)_2]^{b*}$	404,383	95	$[VOCl_2(2,2'\text{-bipy})]^{d}$	371	64
$[VOCl_2(phen)]^{d}$	365	64	$[pyH][VOBr_3(CH_3CN)_2]^{a}$	320,289	40,41
$[pyH][VOBr_3]^{a}$	319	40,41	$[VOBr_2(CH_3CN)_3]^{a}$	316,263	40,41
$[VOBr_2(py)_3]^{a}$	307,257	40,42	$[VOBr_2(dpso)_3]^{a}$	301,266	40,42
$[quinH]_3[VOBr_5]^{a}$	288,268/260	40,41	$[VOBr_2(qn)_2]^{b}$	354,307	90
$[VOBr_2(Ph_3P)_2]^{b}$	347,313	40,42	$[VOBr_2(thiox)_2]^{b}$	347,320	40,42
$[VOBr_2(quin)_2]^{b}$	342,307	40,42	$[Et_4N]_2[VOBr_4]^{b}$	325,274	40,41
$[VOBr_2(py)_2]^{c}$	334	40,42	$[VOBr_2(diox)_2]^{c}$	330	40,42
$[VOBr_2(hmpa)_2]^{c}$	320	40,42	$[Et_4N]_2[VOBr_4]^{c}$	296	40,41
$[VOBr_2(2,2\text{-bipy})]^{d}$	355,345	40,42	$[VOBr_2(dme)]^{d}$	342,326	40,42

Key: a-six-coordinate complexes, b-five-coordinate trigonal bipyramidal complexes, c-five-coordinate square pyramidal complexes, d-complexes with bidentate ligands, *-known structure from X-ray study.

These basic assumptions are useful in predicting the structure of a complex on the basis of its far infrared spectrum. Throughout this section, spectra of the chloride samples have been compared with their bromo-analogues, in order to make vibrational assignments. Where necessary, spectra were recorded for the ionic chlorides([pyH]Cl, etc.) and for the neutral ligands (Ph_3PO, dppe,etc.) to facilitate the assignment of cation and ligand bands.

4.2.1.2 Near Infrared Spectroscopy

There are three principal reasons for measuring the near infrared spectra of the complexes:

(a) To establish the purity of the complex

(b) To establish the bonding mode of the ligand

(c) To establish the nature of the V=O bond.

When a V=O double bond is present in a molecule, a sharp, medium-strength band in the region of about 850-1050 cm^{-1} is observed. Many attempts [eg. 4,21,45,47,48] to correlate the frequency, $\nu(V=O)$, with the other ligands have failed. It is now generally accepted that the exact position of $\nu(V=O)$ is due to many factors and that simple correlation between its position and any other single parameter exists. A broad band between about 900 and 800 cm^{-1} is characteristic of a V=O.....V interaction, and when present is normally indicative of a polymeric structure.

4.2.2. Far Infrared Studies (700-200 cm^{-1})

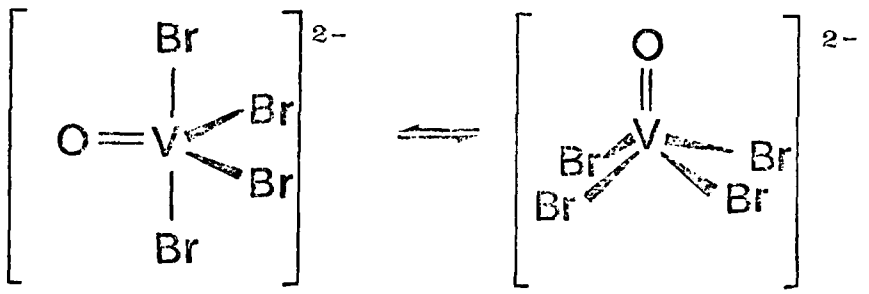
4.2.2.1 Pyridinium Oxotetrachlorovanadate(IV)

In sections 3.5 and 4.1 it was described, in some detail, that two forms of $[pyH]_2[VOCl_4]$, one green and the other blue, had been isolated. In section 4.1 this observation was tentatively interpreted in terms of two geometrical isomers, one of C_{4v} symmetry based on a square pyramid and the other of C_{2v} symmetry (trigonal bipyramidal). Previous studies of the far infrared spectrum of $(Et_4N)_2[VOBr_4]$ [40,41] have distinguished between two such geometrical isomers of the $[VOBr_4]^{2-}$ ion. The equilibrium between the two isomers was shown to be temperature-dependent. Table 4.2 lists the bands observed below 400 cm^{-1} at different temperatures.

Table 4.2 Infrared Spectrum (350-250 cm^{-1}) of $[Et_4N]_2[VOBr_4]$ (units of cm^{-1}) [40,41]

243 K	308 K
325(s)	
300(w)	296(s)
274(s)	

The observations in the far i.r. spectra are interpreted, then, in terms of the equilibrium:



C_{2v} - 243 K C_4v - 308 K

It was not possible, however, to isolate the low temperature form of $[Et_4N]_2[VOBr_4]$.

The far infrared spectrum of $[pyH]_2[VOCl_4]$ recorded for the green form of the complex is different from that recorded for the blue form. Both spectra were obtained at 295 K. The region between 500 cm^{-1} and 250 cm^{-1} is particularly interesting. Table 4.3 details the spectrum in this region for the blue compound (Section 3.5.1), a blue-rich sample containing some green solid and a green-rich sample containing some blue solid (both Section 3.2.3), and the green compound (the first sample isolated in Section 3.5.1). The spectrum for pyridinium chloride has a medium strength band at 395 cm^{-1} but this is by no means as strong a band as that observed for the blue compound at 399 cm^{-1}.

Table 4.3 Far Infrared Spectrum of $[pyH]_2[VOCl_4]$ (units of cm^{-1})

Blue	Blue-rich	Green-rich	Green
399 s	395 m/s	393 m	394 w
356 m	349 s	347 s	344 s
300 m	298 m	298 m	302 m
276 m	278 w	275 w	278 vw

As the sample tends towards a 100% blue sample, the bands at 395-400 cm^{-1} and 275-280 cm^{-1} increase in intensity and the band at 345 cm^{-1} decreases in intensity and shifts to a higher frequency. In Table 4.1 it was reported that $[VOCl_2(NMe_3)_2]$, which is known to have a C_{2v} (trigonal bypyramidal) structure [36], has ν(V-Cl) bands at 404 cm^{-1} and 383 cm^{-1} [95]. Our spectrum can be interpreted as follows: the blue solid as a C_{2v} (trigonal bipyramidal) structure and has ν(V-Cl) bands at 399 and 356, the latter being weaker in intensity than the former, and the green solid has a C_{4v} (square pyramidal) structure with one ν(V-Cl) band at 344 cm^{-1}.

A band of medium strength at 300 cm^{-1} is common to both forms. In the spectrum of the green form it could be assigned as a ν(V-Cl) band, being a weak shoulder characteristic of $VOCl_2$ complexes with C_{4v} symmetry. However, in the spectrum of the blue form the band remains and is unassigned. The band at 276 cm^{-1} is much stronger in intensity for the blue sample, and appears to be characteristic of $VOCl_2$ complexes with C_{2v} (trigonal bipyramidal) symmetry (see section 4.2.8). It is tentatively assigned to a δ(O=V-Cl) bending mode.

4.2.2.2 Other Oxotetrachlorovanadate(IV) complexes

Table 4.4. lists the far infrared spectra of $[Et_4N]_2[VOCl_4]$ and $[Ph_4As]_2[VOCl_4]$. Also listed are the far infrared spectra of tetraethylammonium chloride and tetraphenylarsonium chloride. It is clear that the strong bands observed at 344 cm^{-1} for $[Et_4N]_2[VOCl_4]$ and 346 cm^{-1} for $[Ph_4As]_2[VOCl_4]$ must be assigned as ν(V-Cl) stretching frequencies. All the other bands can be assigned as cation bands. Both $[VOCl_4]^{2-}$ complexes were green in colour and it is not surprising that the frequency of the ν(V-Cl) band is very similar to that obtained for ν(V-Cl) with the green form of $[pyH]_2[VOCl_4]$, namely 344 cm^{-1}. The band, in the form of a shoulder, at ca. 300 cm^{-1} was again observed. This

would suggest that $[VOCl_4]^{2-}$ is square pyramidal, with C_{4v} symmetry in both complexes. Table 4.4 shows that there is a band due to the tetraphenylarsonium cation at 345 cm^{-1} but the 346 cm^{-1} band in $[Ph_4As]_2[VOCl_4]$ spectrum is still assigned to ν(V-Cl) which must mask the other band. $[Me_4N]_2[VOCl_4]$ also shows a very strong band at 346 cm^{-1} assigned as the ν(V-Cl) band, which indicates that the $[VOCl_4]^{2-}$ again has C_{4v} (square pyramidal) symmetry.

Table 4.4 Far infrared spectra of $(Et_4N)_2[VOCl_4]$ and $(Ph_4As)_2[VOCl_4]$ (units of cm^{-1})

ASSIGNMENT	Et_4NCl	$(Et_4N)_2[VOCl_4]$	$(Ph_4As)_2[VOCl_4]$	Ph_4ASCl	ASSIGNMENT
Et_4N^+ band	474 m(sh)	468 w	479 s(sh)	479 m (sh)	Ph_4As^+ band
"	397 w(sh)	-	471 s	467 s	"
"	359 w(sh)	-	454/448 m(sh)	451 m(sh)	"
			-	396 w	"
			367 m(sh)	364 m(sh)	"
ν(V-Cl)	-	344 s	346 s	-	ν(V-Cl)
Et_4N^+ band	303 w(sh)	-	-	345 m	Ph_4As^+ band
ν(V-Cl)		299 m(sh)	299 m(sh)	-	ν(V-Cl)
Unassigned		281 w(sh)	280 w(sh)	-	Unassigned
"		268 w(sh)			

4.2.2.3 $VOCl_2L_n$ complexes

The complexes of the type $[VOCl_2L_n]$ were subject to a similar type of i.r. analysis as those described in Sections 4.2.2.1 and 4.2.2.2. Space limitations forbid discussion of these studies in detail, but the results are summarised in Table 4.5. As discussed in section 4.2.1.1, the complexes (like their bromo analogues) can be classified according to the patterns and frequencies observed for ν(VCl), and this is done in Table 4.5. The $[VOCl_4]^{2-}$ salts are also included, for comparison.

4.2.3 Near Infrared Studies (4000-700 cm^{-1})

4.2.3.1 V=O Stretching Frequencies

Table 4.6 lists the V=O stretching frequencies of some complexes of vanadium(IV) oxide dichloride. It has been shown [40-42] that for complexes of vanadium(IV) oxide dibromide there is a general trend that

$$\nu(V{=}O)_{anionic} > \nu(V{=}O)_{5\ coord} > \nu(V{=}O)_{6\ coord} > \nu(V{=}O)_{bidentate}$$

with the notable exception of $[VOBr_2(py)_2]$. When there are V=O....V interactions, bands appear at lower frequencies and are broad.

Table 4.16 includes a column giving V=O stretching frequencies for $VOCl_2$ adducts quoted in the literature, and a column giving the V=O stretching frequency of the corresponding $VOBr_2$ complex.

The same general trends are observed as for $VOBr_2$ complexes. In many cases the bands observed differ in frequency from those quoted in the literature by a large amount. The value of 994 cm^{-1} is quoted for $[VOCl_2(PhMe_2P)_2]$ although this spectrum was not very satisfactory and the analysis of the compound was not definitive. The V=O band in the spectrum of $[VOCl_2(hmpa)_2]$ comes in the same region as a very strong band due to hexamethylphosphoramide. Two bands were seen at 993 cm^{-1} and 982 cm^{-1}. The 993 cm^{-1} band appeared to be sharper and was assigned as the ν(V=O) band. The ν(V=O) band in the spectrum of $[VOCl_2(dpso)_3]$ comes very close to the ν(S=O) band and it is difficult to make accurate assignments. The ν(V=O) band at 924 cm^{-1} in the spectrum of $[VOCl_2(py)_2]$ is broader than the band at 979 cm^{-1} in the spectrum of $[VOCl_2(py)_3]$. This gives for the chloride complexes, again with the exception of $[VOCl_2(py)_2]$,

$$\nu(V{=}O)_{anionic} \sim \nu(V{=}O)_{5\ coord} > \nu(V{=}O)_{6\ coord}$$

Table 4.5 I.r. data

5-coordinate (Type II)[a]		5-coordinate (Type I)[a]		6-coordinate	
Complex	ν(V-Cl)/cm^{-1}	Complex	ν(V-Cl)/cm^{-1}	Complex	ν(V-Cl)/cm^{-1}
$[VOCl_2(Pn_3P)_2]$	412,356	$[VOCl_2(dppm)]$[b]	394	$[VOCl_2(py)_3]$	356,313
$[VOCl_2(Ph_2MeP)_2]$	409,360	$[VOCl_2(hmpa)_2]$	385	$[VOCl_2(dmso)_3]$	353,321
$[VOCl_2(NMe_3)_2]$	404,383	$[VOCl_2(Ph_3PO)_2]$	384	$[VOCl_2(dpso)_3]$	312,282
$[pyH]_2[VOCl_4]$(blue)	399,356	$[VOCl_2(tmu)_2]$	375		
		$[VOCl_2(py)_2]$	373		
		$[VOCl_2(tmtu)_2]$	372		
		$[VOCl_2(bipy)]$[b]	371		
		$[VOCl_2(phen)]$[b]	366		
		$[Ph_4As]_2[VOCl_4]$	346		
		$[pyH]_2[VOCl_4]$(green)	345		
		$[Et_4N]_2[VOCl_4]$	344		
		$[Me_4N]_2[VOCl_4]$	344		

a See section 4.2

b These complexes have a cis structure

Table 4.6 V=O stretching frequencies for VOX_2 adducts (units of cm^{-1})

COMPLEX	X=Cl			X=Br	
	ν(V=O)	ν(V=O)lit.	Ref	ν(v=0) lit.	Ref
$[VOCl_2(dppm)]$	1011	-	-	-	-
$[VOCl_2(Ph_3PO)_2]$	1006	990	26	-	-
Blue $[pyH]_2[VOCl_4]$	1005	-	-	-	-
Green $[pyH]_2[VOCl_4]$	1004	998,980	37	999	40,41
		1009	72		
		1003	27		
$[VOCl_2(tmu)_2]$	997	998	26	-	-
$[VOCl_2(Ph_2MeP)_2]$	996	-	-	-	-
$[VOCl_2(dppe)]$	995	-	-	-	-
$[Ph_4As]_2[VOCl_4]$	995	-	-	-	-
$[Et_4N]_2[VOCl_4]$	995	1013	75	998	40,41
$[VOCl_2(PhMe_2P)_2]$	994	-	-	-	-
$[VOCl_2(hmpa)_2]$	993	-	-	989	40,42
$[Me_4N]_2[VOCl_4]$	992	-	-	-	-
$[VOCl_2(cy_3P)]$	990	-	-	-	-
$[VOCl_2(tmtu)_2]$	988	-	-	-	-
$[VOCl_2(Ph_3P)_2]$	986	988	27	988	40,42
$[VOCl_2(CH_3CN)_2]$	980	1005	75	-	-
$[VOCl_2(py)_3]$	979	960,955	51	965,959	40,42
$[VOCl_2(dpso)_3]$	949	-	-	968,957	40,42
$[VOCl_2(dmso)_3]$	947	-	-	-	-
$[VOCl_2(py)_2]$	924	920	27	940	40,42

4.2.3.2 Ethanenitrile Stretching Frequencies

$[VOCl_2(CH_3CN)_2]$ was the only complex studied with coordinated ethanenitrile. Table 4.7 lists $\nu(C\equiv N)$ stretching frequencies for uncoordinated ethanenitrile, $VOCl_2(CH_3CN)_2$ and various $VOBr_2$ complexes with coordinated ethanenitrile. $\nu(C\equiv N)$ increases upon coordination as has been reported previously [136] , and the effect of coordination on $\nu(C\equiv N)$ is similar for $[VOCl_2(CH_3CN)_2]$ as for $VOBr_2$ complexes.

4.2.3.3 Complexes of Oxide Ligands, L=O

Table 4.8 shows that the complexes of hexamethylphosphoramide, triphenylphosphine oxide, diphenylsulphoxide, dimethylsulphoxide and tetramethylurea all show a decrease in the $\nu(L=O)$ stretching frequency, indicating that coordination through the oxygen has occurred. Some corresponding values for $VOBr_2$ complexes are listed.

Table 4.7 $\nu(C\equiv N)$ in Ethanenitrile Complexes (units of cm^{-1})

COMPLEX	$\nu(C\equiv N)$	REF
CH_3CN	2295*,2260	136
$VOCl_2(CH_3CN)_2$	2318*,2291	
$VOCl_2(CH_3CN)_2$	2283	75
$VOBr_2(CH_3CN)_3$	2320* 2295	40-42
$(pyH)[VOBr_3(CH_3CN)_2]$	2325*,2320*,2300,2280	40-42

* - a combination band (CH_3 bend + C-C stretch)

Table 4.8 $\nu(L=O)$ for complexes of Oxide Ligands

(L=P,S,C)

COMPLEX	$\nu(L=O)/cm^{-1}$	REF
$VOCl_2(hmpa)_2$	1132	
$VOBr_2(hmpa)_2$	1189	40,42
hmpa	1218	40,42
$VOCl_2(Ph_3PO)_2$	1147,1090	
	1140,1088	53
Ph_3PO	1193	135
	1182	53
$VOCl_2(dpso)_3$	949*	
$VOBr_2(dpso)_3$	968,957*	40,42
dpso	1042	40,42
$VOCl_2(dmso)_3$	1012,993	
	1015,996	53
dmso	1050	53
$VOCl_2(tmu)_2$	1563	
tmu	1648	

* - could be due to $\nu(V=O)$

4.3 ELECTRONIC SPECTRAL STUDIES

4.3.1 Oxotetrachlorovanadate(IV) Complexes

The diffuse reflectance spectra of $[Et_4N]_2[VOCl_4]$, $[pyH]_2[VOCl_4]$ (both green and blue samples), $[Ph_4As]_2[VOCl_4]$, $[pyH]_2[VOCl_4]$.x hmpa (the blue product from 3.2.2), and the impure product containing $[Me_4N]_2[VOCl_4]$ from section 3.7 are listed in Table 4.9.

Drake, Vekris and Wood [37] have previously reported the spectrum of $[Et_4N]_2[VOCl_4]$ as having bands at 13,900 cm^{-1} and 24,100 cm^{-1}. Table 4.9 shows excellent agreement for the lower energy band and only a slight difference for the other.

The green $[VOCl_4]^{2-}$ complexes show a characteristic band at *ca.* 13,700 cm^{-1}. This may be attributed to the $^2B_2 \rightarrow {}^2E$ transition [37,40] which is a transition to an energy level derived from the π-bonding involved in the vanadium-oxygen multiple bond. In the spectra of the two blue $[VOCl_4]^{2-}$ complexes, this bend shifts to higher frequency (15,000-16,000 cm^{-1}). It has been found [40], in a study of anionic oxo-bromo complexes of vanadium(IV), that when V-O....V interactions are present, as in the case of $(pyH)[VOBr_3]$, this characteristic band form is absent. The green $[VOCl_4]^{2-}$ complexes all have a higher energy 'd↔d' band at *ca.* 23,000 cm^{-1}, whereas for the blue complexes this band again shifts to higher frequency and is observed at 25,000-26,000 cm^{-1}. Of the two blue complexes, $[pyH][VOCl_4]$.x hmpa has the higher energy 'd↔d' bands, showing that either this complex has a slightly different symmetry, owing to the presence of the hexamethylphosphoramide, or that the $[pyH]_2[VOCl_4]$ was still slightly contaminated with green form. The blue $[pyH]_2[VOCl_4]$ sample had been separated from green $[pyH]_2[VOCl_4]$ (see section 3.5.1) and it was not possible to eliminate all the green solid in this separation.

4.3.2 Adducts of Vanadium(IV) Oxide Dichloride

Table 4.10 lists the diffuse reflectance spectra of the adducts of $VOCl_2$ studied. If the strongest d↔d band is selected to typify ligand field strength, then some general conclusions can be made. For example, for complexes of the type $[VOCl_2L_2]$, then the ligand field strength order is:

S-donors ≥ O-donors ≥ P-donors ≥ N-donors

For $[VOBr_2L_2]$ complexes, the ligand field strength order was found [40] to be:

O-donors ~ S-donors ≥ P-donors ≥ N-donors

Table 4.9 Diffuse Reflectance Spectra of Oxotetrachlorovanadate(IV) Complexes

COMPLEX	COLOUR	CHARGE-TRANSFER BANDS (kK)	HIGHER ENERGY 'd↔ d' BAND (kK)	LOWER ENERGY 'd↔ d' BAND (kK)
$[Et_4N]_2[VOCl_4]$	Green	44.3,39.0,37.3 sh	23.7/23.1/22.4(triplet),21.6sh	13.9
$[Ph_4As]_2[VOCl_4]$	Green	42.2sh,37.1/36.5(doublet), 31.8	24.0sh,23.3/22.6/21.9(triplet), 21.0sh	13.6
$[pyH]_2[VOCl_4]$	Green	42.7sh,39.0,35.3,31.4sh	23.0sh	13.7
$[pyH]_2[VOCl_4]$	Blue	45.3,43.4,38.9,36.1	25.1sh	15.0,9.1sh
$[pyH]_2[VOCl_4]$.x hmpa	Blue	44.0,38.0,35.5	26.0sh	15.8
$[Me_4N]_2[VOCl_4]/Me_4NCl$	Green/White	43.0,39.8	22.8	13.3

The $VOCl_2$ adduct studied with a sulphur-donor ligand was $[VOCl_2(tmtu)_2]$ and tetramethylthiourea has a multiple carbon-sulphur bond. The $[VOBr_2L_2]$ complexes studied were with ligands such as 1,4-thioxan and tetrahydrothiophen, where π-bonding is not involved in the carbon-sulphur linkage. It is not surprising, then, that tetramethylthiourea showed a higher ligand field strength relative to oxygen donors than the sulphur-donor ligands studied with $VOBr_2$ adducts.

For complexes of the type $[VOCl_2L_3]$ and $[VOCl_2L_2]$, the frequency of the band for six-coordinate complexes is higher than that for five-coordinate complexes.

$[VOCl_2(CH_3CN)_2]$, which has a polymeric six-coordinate environment, has its d↔d band at a high frequency since ethanenitrile has a particularly strong ligand field. This is due to the multiple C≡N bond in ethanenitrile.

All these ligand field effects are summarised in Table 4.11. Ligand field effects on the spectra of $VOBr_2$ adducts are also illustrated in the table. These had been observed previously [40]. In Table 4.10, $[VOCl_2(CH_3CN)_2]$ is entered as a six-coordinate complex as indicated by the i.r. spectrum. $[VOCl_2(cy_3P)]$ is also treated as a six-coordinate species. It seems likely that this complex is polymeric with vanadium-chlorine-vanadium bridging. $[VOCl_2(dppe)]$ is considered to be similar to other phosphine complexes such as $[VOCl_2(Ph_3P)_2]$ and is treated as a five-coordinate species. The spectrum of $[VOCl_2(dpso)_3]$ as reported in Table 4.10 has no higher energy 'd↔d' band, the band being masked by lower energy charge transfer bands. A similar observation is made in the spectra of $[VOCl_2(dmso)_3]$, $[VOCl_2(Ph_3P)_2]$ and $[VOCl_2(py)_2]$. The phosphine complexes seem to have a better resolved band form in the 'd↔d' band region, with extra bands being observed at *ca.* 17,000 cm^{-1}.

4.4 ELECTRON PARAMAGNETIC RESONANCE STUDIES

4.4.1 Solids

Table 4.12 lists the parameters obtained from e.p.r. spectra of powdered samples at room temperature. $[VOCl_2(CH_3CN)_2]$, $[VOCl_2(Ph_2MeP)_2]$, $[VOCl_2(dmso)_3]$, $[pyH]_2[VOCl_4]$ (both the blue and green forms), $[pyH]_2[VOCl_4]$.hmpa and $[Me_4N]_2[VOCl_4]$ all gave simple single first derivative curves. Since $[Me_4N]Cl$ does not give an e.p.r. signal, the signal obtained from the mixture of $[Me_4N]Cl$ and $[Me_4N]_2[VOCl_4]$ can be attributed to $[Me_4N]_2[VOCl_4]$.

Table 4.10 Diffuse Reflectance Spectra of Adducts of $VOCl_2$

COMPLEX	COLOUR	CHARGE-TRANSFER BANDS (kK)	HIGHER ENERGY 'd ⟷ d' BAND (kK)	LOWER ENERGY 'd ⟷ d' BAND (kK)
$VOCl_2(CH_3CN)_2$	Blue	44.2,37.3,30.5sh	23.4sh	14.0
$VOCl_2(hmpa)_2$	Blue-Green	44.6,40.1	23.9	13.5
$VOCl_2(Ph_3PO)_2$	Green	43.8,36.2,33.0sh	24.3/23.7(doublet),23.0sh	14.0
$VOCl_2(cy_3P)$	Green	43.3,38.6	23.9	13.4
$VOCl_2(dpso)_3$	Blue	43.0,36.9/36.0(doublet), 32.4sh,28.3sh	-	13.6,12.1sh
$VOCl_2(dmso)_3$	Blue	44.1,38.3,29.5sh	-	13.4
$VOCl_2(Ph_3P)_2$	Green	42.1sh,36.9,31.0,26.0	-	17.0,12.9/11.9(doublet)
$VOCl_2(py)_2$	Blue-Green	43.0,38.9sh,38.0,37.1, 32.8	-	15.5sh,12.4
$VOCl_2(tmtu)_2$	Blue-Green	44.6,40.6sh,38.9,33.2sh, 32.0	22.8	15.0,14.5sh
$VOCl_2(Ph_2MeP)_2$	Green	42.4sh,38.3,32.6,28.3	23.8sh	17.1sh,16.3,13.4
$VOCl_2(dppe)$	Green	42.8,36.3,34.0sh,28.6	22.6	17.7sh,16.9sh,15.9,13.4

Table 4.11 Ligand Field Effects on Principal d ⟷ d Band (kK)

COMPLEX	PRINCIPAL d ⟷ d BAND
$[VOBr_2(py)_3]$	12.8
$[VOCl_2(py)_2]$	12.4
$[VOBr_2(py)_2]$	11.9
$[VOCl_2(CH_3CN)_2]$	14.0
$[VOBr_2(CH_3CN)_3]$	13.9
$[VOCl_2(dpso)_3]$	13.6
$[VOBr_2(dpso)_3]$	13.4
$[VOCl_2(dmso)_3]$	13.4
$[VOCl_2(cy_3P)]$	13.4
$[VOBr_2(py)_3]$	12.8
$[VOCl_2(tmtu)_2]$	15.0
$[VOCl_2(Ph_3PO)_2]$	14.0
$[VOBr_2(thiox)_2]$	14.0
$[VOBr_2(tht)_2]$	13.7
$[VOBr_2(diox)_2]$	13.7
$[VOBr_2(hmpa)_2]$	13.7
$[VOBr_2(thf)_2]$	13.6
$[VOCl_2(hmpa)_2]$	13.5
$[VOCl_2(Ph_2MeP)_2]$	13.4
$[VOCl_2(dppe)]$	13.4
$[VOCl_2(Ph_3P)_2]$	12.9
$[VOBr_2(Ph_3P)_2]$	12.9
$[VOCl_2(py)_2]$	12.4
$[VOBr_2(py)_2]$	11.9
$[VOBr_2(quin)_2]$	11.5

* - this sample of $[VOCl_2(py)_2]$ was the sample prepared as described in 3.9.2 and left for two months, whence its i.r. spectrum was similar to that of the $[VOCl_2(py)_2]$ obtained in 3.9.1.

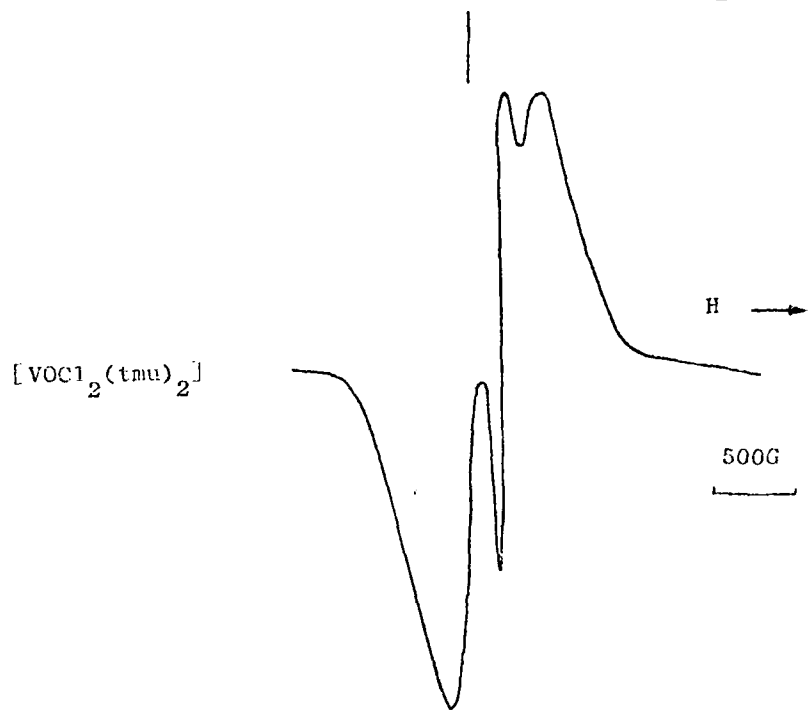
$[VOCl_2(tmu)_2]$ and $[VOCl_2(tmtu)_2]$ both appeared to give two superimposed first derivative peaks, all illustrated in Fig. 4.1. This could be due either to the vanadium(IV) atoms being in two different environments in the compound, or to a minimal amount of hyperfine structure following the interaction of the unpaired electron with the $^{51}V(I=7/2)$ nucleus. The e.p.r. spectrum for $[VOCl_2(dppe)]$ as illustrated in Fig 4.2, has a shoulder in the central region of, what would otherwise be, a normal first-derivative curve.

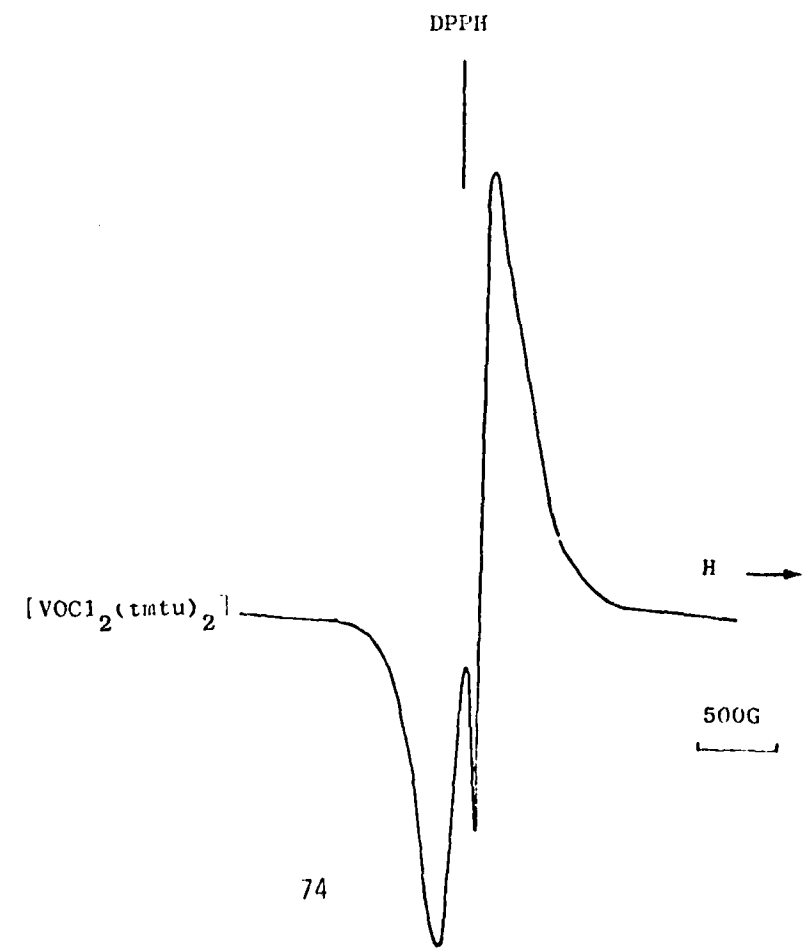
$[VOCl_2(Ph_3PO)_2]$, $[VOCl_2(hmpa)_2]$, $[VOCl_2(Ph_3P)_2]$, $[VOCl_2(cy_3P)]$, $[VOCl_2(dpso)_3]$, $[VOCl_2(dppm)]$, $[Et_4N]_2[VOCl_4]$ and $[Ph_4As]_2[VOCl_4]$ all gave fine structure in their e.p.r. spectra, and their room temperature spectra are shown in Figs. 4.3-4.6. Fine structure has been observed previously [89] for $[VOBr_2(Ph_3P)_2]$, $[VOBr_2(dpso)_3]$, $[VOBr_2(hmpa)_2]$ and $[Et_4N]_2[VOBr_4]$. The fine structure observed can be explained in terms of the complexes behaving as magnetically dilute systems, owing to the presence of very bulky ligands (in the cases of $[VOCl_2(Ph_3PO)_2]$, $[VOCl_2(dpso)_3]$ $[VOBr_2(hmpa)_2]$ etc) or counter-ions (in the cases of $[Ph_4As]_2[VOCl_4]$ and $[Et_4N]_2[VOX_4]$, where X=Cl or Br) around the central ion. Magnetically dilute systems would not be subject to the relaxation processes, involving interactions of the unpaired electron spin moment with electron and nuclear spin moments in neighbouring molecules, to the same extent as magnetically non-dilute spin systems.

Of the solids, $[Ph_4As]_2[VOCl_4]$ and $[VOCl_2(Ph_3PO)_2]$ showed the most complex and well-resolved fine structure. The tetraphenylarsonium cation was the largest counter-ion studied and triphenylphosphine oxide the most bulky ligand. This confirms the dependence of fine structure on size of counter-ion or ligand. The fine structure observed in the case of $[VOCl_2(cy_3P)]$ is only well resolved in the central region of the spectrum. At high and low field extremes, the masking of the structure could be attributed to the polymeric nature of the $VOCl_2(cy_3P)$ complex.

The spectrum of $[Ph_4As]_2[VOCl_4]$ at room temperature was found to be extremely similar to the spectrum of $[Ph_4As]_2[VOCl_4]$ in ethanonitrile at 128 K (see Figs 4.6 and 4.7) and these spectra will be discussed in section 4.4.2.

Fig. 4.1 E.p.r. spectra of powdered samples of $[VOCl_2(tmu)_2]$ and $[VOCl_2(tmtu)_2]$





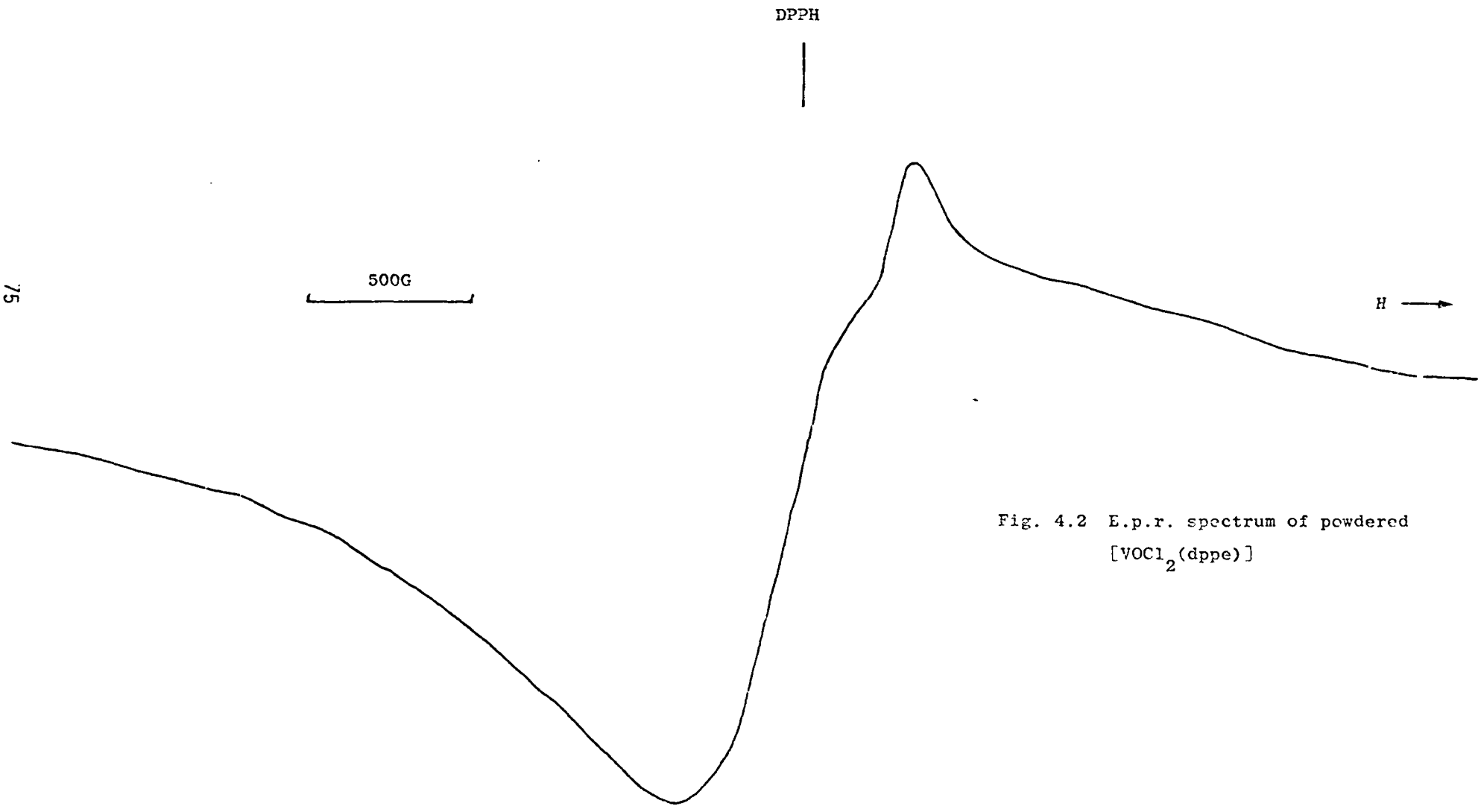


Fig. 4.2 E.p.r. spectrum of powdered $[VOCl_2(dppe)]$

Table 4.12 includes g-values obtained from e.p.r. spectra of $VOBr_2$ adducts [89] and these are compared with the results for $VOCl_2$ adducts. All the complexes in Table 4.12 gave simple first-derivative curves except for $[VOCl_2(tmu)_2]$ and $[VOCl_2(tmtu)_2]$. For these compounds, there appeared to be two superimposed first derivative curves, one very broad and one very sharp. An alternative interpretation of the spectrum would be that only one line of fine structure was seen in the spectrum, which otherwise was a simple first derivative curve. The g values are all in the 1.990-2.005 range except for $[VOBr_2(dmf)]$ and $[Fecp_2][VOBr_3]$. There are no trends observed due to the donor-atom of the ligand, size of the ligand, or stereochemistry of the complex. Values of g_{iso} for $[VOCl_2(Ph_3PO)_2]$, $[VOCl_2(cy_3P)]$, $[VOCl_2(Ph_3P)_2]$, $[VOCl_2(Ph_2MeP)_2]$, $[VOCl_2(dppe)]$ and $[Ph_4As]_2[VOCl_4]$ are quoted in section 4.4.2. These values were calculated from solution e.p.r. spectra. Computer simulation studies were used for calculating g values from spectra of powdered samples, where fine structure was observed. The only computer simulation carried out on such a spectrum concerned the spectrum of $[Ph_4As]_2[VOCl_4]$ and the result is illustrated in Fig 4.8. The simulation gave g values and A values as follows:

$g_{\parallel} = 1.9609$ $\quad A_{\parallel} = 182.8$ G

$g_{\perp} = 1.9866$ $\quad A_{\perp} = 74.1$ G

From these values, g_{iso} and A_{iso} values can be calculated giving the results below.

$g_{iso} = 1.9780$ $\quad A_{iso} = 110.4$ G

These values may be compared with those obtained for the computer simulation of the low-temperature solution e.p.r. spectrum of $[Ph_4As]_2[VOCl_4]$ discussed in 4.4.2.

The g value for $[VOCl_2(Ph_2MeP)_2]$ is quoted in Table 4.21 and solution e.p.r. studies are also discussed in section 4.4.2 The different studies give two different g values for this complex.

Fig. 4.3 E.p.r. spectra of powdered samples of $[VOCl_2(hmpa)_2]$ and $[VOCl_2(Ph_3PO)_2]$

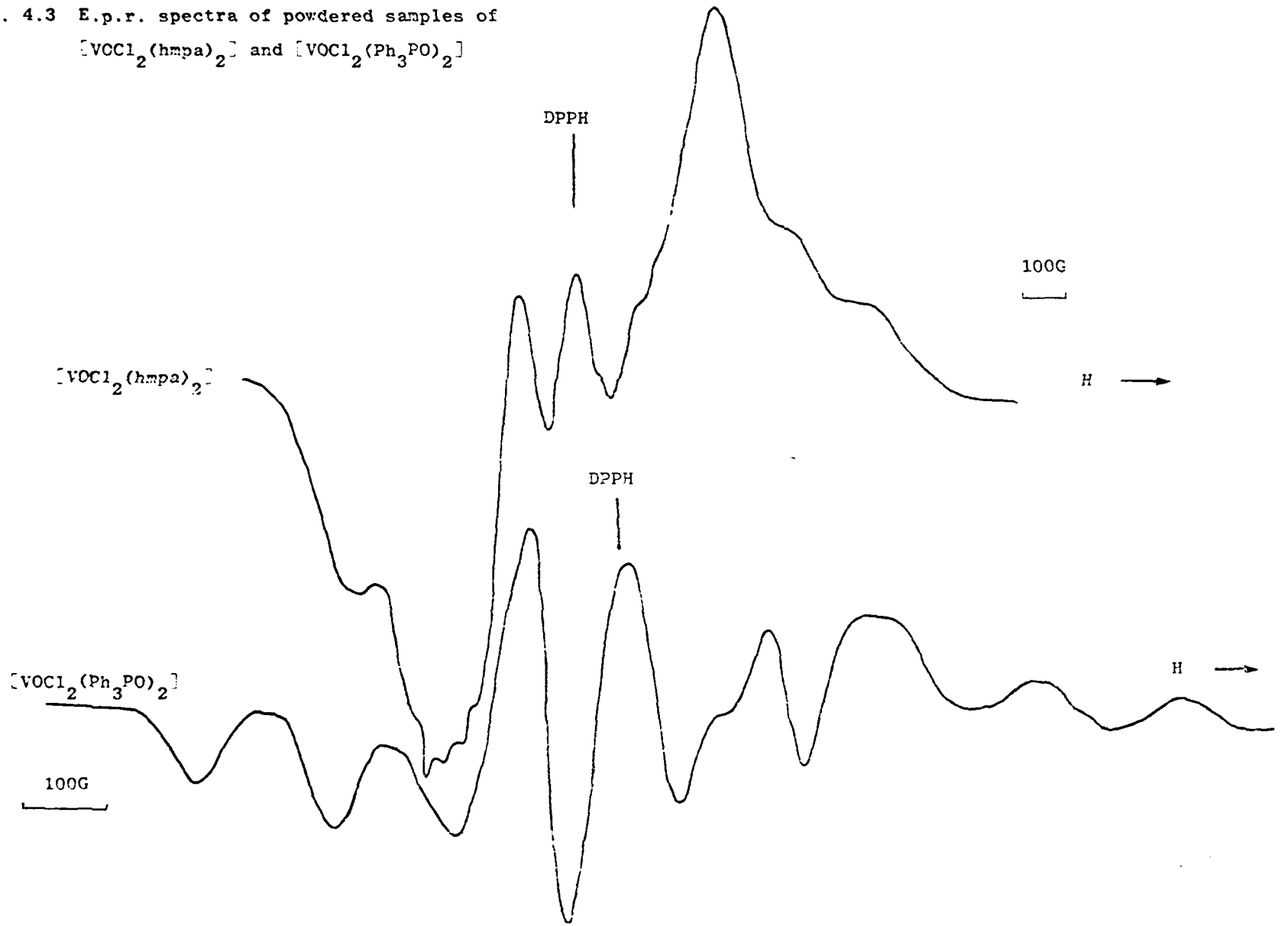


Fig. 4.4 E.p.r. spectra of powdered samples of $[VOCl_2(Ph_3P)_2]$ and $[VOCl_2(cy_3P)]$

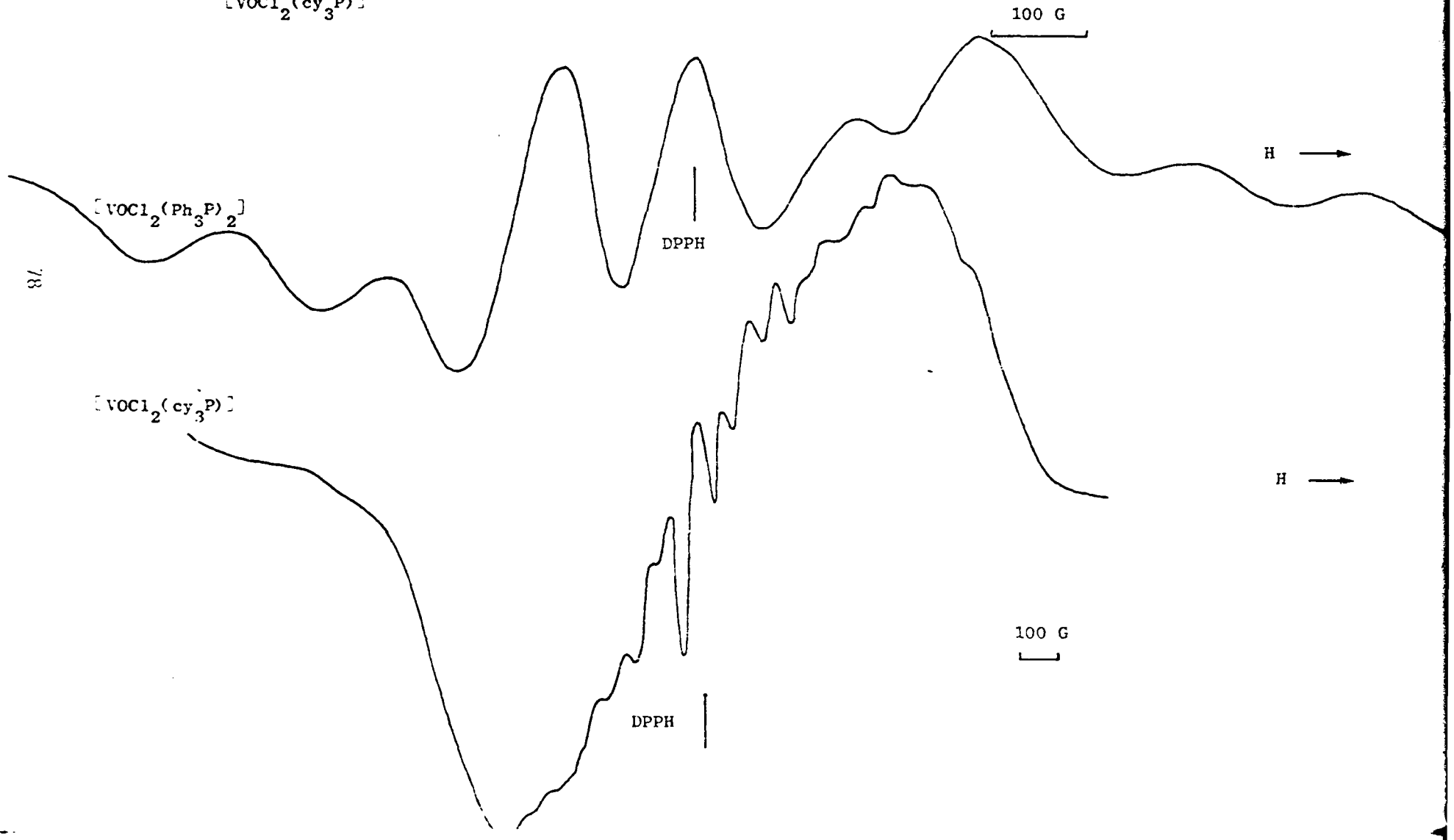


Fig. 4.5 E.p.r. spectra of powdered samples of $[VOCl_2(dpso)_3]$ and $[VOCl_2(dppm)]$

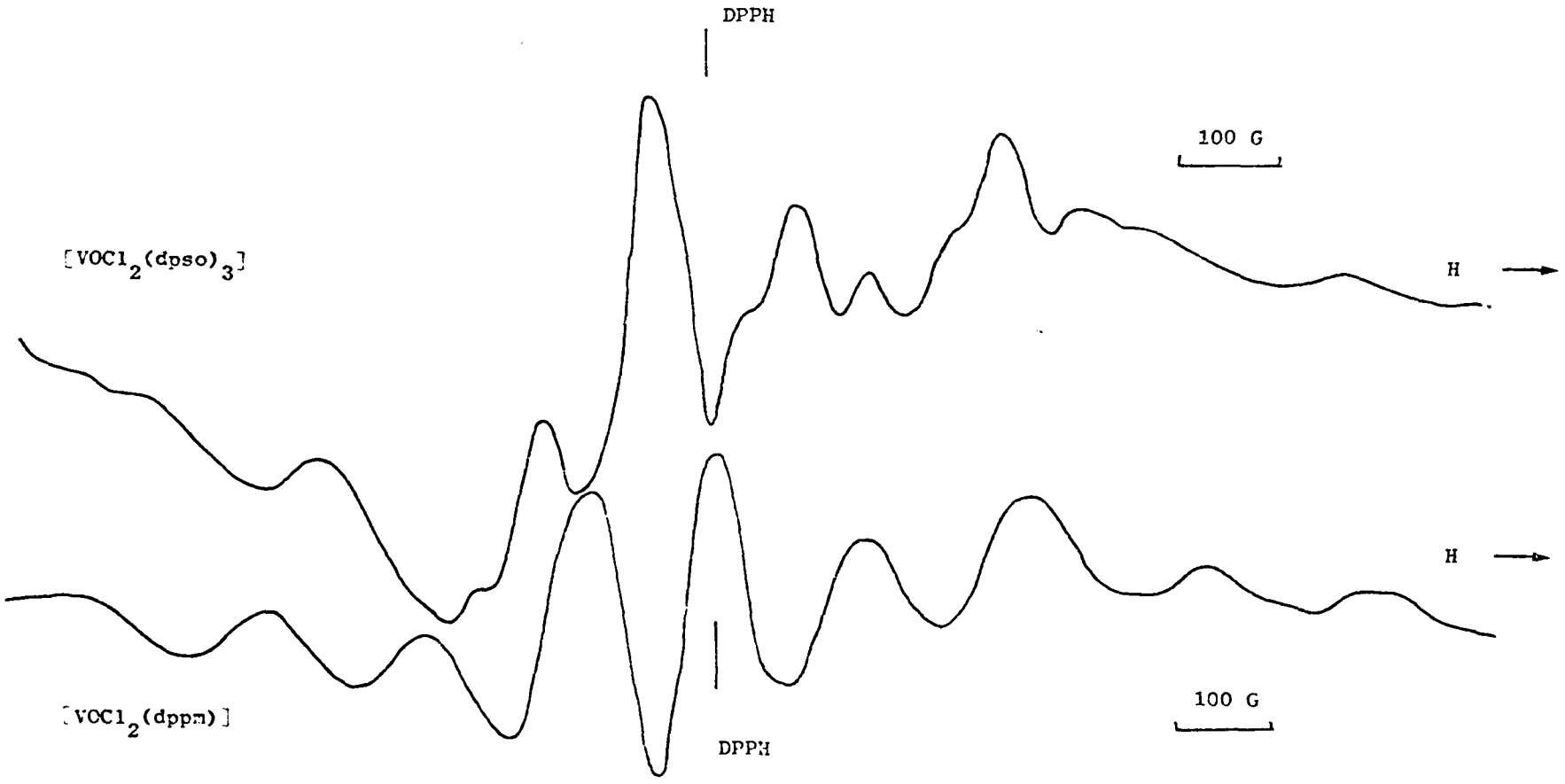


Fig. 4.6 E.p.r. spectra of powdered samples of $[Et_4N]_2[VOCl_4]$ and $[Ph_4As]_2[VOCl_4]$

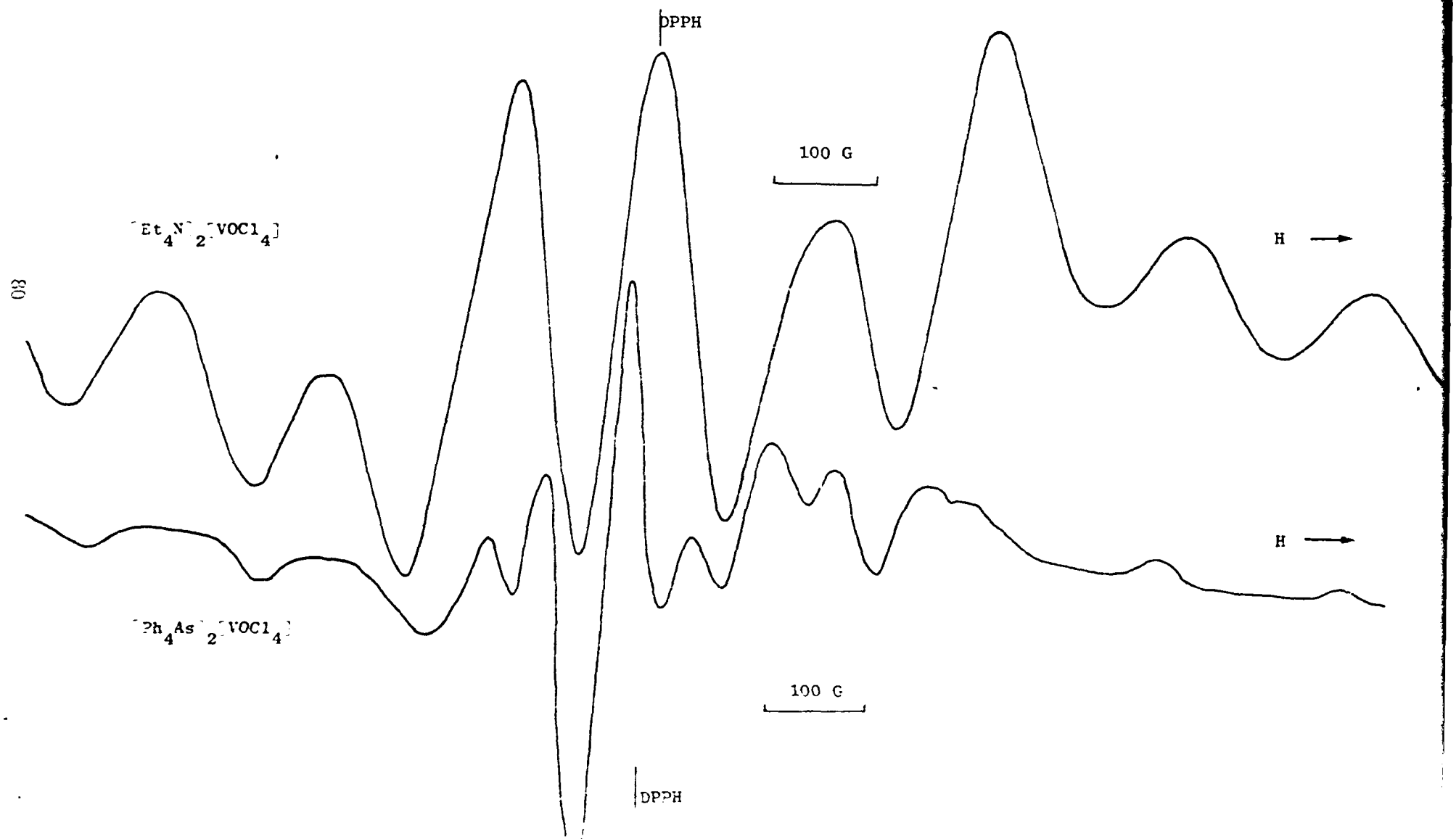
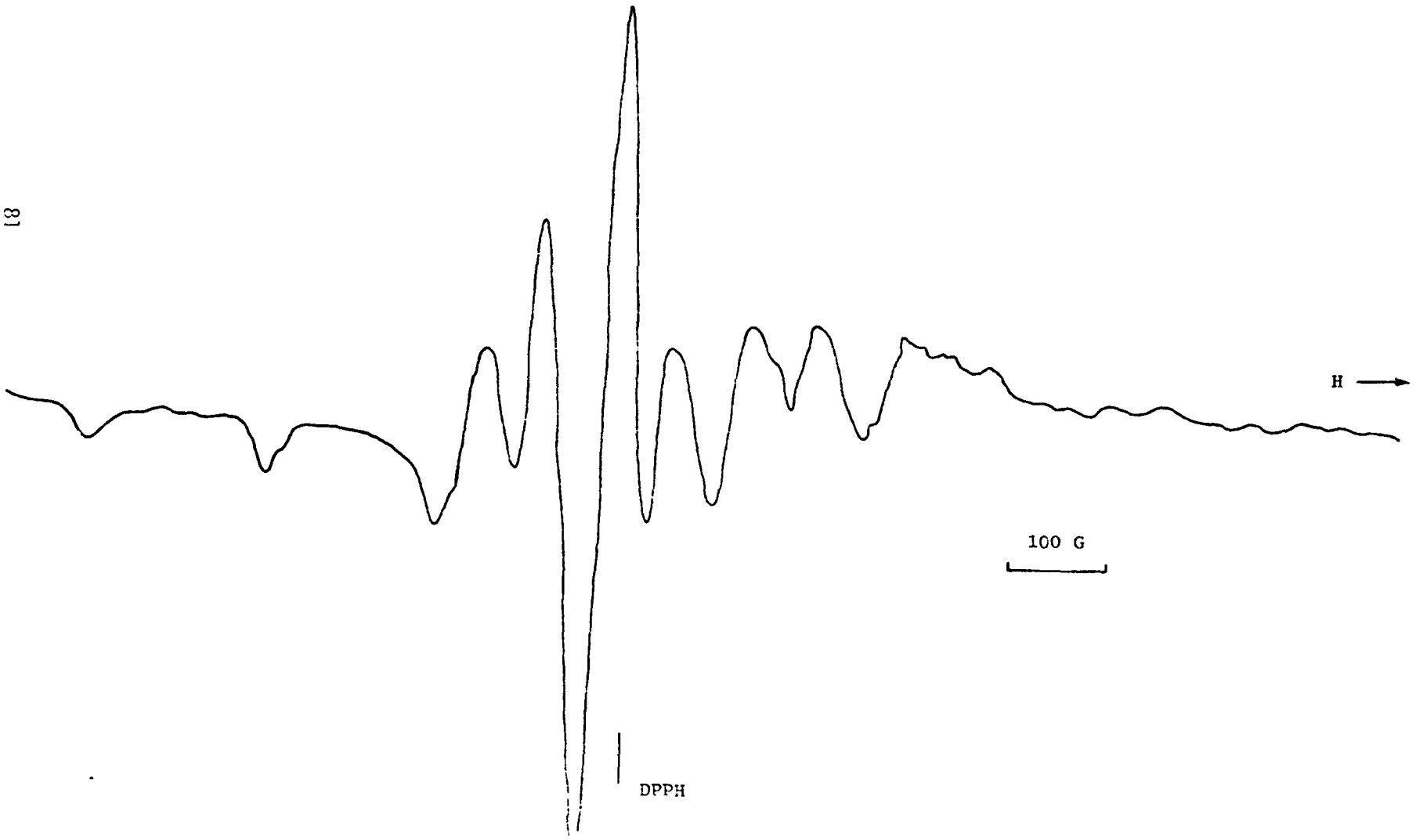


Fig. 4.7 E.p.r. spectrum of $[Ph_4As]_2[VOCl_4]$ in ethanenitrile at 128 K



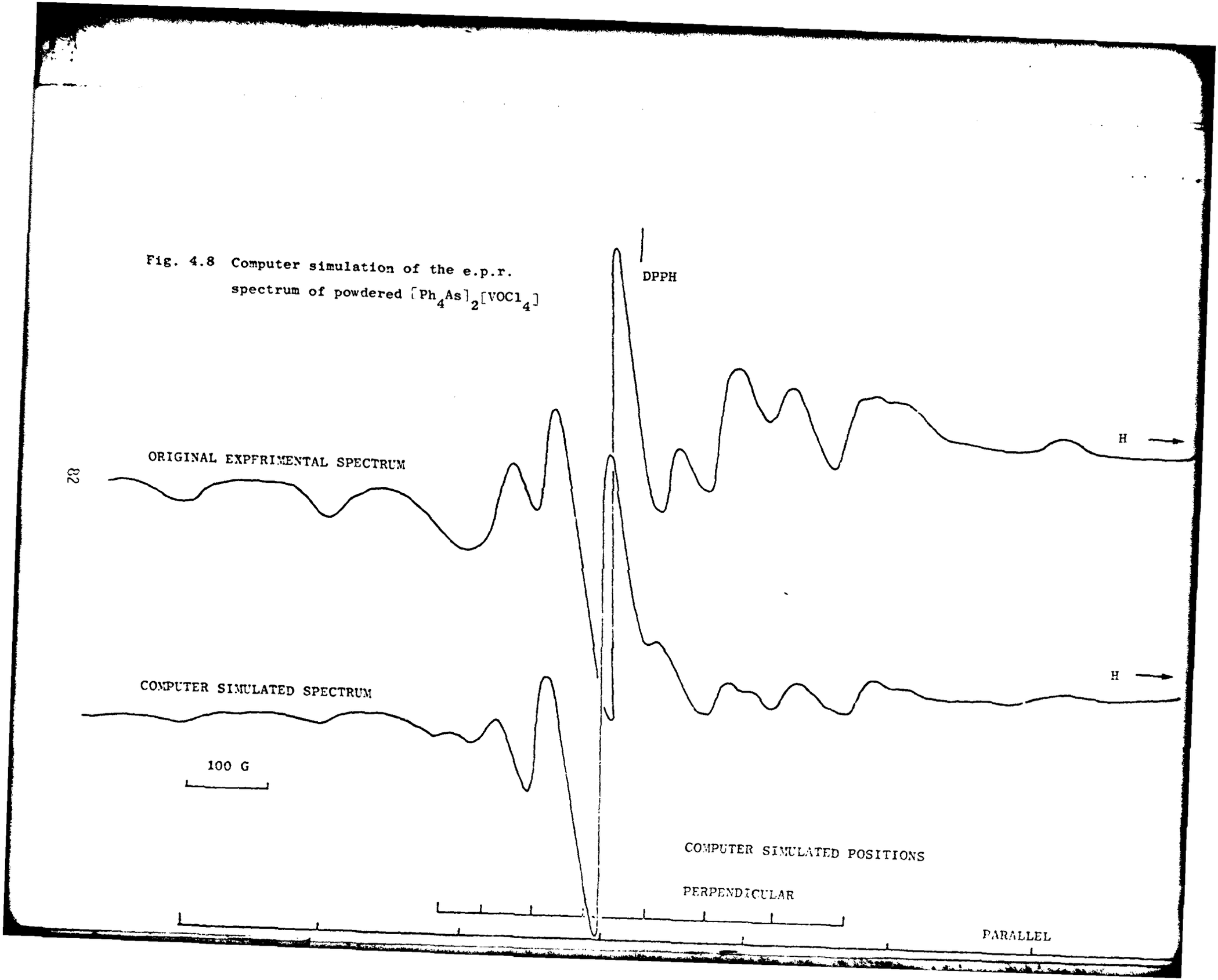


Fig. 4.8 Computer simulation of the e.p.r. spectrum of powdered $[Ph_4As]_2[VOCl_4]$

Table 4.12 E.p.r. results from powdered samples (298K)

$VOBr_2$ complex	g	$VOCl_2$ complex	g
$[Fecp_2]$ $VOBr_3$	2.015	Green $[pyH]_2[VOCl_4]$	2.004
$[VOBr_2(thiox)_2]$	2.005	$[VOCl_2(dmso)_3]$	2.001
$[VOBr_2(quin)_2]$	2.001	Blue $[pyH]_2[VOCl_4]$.hmpa	1.998
$[VOBr_2(4\text{-}pic)_3]$	1.998	Blue $[pyH]_2[VOCl_4]$	1.997
$[VOBr_2(diox)_2]$	1.997	$[VOCl_2(Ph_2MeP)_2]$	1.996
$[VOBr_2(py)_3]$	1.995	$[Me_4N]_2[VOCl_4]$	1.995
$[VOBr_2(py)_2]$	1.992	$[VOCl_2(tmtu)_2]$	1.995/1.993
$[quinH]_3[VOBr_5]$	1.991	$[VOCl_2(tmu)_2]$	1.994/1.996*
$[VOBr_2(dme)]$	1.970	$[VOCl_2(CH_3CN)_2]$	1.992

* See text for explanation of two values

4.4.2 Solutions

Table 4.13 lists the parameters obtained from e.p.r. spectra in either ethanenitrile (in the case of $[Ph_4As]_2[VOCl_4]$ and $[VOCl_2(Ph_3PO)_2]$ or tetrahydrofuran. Spectra were recorded at room temperature and at *ca.* 138 K. The isotropic spectra of all the complexes studied showed eight distinct lines as anticipated, whereas the anisotropic spectra all exhibited complex fine structure. No ligand hyperfine structure was observed in the spectra of the various phosphine complexes studied. The values of parameters g_{iso}, A_{iso}, $g_{\parallel}$, $A_{\parallel}$, $g_{\perp}$ and $A_{\perp}$ were calculated using computer simulation as described in section 2.5. Parameters calculated previously [40,89] for $VOBr_2$ complexes are listed in Table 4.13 for comparison.

The g_{iso} values calculated from the e.p.r. solution spectra are typically 1.97. The g_{iso} values quoted in Table 4.12 for those powdered samples which gave simple first-derivative curves, were of the order of 1.995. It is not reasonable to expect these values to coincide, since the factors which cause line-broadening and lead to simple first-derivative curves, are not present in solution. This being so, a difference in g-values might be expected.

The A_{iso} values for the various solutions of $[VOBr_2(Ph_3P)_2]$ in tetrahydrofuran or methylbenzene are interesting. It has been postulated [89] that in tetrahydrofuran, the possibility of the following equilibrium exists:

$$[VOBr_2(Ph_3P)_2] \underset{Ph_3P}{\overset{thf}{\rightleftharpoons}} [VOBr_2(Ph_3P)(thf)] \underset{Ph_3P}{\overset{thf}{\rightleftharpoons}} [VOBr_2(thf)_2]$$

At any one time, then, more than one species will be present in solution. The addition of excess ligand will shift the equilibrium to the left, but the e.p.r. signal observed is always a time-averaged signal, due to the various species present. The species responsible for the e.p.r. signal giving an A_{iso} value of 106 G in tetrahydrofuran is $[VOBr_2(thf)_2]$. However, when either excess triphenylphosphine is added, or a non-coordinating solvent such as methylbenzene is used, a different species (probably $VOBr_2(Ph_3P)_2$) gives an e.p.r. signal with a higher A_{iso} value of 111 or 113 G. The signal observed could be time-averaged for several species, but clearly the equilibrium position shifts. This type of equilibrium could also occur for solutions in ethanenitrile, which is a coordinating solvent.

Table 4.13 E.p.r. results from solution samples

A. ISOTROPIC SPECTRA DATA

Complex	Solvent	g_{iso}	A_{iso}/G
$[VOCl_2(Ph_3PO)_2]$	CH_3CN	1.966	109.8
$[Ph_4As]_2[VOCl_4]$	CH_3CN	1.969	109.2
$[VOCl_2(cy_3P)]$	thf	1.975	106.4
$[VOCl_2(Ph_3P)_2]$	thf	1.965	107.6
$[VOCl_2(dppe)]$	thf	1.967	118.8
$[VOCl_2(Ph_2MeP)_2]$	thf	1.966	119.5
" (+ added Ph_2MeP)	thf	1.970	121.6
$[Fe(cp)_2][VOBr_3]$	CH_3CN	1.989	104
$[Et_4N]_2[VOBr_4]$	CH_3CN	1.996	100
$[pyH]_2[VOBr_4]$	CH_3CN	2.005	100
$[VOBr_2(Ph_3P)_2]$	thf	1.985	106
$[VOBr_2(Ph_3P)_2]$ (+ added Ph_3P)	thf	1.987	111
$[VOBr_2(Ph_3P)_2]$ (+ added Ph_3P)	$PhCH_3$	1.977	113
$[VOBr_2(py)_3]$	py	1.979	98
$[pyH][VOBr_3(CH_3CN)_2]$	CH_3CN	1.998	99
$[VOBr_2(py)_3]$	$PhCH_3$	1.989	103

B. ANISOTROPIC SPECTRAL DATA

Complex	Solvent	$g_{\parallel}$	$g_{\perp}$	$g_{iso(calc)}$	$A_{\parallel}$/G	$A_{\perp}$/G	$A_{iso(calc)}$/G
$[VOCl_2(Ph_3PO)_2]$	CH_3CN	1.939	1.973	1.962	199.37	79.55	119.5
$[Ph_4As]_2[VOCl_4]$	CH_3CN	1.959	1.984	1.976	184.05	75.60	111.8
$[VOCl_2(Ph_3P)_2]$	thf	1.955	1.983	1.974	180.36	72.61	108.5
$[VOCl_2(dppe)]$	thf	1.947	1.973	1.964	227.33	91.48	136.8
$[VOCl_2(Ph_2MeP)_2]$	thf	1.957	1.986	1.977	200.77	79.39	119.9
$[VOCl_2(cy_3P)]$	thf	1.945	1.973	1.963	196.40	78.45	118.4
$[VOBr_2(Ph_3P)_2]$	$PhCH_3$	1.967	1.976	1.973	184	74	111
$[VOBr_2(py)_3]$	$PhCH_3$	2.010	1.984	1.993	182	70	101

Of the six $VOCl_2$ adducts studied, $[Ph_4As]_2[VOCl_4]$ is the only one which should not be affected in this way, since there are no neutral ligands to be displaced by the coordinating solvents. Coordination of a sixth ligand could, however, occur giving an ion of the type $[VOCl_4L]^{2-}$. The data quoted in Table 4.13, for $[Ph_4As]_2[VOCl_4]$ can be compared with the data obtained by computer simulating the e.p.r. spectrum of the powdered compound (see section 4.4.1). The values are similar and the species present in solution is clearly, therefore, $[Ph_4As]_2[VOCl_4]$.

If, for the other complexes, we assume that an A_{iso} value of <110 G is indicative of species, predominantly of the type $[VOCl_2(thf)_2]$ or $[VOCl_2(CH_3CN)_2]$, and an A_{iso} value of >110 G indicates the formation of complexes of the type, $[VOCl_2(thf)L]$ or $[VOCl_2L_2]$, then various conclusions can be drawn. These assumptions are based on the results for $[VOBr_2(Ph_3P)_2]$ in tetrahydrofuran and methylbenzene discussed earlier.

$[VOCl_2(Ph_3P)_2]$ appears to exist in tetrahydrofuran solution as $[VOCl_2(thf)_2]$, both at room temperature and at 138 K. This would explain the lack of ligand hyperfine structure (due to coordinated phosphine ligand) in the e.p.r. solution spectra of the complex.

The high A_{iso} values for $[VOCl_2(Ph_2MeP)_2]$ both in the isotropic and anisotropic data suggests the complex in solution contains at least one coordinated phosphine ligand. If at least one phosphine ligand is coordinated, as seems likely, then it is surprising that no ligand hyperfine structure is observed. The extra methyldiphenylphopshine added has little effect on the g_{iso} and A_{iso} values (see Table 4.13). This could be because the species present already is $[VOCl_2(Ph_2MeP)_2]$, or it could indicate that the equilibrium constant for the coordination of the second phosphine ligand is such that this does not occur to a large extent under the conditions in which the addition of excess ligand was carried out.

$[VOCl_2(Ph_3PO)_2]$ and $[VOCl_2(cy_3P)]$ both have A_{iso} values of <110 G at room temperature and values of >115 G at 138 K. At room temperature the e.p.r. signals are likely to be due to $[VOCl_2(CH_3CN)_2]$ and $[VOCl_2(thf)_2]$ respectively. As the solutions are cooled gradually by blowing cold nitrogen gas over the sample (see section 2.5), the complexes $[VOCl_2(Ph_3PO)_2]$ and $[VOCl_2(cy_3P)]$ could be formed. Both these complexes are relatively insoluble as described in the preparative section (Chapter 3) and it is perhaps reasonable to postulate that, as the solution gets more concentrated on gradual freezing of the solvent, the equilibrium shifts

so as to favour the formation of these complexes.

$[VOCl_2(dppe)]$ has A_{iso} values of 118.77 and 136.76 respectively at room temperature and 138 K. Neither of these values can be due to the $[VOCl_2(thf)_2]$ complex, so it is possible that the room temperature signal is due to the mixed complex, $[VOCl_2(dppe)(thf)]$. The e.p.r. spectrum recorded at 138 K is then assigned to the $[VOCl_2(dppe)]$ complex. $[VOCl_2(dppe)]$ has again been shown to be relatively insoluble in tetrahydrofuran and will form as the solution becomes more concentrated at low temperatures. The fact that the $[VOCl_2(dppe)]$ complex has an A_{iso} value of 136.76 and that $[VOCl_2(dppe)(thf)]$ has an A_{iso} value of 118.77 does not necessitate the reassignment of all the other complexes studied. As stated previously, all the e.p.r. signals seen are time-averaged signals for all the species present. Although the predominant species in a solution giving an e.p.r. signal with an A_{iso} value of *ca.* 120 G may well be of the type, $[VOCl_2L(thf)]$, no definite conclusions can be drawn from the limited experimental evidence available.

Neither $[VOCl_2(Ph_2MeP)_2]$ (due to the relatively small ligand), nor $[VOCl_2(dppe)]$ (due to its bridged polymeric structure in the solid state) showed fine structure in the e.p.r. spectra of the powdered complexes so comparisons could not be made for these complexes.

Table 4.13 shows that $[VOBr_2(Ph_3P)_2]$ and $[VOBr_2(py)_3]$ both remain unchanged as cooling is carried out. Methylbenzene is a non-coordinating solvent, but, comparing the A_{iso} values for $[VOBr_2(py)_3]$ in pyridine and methylbenzene, it seems likely that the equilibrium

$$[VOBr_2(py)_3] \underset{py}{\overset{PhCH_3}{\rightleftharpoons}} [VOBr_2(py)_2] + py$$

exists [89]. The e.p.r. signal with an A_{iso} value of 103 for the methylbenzene solution is due to $[VOBr_2(py)_2]$, whereas the A_{iso} value of 99, for the pyridine solution, is due to the six coordinate complex, $[VOBr_2(py)_3]$.

Finally, it is possible that, by employing a more rapid cooling technique such as plunging the e.p.r. sample tube into liquid nitrogen different species will be "trapped" in the frozen solutions from the complexes studied when gradual cooling by cold nitrogen gas is used.

All the g and A values quoted in Table 4.13 were calculated by computer simulation of the spectra concerned. In every case the simulated spectrum approximated to the original spectrum and Figs 4.9 and 4.10 show two typical cases, the spectra of $[Ph_4As]_2\ [VOCl_4]$ and $[VOCl_2(Ph_3PO)_2]$ solutions in ethanenitrile at 138 K, and the corresponding simulations. The arrows on the original spectra indicate the positions measured to provide the input data for the computer program (see section 2.5). The two sets of eight positions measured correspond to the eight 'parallel' and eight 'perpendicular' lines.

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ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY OF VANADIUM (IV) C--ETC(U)
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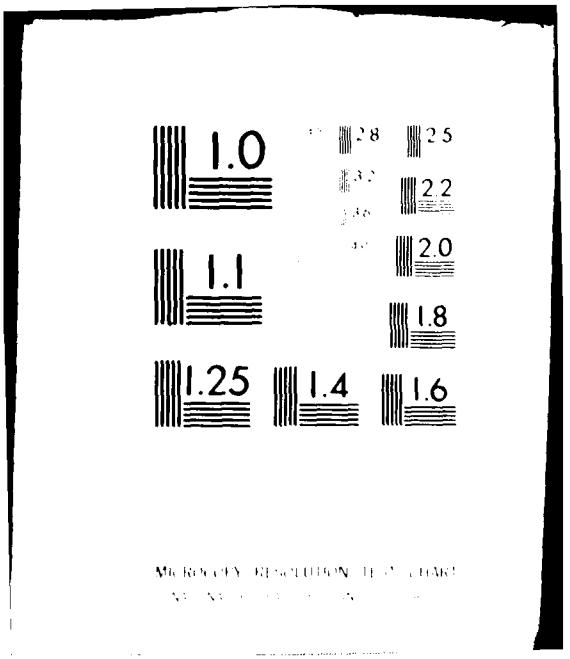
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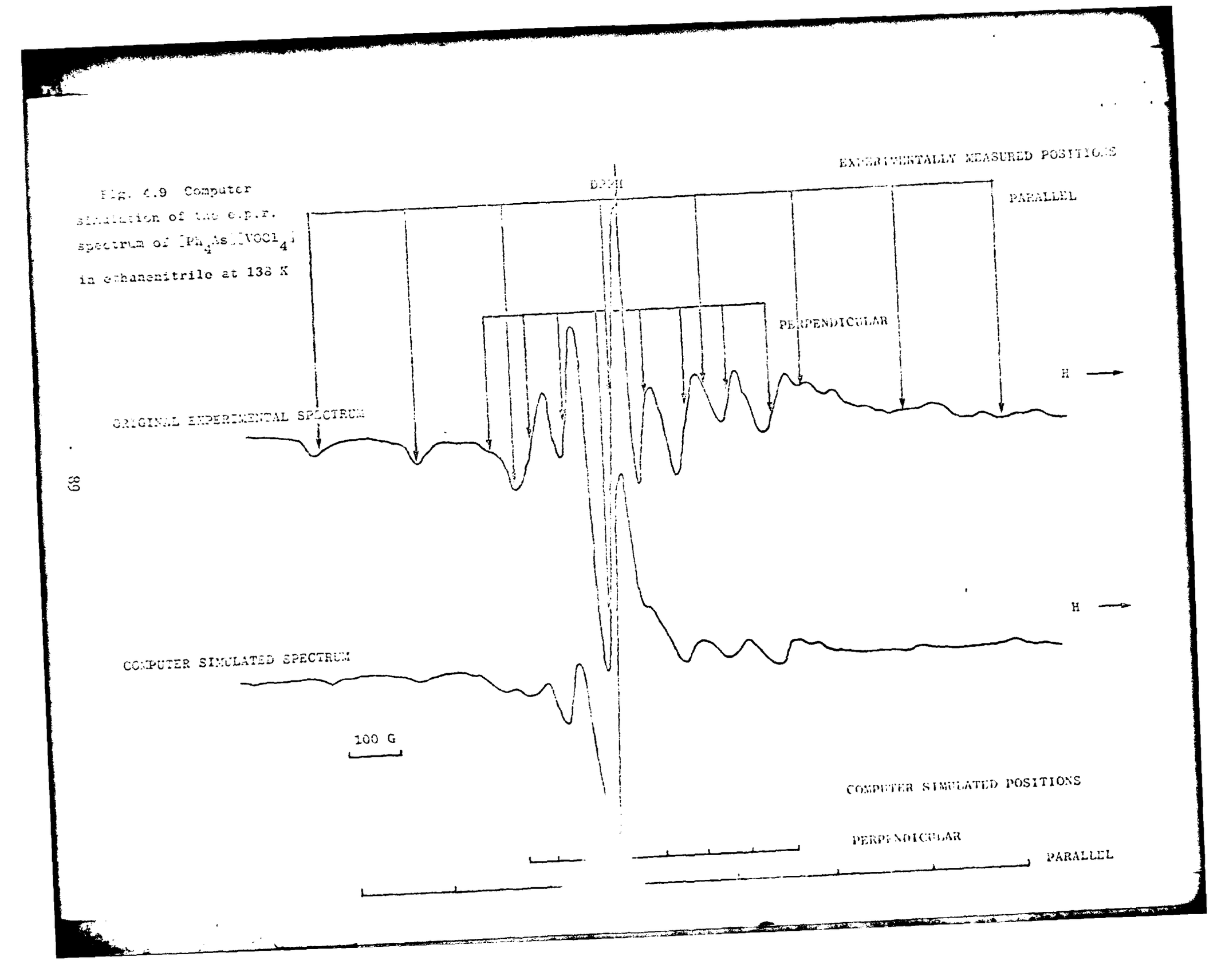
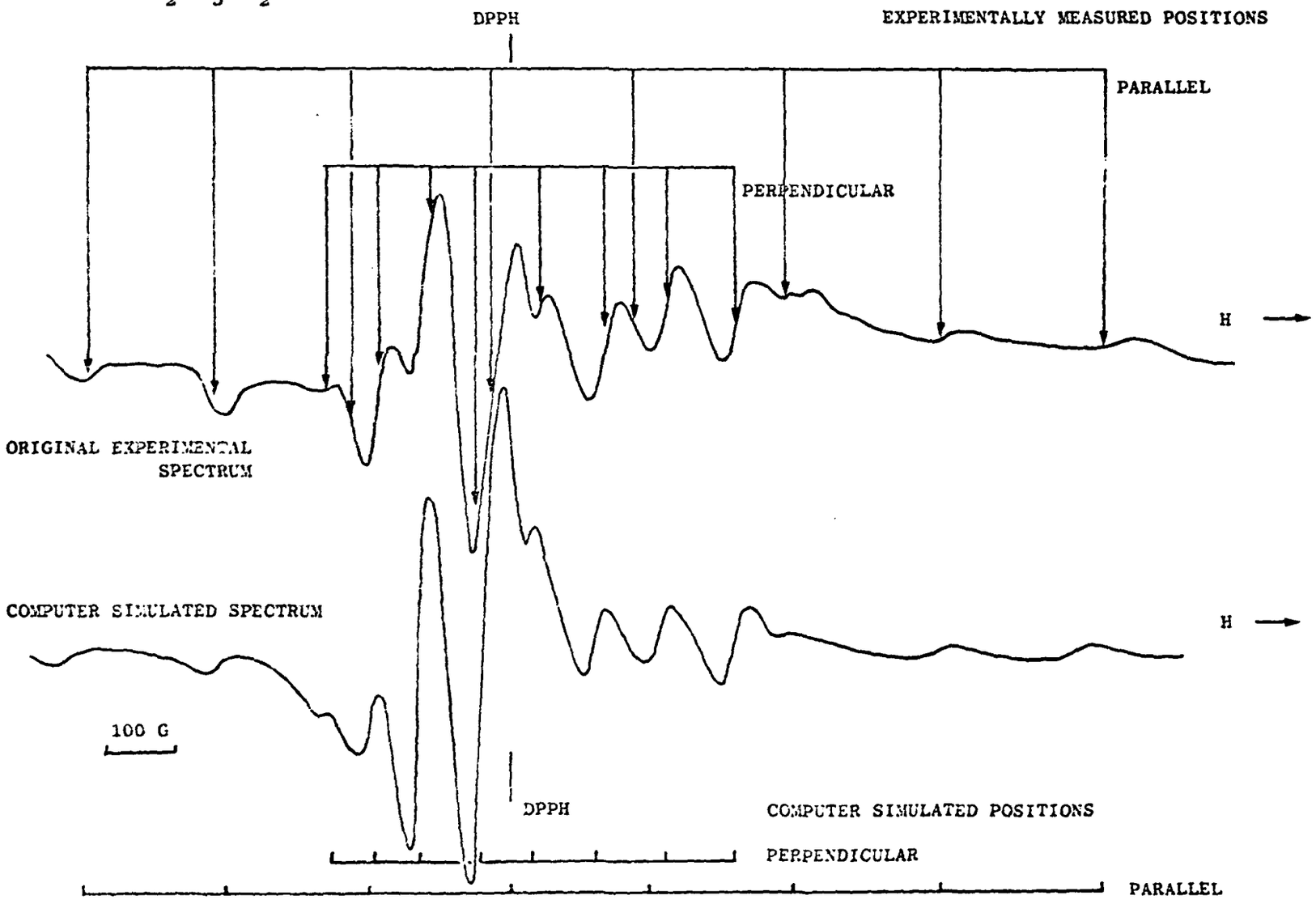


Fig. 4.9 Computer simulation of the e.p.r. spectrum of $[Ph_4As][VOCl_4]$ in ethanenitrile at 138 K

Fig. 4.10 Computer simulation of the e.p.r. spectrum of $[VOCl_2(Ph_3PO)_2]$ in ethanenitrile at 138 K



SECTION 5 : CONCLUSIONS AND SUMMARY

5.1. INTRODUCTION

Many complexes of the types $A_2[VOCl_4]$ (where A is a cation) and $[VOCl_2L_n]$ (where L is a neutral monodentate or bidentate ligand and n is 1,2 or 3) were prepared by means of a ligand exchange method using $[VOCl_2(CH_3CN)_2]$ as starting material. This method proved to be an extremely successful synthetic route to a wide range of complexes. It was, however, not possible to form complexes with triphenylstibine, triphenylarsine or triphenylamine. This was due to the fact that the solvents, ethanenitrile or tetrahydrofuran, coordinated more readily than the stibine, arsine or amine concerned. Five phosphine complexes were prepared, analysed and studied.

5.2. ANIONIC COMPLEXES

Three $[VOCl_4]^{2-}$ complexes, namely $[Et_4N]_2[VOCl_4]$, $[pyH]_2[VOCl_4]$ and $[Ph_4As]_2[VOCl_4]$ were prepared. In addition to these, $[Me_4N]_2[VOCl_4]$ was prepared in admixture with $[Me_4N]Cl$.

$[Et_4N]_2[VOCl_4]$, $[Ph_4As]_2[VOCl_4]$ and $[Me_4N]_2[VOCl_4]$ were green. The diffuse reflectance spectra of these three complexes all had strong 'd ↔ d' bands at *ca.* 13700 cm^{-1}, and the far infrared spectra contained one strong band (and a lower energy shoulder) assigned as a ν(v-Cl) stretching frequency. This strong band always occurred in the 345 cm^{-1}, region, and suggested that the $[VOCl_4]^{2-}$ ion in these complexes had a square pyramidal (C_{4v}) symmetry.

$[pyH]_2[VOCl_4]$ was green in colour at room temperature but predominantly blue at 243 K. The green and blue forms of the complex were studied separately. The green form had similar i.r. and diffuse reflectance spectra to the three green $[VOCl_4]^{2-}$ complexes discussed above. The blue form had a strong i.r. band at 400 cm^{-1} and a weaker band at 360 cm^{-1}, both of which were assigned as ν(V-Cl) bands. This result suggests an equilibrium between two geometric isomers of the $[VOCl_4]^{2-}$ ion, similar to that observed previously for $[VOBr_4]^{2-}$ [40,41] and for $[VOF_4]^-$ [125] . The green isomer, on the basis of its i.r. spectrum, has C_{4v} symmetry (square pyramidal), and the blue isomer has C_{2v} symmetry (trigonal bipyramidal). There were differences in the diffuse reflectance spectra also. The green $[VOCl_4]^{2-}$ complexes have a strong 'd ↔ d' band at *ca.* 13700 cm^{-1} whereas blue $[pyH]_2[VOCl_4]$ has a 'd ↔ d' band at 15000 cm^{-1}. $[VOCl_2(NMe_3)_2]$, which is known to have trigonal bipyramidal symmetry [36], has its major 'd ↔ d' band at 13150 cm^{-1} [36],

but $[VOCl_2(py)_2]$, which, on the basis of its i.r. spectrum, has square pyramidal symmetry has a 'd ⟷ d' band at 12400 cm^{-1}. Although trimethylamine and pyridine are different ligands, they are both nitrogen-donors and these two results, together with the $[VOCl_4]^{2-}$ i.r. frequencies quoted, would suggest that for complexes with similar ligands, those with trigonal bipyramidal symmetry have their major 'd ⟷ d' band at higher frequencies than those with square pyramidal symmetry. $[pyH]_2[VOCl_4].x$ hmpa is blue and has similar i.r. and diffuse reflectance spectra to the blue form of $[pyH]_2[VOCl_4]$. The hexamethylphosphoramide present stabilises the blue $[VOCl_4]^{2-}$. Both blue complexes give an extra band in their i.r. spectra at *ca.* 275 cm^{-1} which is tentatively assigned as a δ(O=V-Cl) bending frequency. This band is absent in the spectra of the green complexes.

Attempts to form anionic complexes of the types $[VOCl_3L_2]^-$, $[VOCl_3L]^-$ and $[VOCl_4L]^{2-}$ were unsuccessful. The ligands used in these attempts were hexamethylphosphoramide and triphenylphosphine oxide, but despite varying the relative proportions of the reagents, the only products formed were $[pyH]_2[VOCl_4]$, $[VOCl_2(hmpa)_2]$ and $[VOCl_2(Ph_3PO)_2]$.

5.3. NEUTRAL COMPLEXES

All the neutral complexes prepared were five- or six-coordinate. On the basis of their formulae, three of the complexes prepared, $[VOCl_2(cy_3P)]$, $[VOCl_2(dppm)]$ and $[VOCl_2(dppe)]$ might have been expected to be four coordinate but this was not the case. $[VOCl_2(cy_3P)]$, on the evidence of its i.r. spectrum has a six-coordinate polymeric structure with bridging through chlorine atoms. The e.p.r. spectrum of $[VOCl_2(dppm)]$ suggests an absence of bridging in the molecule and the i.r. spectrum confirms that the bidentate ligand is acting as a chelate, and that the molecule has square pyramidal (C_{2v}, in this case) symmetry. In contrast, the e.p.r. spectrum of powdered $[VOCl_2(dppe)]$ suggests that bridging dppe is present, and the i.r. spectrum suggests that the bridging is through the phosphine ligands.

The five-coordinate complexes have either trigonal bipyramidal (C_{2v}) or square pyramidal (C_{2v}) symmetry (see Table 4.5). The infrared spectrum of $[VOCl_2(CH_3CN)_2]$ suggests that it has neither of these symmetries, but rather a six-coordinate polymeric structure with chlorine bridging, in the solid state.

Apart from $[VOCl_2(cy_3P)]$ and $VOCl_2(CH_3CN)_2$, the only other

six-coordinate species prepared were $[VOCl_2(dpso)_3]$, $[VOCl_2(dmso)_3]$ and $[VOCl_2(py)_3]$.

In the $VOBr_2$ system the ionic $[VO(dmso)_5\ Br_2]$ has been prepared [40,42] but it was not possible to prepare the chloro-analogue.

5.4. ELECTRON PARAMAGNETIC RESONANCE STUDIES

The results confirm that the amount of hyperfine structure seen in the e.p.r. spectrum of a powdered sample of an oxodihalovanadium(IV) complex depends on the size of the counter-ion or ligand present with large counter-ions or ligands leading to more fine structure. $[Ph_4As]_2[VOCl_4]$ and $[VOCl_2(Ph_3PO)_2]$, in particular, gave spectra which were very similar to those obtained under truly anisotropic conditions (*ie*: in a frozen solution). Computer simulation of the spectrum of $[Ph_4As]_2\ [VOCl_4]$ enabled $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, $A_{\perp}$, g_{iso} and A_{iso} values to be calculated. $[VOCl_2(dppe)]$ did not give fine structure in its e.p.r. spectrum because of its bridged polymeric structure in the solid state. The compounds which gave rise to fine structure were:

$[VOCl_2(hmpa)_2]$, $[VOCl_2(Ph_3PO)_2]$, $[VOCl_2(Ph_3P)_2]$, $[VOCl_2(cy_3P)]$, $[VOCl_2(dpso)_3]$, $[VOCl_2(dppm)]$, $[Et_4N]_2[VOCl_4]$ and $[Ph_4As]_2[VOCl_4]$.

The results for the e.p.r. solution spectra were particularly interesting. At room temperature all the complexes studied gave eight-line spectra typical of vanadium(IV). However, no ligand hyperfine structure was observed due to coordinated phosphine ligands. This result was interpreted in terms of the phosphine ligands being displaced by coordinating solvent molecules.

The A_{iso} values for the spectra at room temperature, taken together with those recorded for frozen solutions at 138 K, indicated that there were a variety of species present and that equilibrium of the following form existed.

$$[VOCl_2L_2] \underset{L}{\overset{thf}{\rightleftharpoons}} [VOCl_2L(thf)] \underset{L}{\overset{thf}{\rightleftharpoons}} [VOCl_2(thf)_2]$$

Often, A_{iso} values calculated, by means of computer simulation, for low-temperature solution e.p.r. spectra, were higher than those calculated for the same solutions at room temperature, suggesting that, to some extent, ligand molecules had displaced solvent molecules. All e.p.r. signals were time-averaged signals for several species and it was not

possible to assign a particular A_{iso} value unambiguously to a given species.

The complex $[Ph_4As]_2\ [VOCl_4]$ was obviously present in ethanenitrile solution both at room temperature and at 138 K. The various g and A values obtained for the solution of the complex were similar to those obtained for the powdered sample.

	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$A_{\parallel}$ /G	$A_{\perp}$/G	A_{iso}/G
Solid	1.961	1.987	1.978*	182.8	74.1	110.3*
Solution (295 K)	-	-	1.969	-	-	109.2
Solution (138 K)	1.959	1.984	1.976*	184.0	75.6	111.7*

* - calculated value

The actual e.p.r. spectrum recorded for the solution of $[Ph_4As]_2\ [VOCl_4]$ in ethanenitrile at 138 K was very similar to that of the powdered sample. Whereas, with other oxodihalovanadium(IV) species, the actual species responsible for e.p.r. signals from solutions is in doubt, with $[Ph_4As]_2[VOCl_4]$ there is no such doubt and spectral parameters can be calculated and assigned unambiguously, from either the spectrum of the powdered sample, or the spectrum of the solution at 138 K, by means of a computer simulation.

The A_{iso} values for the spectra of $[VOCl_2(Ph_3P)_2]$ and $[VOCl_2(Ph_2MeP)_2]$ solutions in tetrahydrofuran showed the methyldiphenylphosphine ligand to be coordinated to a greater extent than triphenylphpsphine in solution. 1,2-bis(diphenylphosphino)ethane was coordinated to a greater extent at 138 K than at room temperature on the basis of the A_{iso} values for the $[VOCl_2(dppe)]$ solution in tetrahydrofuran. Similarly the ligands in both $[VOCl_2(Ph_3PO)_2]$ and $[VOCl_2(cy_3P)]$ appeared to be displaced by solvent at room temperature, but to be coordinated to some degree at 138 K.

These results, showing the existence of equilibria involving ligand displacement by solvent molecules, shed doubt on many past solution studies of oxodihalovanadium(IV) complexes.

5.5 FINAL SUMMARY

The aim of this project was to prepare and characterise various complexes, either of the type $[VOCl_2L_n]$ (where L is a neutral monodentate or bidentate ligand) or A_2 $[VOCl_4]$ (where A is a cation), with the prime objective of examining their electron spin resonance spectra.

$[VOCl_2(CH_3CN)_2]$ was prepared by a standard method and was then used as starting material in the preparation, by ligand exchange, of $[VOCl_2L_2]$ (L=hmpa, Ph_3PO, py, Ph_3P, tmu, tmtu, Ph_2MeP or $PhMe_2P$), $[VOCl_2L_3]$ (L=py, dpso, or dmso), $[VOCl_2L]$ (L=cy_3P, dppm or dppe) and A_2 $[VOCl_4]$ (A= $[Et_4N]$, $[pyH][Me_4N]$ $[Ph_4As]$) Although it proved impossible to prepare complexes with stibine and arsine ligands by this method, the synthetic route used proved, on the whole, to be extremely successful. Of the complexes prepared, only the structure of $[VOCl_2(tmu)_2]$ was known, this having square-pyramidal (C_{2v}) symmetry.

The far infrared spectra of the complexes were recorded and used to classify the complexes according to their structures. $[VOCl_2(cy_3P)]$, $[VOCl_2(CH_3CN)_2]$ and $[VOCl_2L_3]$ (L=dpso, dmso or py) were shown to have six-coordinate structures. $[VOCl_2(dppm)]$, $[VOCl_2L_2]$ (L=hmpa, Ph_3PO, py, tmu or tmtu) and A_2 $[VOCl_4]$ (A=$[Et_4N]$,$[Me_4N]$, $[Ph_4As]$ or $[pyH]$ based on a square pyramid $[VOCl_2(dppe)]$,$[VOCl_2L_2]$ (L=Ph_3P, Ph_2MeP or $PhMe_2P$) and blue $[pyH]_2$ $[VOCl_4]$ also had five-coordinate structures, but based on a trigonal bipyramid. Far infrared spectra of $VOCl_2$ adducts had never previously been studied in any great detail, and had not been used for structural assignment.

During this study, it became clear that two forms of the anion $[VOCl_4]^{2-}$ existed in the complex $[pyH]_2[VOCl_4]$. A blue form of the complex was stable at 243 K, and a green form at 295 K. Far infrared studies showed the $[VOCl_4]^{2-}$ ion to have different symmetries in the two complexes both of which were isolated and studied.

Diffuse reflectance spectra were recorded for most of the complexes prepared. These revealed slight differences in the 'd $\leftrightarrow$ d' band region which could be attributed to the different symmetries of the complexes. The expected trends in ligand field strength were also observed for the various ligands studied.

The principal physical technique employed in the study of these complexes, however, was electron paramagnetic resonance spectroscopy. It was hoped that this study would reveal some correlation between the structure of a species in the solid state and its structure in solution. It was also hoped that a study of various complexes in the solid state, would provide

an explanation for the appearance of hyperfine structure in the spectra of previously studied $VOBr_2$ adducts.

Hyperfine structure was observed in the spectra of powdered samples of $[VOCl_2L]$ (L = cy_3P or dppm), $[VOCl_2L_2]$ (L = hmpa, Ph_3PO or Ph_3P), $[VOCl_2(dpso)_3]$ and $A_2[VOCl_4]$ (A = $[Et_4N]$ or $[Ph_4As]$). The e.p.r. spectra recorded for other complexes did not show fine structure and this fact suggested that the amount of hyperfine structure observed depends on the size of the counter-ion or ligand present. For the first time, with the spectrum of $[Ph_4As]_2[VOCl_4]$, it was possible to analyse the hyperfine structure observed, computer simulate the spectrum, and obtain spectral parameters for a sample in the polycrystalline solid state. Spectral parameters were also obtained, by means of computer simulation, for the solution of $[Ph_4As]_2[VOCl_4]$ in ethanenitrile both at 295 K and at 138 K and, hence, it was possible to compare the species present in the solid state with that present in solution.

Finally a study of the e.p.r. spectra of solutions of some of the complexes was undertaken. The phosphine complexes, previously unknown, had been prepared in the hope that ligand hyperfine splittings due to interactions with phosphorus ($I=\frac{1}{2}$) atoms, would be observed in the isotropic spectra. No ligand hyperfine splittings were observed, suggesting that displacement of the phosphine ligands by coordinating solvent molecules was taking place. Observations previously made for the solution of $[VOBr_2(Ph_3P)_2]$ in tetrahydrofuran had suggested that the following equilibria existed:

$$[VOBr_2(Ph_3P)_2] \underset{Ph_3P}{\overset{thf}{\rightleftharpoons}} [VOBr_2(Ph_3P)(thf)] \underset{Ph_3P}{\overset{thf}{\rightleftharpoons}} [VOBr_2(thf)_2]$$

Studies on solutions of various oxodichlorvanadium(IV) complexes in ethanenitrile or tetrahydrofuran suggested the widespread existence of such equilibria. Computer simulations of the e.p.r. spectra were used to calculate the various spectral parameters. Results suggested a correlation between the isotropic hyperfine splitting constant (A_{iso}) and the nature of the species present insolution. By recording spectra at both 295 K and 138 K, it became apparent that the equilibria were temperature-dependent, and that different species often predominated at the different temperatures.

These results, indicating the variety of species present in solution, shed a great deal of doubt on many solution studies of oxodihalovanadium(IV) complexes reported in the literature. This is a system which merits further detailed attention.

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