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One Dimensional X-ray Diffraction Techniques
as a Routine Stereo-chemical Tool

Final Technical Report Number 1, 1 November 1961 (revised)

for the period

1 November 1960 to 31 October 1961

Contract Number DA-91-591-EUC-1633

by R.S. Nyholm

Peter Pauling

G.B. Robertson

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SUMMARY

The objective of this investigation is to determine as much as possible about the structures of compounds or groups of compounds from a consideration of functions directly calculable from the x-ray diffraction patterns of powdered samples of the compounds. In particular, the study of coordination compounds and complex ions concerns the number and arrangement of ligands about the central coordinated metal ion. The investigation involves the preparation of techniques for showing that a compound or group of compounds has a particular coordination arrangement by considering and comparing the intensity distribution and radial distribution curves obtained experimentally from the compounds and by comparing the curves obtained from observable data with corresponding curves calculated from proposed molecular structures

Toward this end x-ray powder diffraction photographs have been taken of several series of compounds, the members of a series involving slight changes from one compound to another such as isomorphous substitution of the various elements or slight modifications of the structures. These series include M^{II} dipyrindine dihalide where M^{II} is a divalent transition metal such as Mn, Fe, Co, Ni, Zn and the halide Br^- or Cl^- ; a series of cis and trans octahedral compounds such as (cobalt bis-ethylenediamine dihalide) X^- ; a series of eight coordinated compounds M^{IV} bisdiarsine tetrachloride where M^{IV} is Ti, V, Zr or Hf, and diarsine is a ditertiary arsine chelate group; and a series of compounds containing the complex ions $(M^{III}Cl_6)^{3-}$ or

$(M_2^{III}Cl_9)^{3-}$ where M is Cr, Mo or W.

Several computer programmes have been written to treat these data and to aid in their interpretation. These include a programme that calculates and sorts by their magnitude $\sin^2 \theta/\lambda^2$ and functions thereof for a given crystallographic unit cell and the structure factor and functions thereof for a given structure. This programme has been found to be of general usefulness in the study of crystal structures. A programme has been written which treats the one dimensional x-ray diffraction data in various ways and calculates the Fourier transform of the data, the radial distribution curve. This programme has been used in the preliminary treatment of some of the data that has been collected.

In the course of this work, a certain amount of single crystal x-ray diffraction work has been carried out. This includes the solution of the structure of titanium bisdiarsine tetrachloride and its isomorphs. A preliminary paper has been published (Nature, 192, 222 (1961); J. Chem. Soc. 1962, in press) and fairly complete diffraction data has been collected for a complete and accurate analysis of the structure. A large amount of data for the compound potassium platinum bisacetyl-acetone chloride $K(Pt(C_5H_7O_2)_2Cl)$ has been collected and a trial structure based on the projection data proposed.

1. The Problem

a) Preamble. As outlined in our original proposal the object of this investigation has been

"to develop the routine use in favourable cases of the radial distribution curve of electron density to determine a certain amount of structural information about coordination compounds and complex ions in the solid state and in solution. The proposal involves an evaluation of the general usefulness of the method."

As will become clear in this report the work has involved the use of both single crystal and powder techniques to establish structures as quickly as possible and to enable comparisons to be effected.

b) Desired information on the structure of compounds.

Given the number of ligands attached to a central metal atom (the coordination number), there are three main kinds of information concerning the structure of compounds of interest to us: (i) interatomic distances, (ii) interatomic angles and (iii) molecular conformation. Thus, in the case of a complex of the general formula $MCl_2 \cdot 2\text{pyridine}$, we first wish to know whether the metal atom is four-coordinate or six-coordinate, in the latter instance via halogen bridging forming an infinite polymeric structure. Given that the compound is monomeric and hence four-coordinate, one wishes to know whether the bonds are arranged so as to form a square or a tetrahedron of atoms around the central metal atom. There remains the need for data as to bond lengths so as to enable one to infer something about the nature of the bond, whether

it is essentially ionic or covalent and if the latter, the degree of double bonding if any; and finally the conformation of the molecule or complex ion as a whole.

A wide range of physical methods have been developed and applied to inorganic compounds during the past few years to enable one to infer the structure of molecules. Traditional methods involving thermodynamic activities of the substance dissolved in a suitable solvent lead to molecular weights; similarly electrical conductivity studies on solutions and melts yield complementary information. More recently one has seen the wide-spread application of the measurement of infra-red, visible and ultraviolet spectra for structural purposes as well as the use of electric dipole moment and magnetic susceptibility measurements. Other spectral techniques include nuclear magnetic resonance and electron spin resonance methods. The definitive technique, however, and unfortunately the most time consuming, are the methods of x-ray diffraction analysis. Where possible, the x-ray method must be regarded as the final arbiter of structure.

The time taken for many single structures forces one either to limit the number of structures which can be determined in a given time or to look for modifications of standard x-ray techniques which will enable one to obtain a certain minimum of essential structural information quickly. In the study of coordination compounds, this minimum structural information would be the coordination number and stereochemistry of the central metal atom only with perhaps limited accuracy and without know-

ledge of the other atoms present.

The physical techniques other than x-ray methods mentioned above do indeed give a good deal of reliable information but constantly one finds unexpected results when a full x-ray study is made. Thus in 1939¹ it was generally assumed that in bivalent nickel, palladium and platinum compounds diamagnetism was diagnostic of a square co-planar four-coordinate metal II complex whereas paramagnetism with two unpaired electron spins indicated either an octahedral or a tetrahedral arrangement. It is now known from x-ray diffraction studies that quite a number of diamagnetic nickel II compounds are in fact five-coordinate (for example $\text{NiBr}_2 \cdot \text{Triarsine}$ ² which is square pyramidal) or, in the case of Pd, six-coordinate (for example $\text{PdI}_2 \cdot 2\text{Diarsine}$ which is tetragonally coordinated³.) On the other hand, it was only recently that tetrahedrally coordinated bivalent nickel was established in the compounds $\text{NiBr}_2 \cdot 2\text{Ph}_3\text{P}$ ⁴ and $(\text{Ph}_3\text{MeAs})_2\text{NiCl}_4$ ⁵.

Several groups of compounds have been prepared recently in these laboratories for which a certain amount of structural information is required, in particular the arrangement of metal atoms and their coordinated ligands, and for which an unambiguous structure assignment has not been possible by the usual physical chemical non diffraction methods. Several of these groups have been partially examined by the techniques involved in this investigation.

A series of compounds of the form
 $(\text{M}_3(\text{CH}_3\text{COO})_6(\text{OH})_2)\text{Cl} \cdot 8\text{H}_2\text{O}$ where M is iron III or chromium III

and similar compounds have been prepared by Mr. A. Earnshaw and the magnetic properties of these compounds cannot be understood without knowledge of the atomic arrangement. A structure has been predicted ⁶ but cannot be confirmed without a diffraction study.

Many workers in these laboratories have, since 1950, prepared a large number of compounds of the general form $(MX_2 \cdot 2\text{Diarsine})Y$, where M is a divalent metal, X a halide and Y an anion and wish to know whether these compounds are cis or trans octahedral complexes or perhaps tetragonally or otherwise distorted from an octahedral arrangement of ligands.

Dr. E. Coffee has prepared a number of compounds which it is thought contain metal - metal bonds. Among these are $(\text{Ph}_3\text{PAu})_2$, (two forms), $\text{Ph}_3\text{P-Au-Mn}(\text{CO})_5$, $(\text{Ph}_3\text{PAu})_2\text{Fe}(\text{CO})_4$ and $\text{Ph}_3\text{Au-Co}(\text{CO})_4$. Metal - metal bonds in inorganic compounds are little understood, and not only is it difficult to prove the existence of such bonds without a diffraction study, but the interatomic distances and angles need to be determined.

Dr. N. Gill has prepared a series of compounds of transition metals of the form $\text{MX}_2 \cdot 2\text{pyridine}$ where X is a halide. The possible arrangements of the ligands about the metal atom are octahedral, tetragonal, square or tetrahedral. Theoretical predictions of the expected coordination have been made, and the structures inferred from the absorption spectra and magnetic susceptibilities of the compounds. The actual structures cannot be known for sure without quantitative diffraction studies nor

can correlations between the physical properties of the substances with the atomic structure be made.

c) Information available from one dimensional diffraction data

The x-ray diffraction pattern of a crystalline powder, a gaseous, liquid or amorphous material must have spherical symmetry, i.e. it is a one dimensional function. Obviously one can obtain only one dimensional structural information from such a diffraction pattern, that is, only information about the distances between atoms but not about their relative orientation except in so far as this affects distances. The diffraction pattern can be obtained photographically in a suitable camera or measured directly with some sort of photon counter. The Fourier transform of the data so obtained can be calculated with no assumptions about the structure of the substance involved,* and in some cases, this Fourier transform, or radial distribution curve, can be interpreted in terms of the atomic structure of the substance. We shall use the term "intensity distribution curve" (IDC) to refer to the diffraction pattern of a substance (in reciprocal space) whether observed or calculated and the term "radial distribution curve" (RDC) to refer to real space functions, whether derived from the atomic structure or the Fourier transform of the observed intensity distribution curve.

The radial distribution curve represents the average environment of the average atom of the substance (where the aver-

* Cf. p.10 for a modification of this point

age refers to the electron density or atomic number of the atom) and must be interpreted in terms of structure as such. Often the number of structural parameters exceeds the number of data available, and a unique interpretation cannot be made. This is because the structure involves orientation and distances whereas the RDC gives information only about distances. None the less, if a trial structural model can be proposed, the radial distribution curve of the model can readily be calculated and compared with that obtained from the observed diffraction data. If the two curves agree well, the model is likely to be correct, or, alternatively, it may be possible to show that a proposed model or groups of models does not agree with the observed data.

The radial distribution curve can be modified in various ways; the intensity distribution curve may be divided by the sum of the squares of the atomic scattering factors to produce the average environment of the average atom in terms of atoms instead of in terms of electron density. The sum of the squares of the atomic scattering factors should be subtracted from intensity distribution curve (equivalent to removing the origin peak from the Patterson function) but this requires knowing the absolute scale of the IDC.

The intensity distribution curve itself cannot be interpreted in physical terms, but some investigators consider the comparison of observed and calculated IDC's a more sensitive test of the correctness of a proposed model than the comparison of RDC's? We do not yet know if this is generally true.

d) The application of one dimensional diffraction data to coordination chemistry. The RDC is often difficult to interpret. It represents the average environment of the average atom in terms of atomic number and consequently in those problems in which the atom of major interest has a large atomic number, the RDC is weighted to show information about the heavy atom. This is often the case in the study of coordination compounds. Furthermore, often the ligands, e.g. arsenic, have a high atomic number, and in these cases the metal-arsenic and arsenic-arsenic interactions will appear strongly in the RDC. In addition, the study of coordination compounds usually involves the study of many similar compounds in which the coordinated metal atom is changed, for example from Cr to Mo or W, and/or where the ligands are changed, for example from Cl to Br or I. In these cases, by comparison of the RDC's from the several compounds, the peaks corresponding to interactions between the atoms which are changed and themselves and the other atoms will change, allowing an unambiguous interpretation of these interactions.

In those cases where several compounds are available are where the atoms of major interest are of high atomic number, the application of the RDC method should readily give a good deal of stereochemical information. The information is not definitive, that is, it is open to alternative interpretations, but the technique should in favourable cases be at least as valuable as the indirect physical methods currently used. The success of the general use of the methods, given suitable

compounds, is the availability of an easily used procedure for obtaining the data and treating it numerically.

2. The facilities prepared for this investigation.

a) The collection of x-ray powder diffraction photographs.

We have been using a Philips 114.83 mm diameter camera and x-ray generator with copper and chromium radiations for the collection of the data. The camera, of the collimator type, is very easy to use. For the RDC method, one does not want particularly high resolution in the photographs, but the signal to noise ratio is very important. We have performed some experiments to see what can be done to raise the signal to noise ratio in this experimental setup. The camera as it stands does not have a very good signal to noise ratio; it cannot be evacuated and the film is uncovered. The problem is often aggravated by the existence of atoms which fluoresce in the most convenient radiation, copper, and we have tried using chromium radiation instead. The tube loading of a chromium tube is low and the exposure times very long. In general photographs taken with copper radiation are better even in the presence of atoms which fluoresce. We put black paper between the sample and the film which absorbs the longer wavelength fluorescence radiation more than the characteristic coherent radiation. In an attempt to increase the signal to noise ratio we have designed modifications to the camera to allow it to be evacuated or filled with

helium and to place the filter between the sample and the film (as used at the Bell Laboratories, personal visit Aug. 1961). These modifications, however, have not been completed.

The use of direct x-ray photon counters has much to recommend it. Crystal monochromators can be used between the sample and the detector and a pulse height analyser used with a proportional or scintillation counter. These greatly increase the signal to noise ratio of the experiment by decreasing the detector bandwidth compared to the wide bandwidth of photographic film. The geometry of the experimental setup can be controlled and the determination of the absolute scale of the IDC more easily made. We are designing at present an automatic counter for the collection of one dimensional diffraction data from powders and liquids. The device would use Bragg-Bentano focusing geometry and would automatically collect diffraction data and prepare punched paper tape for the computer.

Lists of compounds for which photographic data have been collected are given in part 3.

b) The measurement of such photographs and the preparation of the data for treatment by the computer. We have been using a Joyce-Loebl recording densitometer for the measurement of the diffraction photographs. The densitometer has two mechanically linked tables, one holding the film and one the recording paper. The ratio of their linear movement is 1, 2, 5, 10.

20 and 50 to 1; we generally use the ratio 2:1. The light beam is split, one part travelling through condensers, the

film, a microscope (16 mm lens) and the other through an optical density wedge. The two beams are sampled by a chopper and the difference signal drives a motor connected to a carriage carrying the wedge and a pen. The film and recording paper can be traversed by hand or generally by a motor; we use the slowest speed. We have found that the pen record is most satisfactory with the instrument control set feedback 5, motor speed 2, slit width 30 μ , slit height 500 μ .

The instrument is not ideal for the measurement of the photographs but we know of none better. The area of photograph seen at any one time is small, so small that individual grains in the film cause noise in the record curve. The slit width cannot be made too wide or the space between diffraction lines cannot be measured in complicated photographs. It is important to measure the interline areas because they give a measure of the background of the photograph.

We are using this instrument for the measurement of these photographs, but these problems could be eliminated by the use of a counter instrument as suggested in part 2 a).

c) The calculation of functions of the data: the radial distribution curve. We have written and modified an autocode programme for the University of London Mercury computer to read the intensity data, correct it for Lorentz and polarization factors, and to calculate a modified radial distribution curve. The programme calculates

$$rD(r) = \sum_{s_{\min}}^{s_{\max}} I \frac{2\sin(2\theta)\sin\theta}{1+\cos^2(2\theta)} \frac{e^{-Bs^2}}{\sum_{\text{atoms}} f_i^2} \sin(4\pi rs)$$

where $s = (\sin\theta)/\lambda$

The programme does not determine the absolute scale of the data nor subtract the intra atomic coherent scattering. The programme is easily modified and a complete description of it is given in Appendix I.

d) The calculation of intensity distribution curves and radial distribution curves for proposed structural models.

There are two ways of calculating the radial distribution curve of a structural model. The first is to consider the model and to sum the products of the atomic number (and to put in an exponential or other function for the atomic shape) for all atom pairs (that is to do the calculation in real space) and the other is to first calculate the diffraction pattern of the model and then to calculate the Fourier transform of this diffraction pattern as is done with the observed data. We have decided to use the latter method. It has the advantage that the intensity distribution curve is produced automatically during the course of the calculation. In addition modifications to the radial distribution curve and the handling of the electron density of atoms are more easily accomplished by the usual crystallographic techniques by going into reciprocal space and then back into real space. To this end we have written a programme that calculates the interplanar spacings for a given unit cell, sorts

them according to the magnitude of $\sin^2\theta$ and punches them and functions of them. The programme will also calculate the structure factor for a given structure and produce it and some functions thereof. The IDC of a proposed molecular structure as distinct from a proposed crystal structure can be calculated by putting the molecular structure in a large artificial unit cell. The second part of this programme to calculate the RDC of the structural model by doing a Fourier summation on the calculated IDC stored in the computer has not yet been written.

This programme has turned out to be of great value in general single crystal investigations. The single crystal with which one actually performs a diffraction experiment is not a large sample of the gross substance available. Particularly with the unstable substances of current interest, the individual crystal may be something other than the rest of the material available with which one has made physical measurements. The method of ensuring that the individual crystal used for a diffraction experiment is to index a powder diffraction photograph taken with a representative sample of the substance in terms of the unit cell obtained from the single crystal investigation and see if they correspond. This can readily be done with the programme available. It sorts the planes in the order in which they appear on the powder photograph. We have used the programme to calculate spacings for the compounds Ph_3PAu two forms, $\text{TiCl}_4 \cdot 2\text{Diarsine}$, $\text{KPt}(\text{acac})_2\text{Cl}$, $\text{Zr}(\text{acac})_3\text{Cl}$, $\text{CuCl}_2 \cdot 2\text{pyridine}$ and bromine bisquinilin perchlorate. Very little is known about this last very unstable compound, on

which we have done some work, and of the two crystalline forms found (one is something else) we were able to show that one form is characteristic of the material as a whole. A complete description of this programme is given in Appendix II.

e) The comparison of the radial distribution curves of substances with their known structures. Since the unique interpretation of the experimentally determined RDC is usually difficult or impossible, a great deal of the success of the method involves being able to suggest possible structures and to test these suggestions. The method of testing has been described in part 1 b) and the calculations in part 2 d). We have, however, found in the course of our investigations that some structural data could be determined in particular cases quickly by a short single crystal investigation or that the coordination state was so unusual as to require us to make a single crystal investigation in order to test our results. The experimental facilities available in the laboratory include an integrating Weissenberg camera and a Buerger precession camera. The major computer programmes for single crystal work, a Fourier synthesis programme and a least squares programme, are available by courtesy of O.S. Mills and J.S. Rollett. We have written a few fairly minor programmes to facilitate this work. These are

1) a programme that does a polynomial interpolation in a widely spaced tabulated table of atomic scattering factors and produces a table of f with variable intervals in $\sin \theta$ or $\sin^2 \theta$ to be used with our IDC programme (section 2 d) and Appendix II) and with

Rollett's structure factor least squares programme.

2) a programme which produces the coordinates on a square grid of any perspective view of any crystal structure.

3) two subroutines of general use which are used in our other programmes.

a) a very fast sin and cos routine which determines both the sin and cos of $2\pi X$ to 1 part in 1000 is about 3 msec, and

b) a similar fast programme which determines e^X to 1 part in 1000 in the range $-9 \leq X \leq 8$.

3. The compounds and groups of compounds considered and results obtained.

a) Cis and trans octahedral compounds of transition metals, mostly of the form $(MX_2 \cdot 2Diarsine)Y$. A group of compounds prepared by Professor S. Yamada and Mr. Gordon Rodley has been partially studied. These compounds are generally octahedral complexes of transition metals, primarily cobalt, which it is thought exist in both the cis and trans forms. The differences between the radial distribution curves of the cis and trans forms of octahedral complexes are not great, yet it is thought by the comparison of such curves from several compounds in which the central metal atom and the ligands are substituted by atoms of different atomic number, a classification of the compounds as to which are cis and which trans will be possible. Calculated

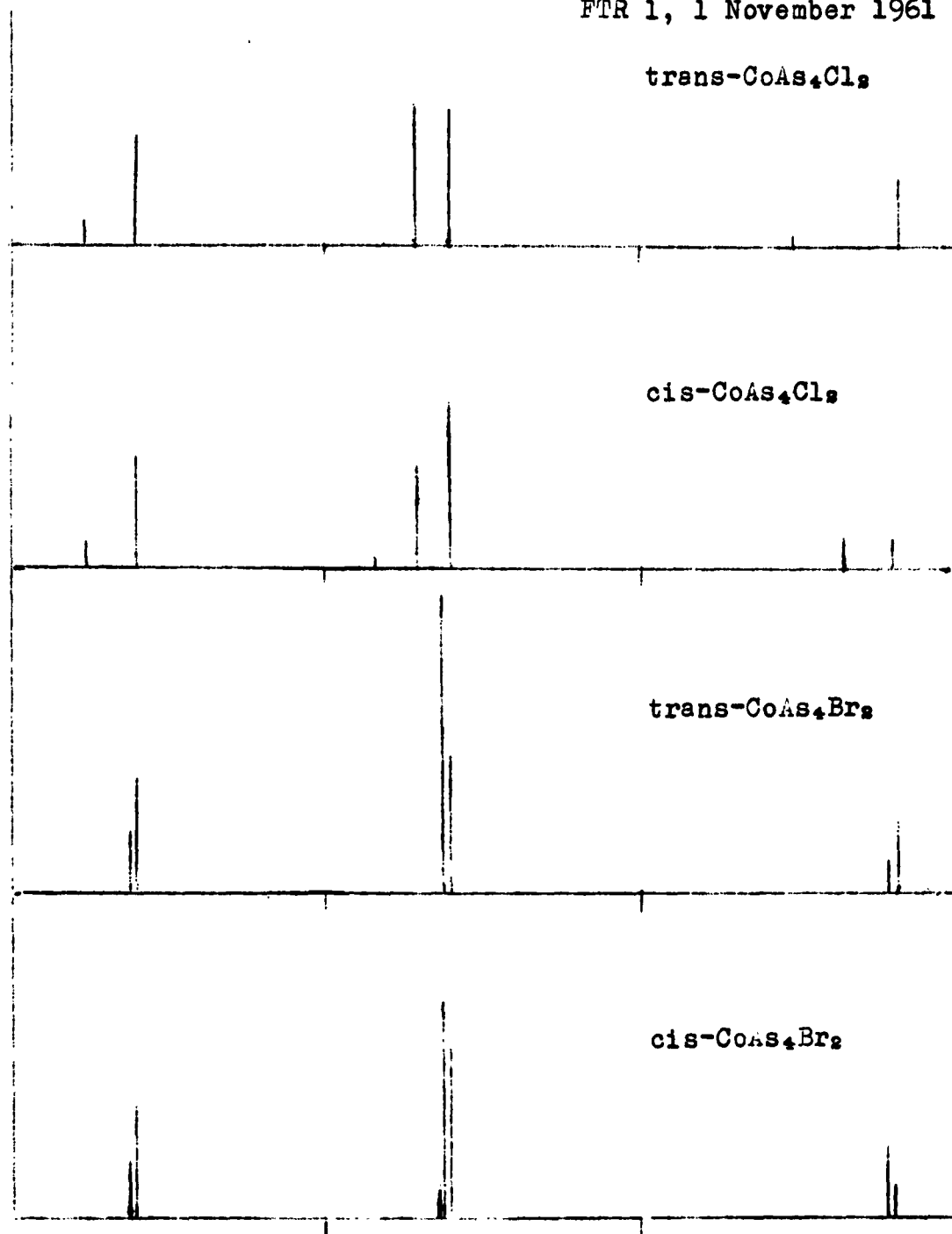


Figure 1. Calculated point atom interactions (simple RDC's) for cis and trans octahedral cobalt Diarsine complexes.

point atomic interactions (the simple form of the RDC) are shown in figure 1, for the cis and trans forms of CoAs_4Cl_2 and CoAs_4Cl_3 . Powder diffraction photographs of these compounds have been made as shown in table 1.

Table 1. Powder photographs available of
cis trans octahedral complexes.

Compound	Radiation	Intensity range available (hours exposure)	Prepared by
cis $(\text{CoD}_2\text{Cl}_2)\text{ClO}_4$	Cu	1.5 - 6	SY
	Cr	11 - 19	
cis $(\text{CoD}_2\text{Br}_2)\text{ClO}_4$	Cr	6 - 16	SY
trans $(\text{CoD}_2\text{Cl}_2)\text{ClO}_4$	Cu	1/3 - 3	SY
	Cr	6	
trans $(\text{CoD}_2\text{Br}_2)\text{ClO}_4$	Cu	1/2 - 2	SY
	Cr	16	
trans $(\text{RhD}_2\text{Cl}_2)\text{ClO}_4$	Cu	1/2 - 2.5	SY
$(\text{NiD}_2\text{Cl}_2)\text{ClO}_4$	Cu	1/3 - 3	SY
$(\text{CoD}_2\text{Cl}_2)\text{Cl}$	Cu		GR
$(\text{CoD}_2\text{I}_2)\text{I}$	Cu		GR
$(\text{NiD}_2\text{Cl}_2)\text{Cl}$	Cu	2 1/2	GR
$(\text{RhD}_2\text{Cl}_2)\text{Cl}$	Cu		GR
$(\text{IrD}_2\text{Cl}_2)\text{Cl}$	Cu	2	GR
$(\text{RhD}_2\text{I}_2)\text{I}$	Cu		GR
$(\text{IrD}_2\text{Cl}_2)\text{Cl}$ (insoluble)	Cu		GR
$(\text{IrD}_2\text{Cl}_2)\text{Br}$ (insoluble)	Cu		GR

Table 1 (Continued)

Compound	Radiation	Intensity range available (hours exposure)	Prepared by
(CoD ₂ Cl ₂)	Cu	4	GR
(NiD ₂ Cl ₂)	Cu	2½	GR
NiD ₂ (NO ₃) ₂	Cu	2	GR
CoD ₂ (NO ₃) ₂	Cu	2	GR
CoD ₂ (ClO ₄) ₂ type A	Cu	2	GR
NiD ₂ (ClO ₄) ₂ type A	Cu	2	GR
CoD ₂ (ClO ₄) ₂ type B	Cu	2	GR
NiD ₂ (ClO ₄) ₂ type B	Cu	2	GR
FeD ₂ (ClO ₄) ₂	Cu	1	GR
cis (Coen ₂ Cl ₂)Cl	Cu	1/3 - 3	SY
trans (CoenCl ₂)ClO ₄	Cr	6	SY

D = Diarsine, (C₆H₄)(As(CH₃))₂

en = ethylenediamine

SY prepared by Professor S. Yamada

GR prepared by Mr. Gordon Rodley in these laboratories.

The statement of the isomer of the compound is that of Professor Yamada based upon a study of the absorption spectra of the compounds. We hope to confirm or correct this assignment by means of the present study; detailed measurements on these photographs and the calculations of the radial distribution curves are in progress.

another series of compounds is that of the MX₂.2pyridine

where X is Cl, Br or I prepared by Dr. Naida Gill. X-ray powder diffraction photographs have been taken of the compounds

Crpy ₂ Cl ₂	Mnpy ₂ Br ₂	COPY ₂ I ₂
Mnpy ₂ Cl ₂	COPY ₂ Br ₂	Znpy ₂ I ₂
Fepy ₂ Cl ₂	COPY ₂ Br ₂	
COPY ₂ Cl ₂		
Nipy ₂ Cl ₂		
COPY ₂ Cl ₂		
Znpy ₂ Cl ₂		

These compounds have been classified into groups according as the central metal atom is octahedrally, tetragonally or tetrahedrally coordinated by consideration of the spectra and magnetic susceptibility of the compounds and a qualitative judgement of the x-ray diffraction photographs. In order to make this classification as quantitative as possible we are measuring these photographs and calculating the radial distribution curves from them but this has not yet been done. The crystal structures of some of these compounds are known, and so it is possible to calculate the expected diffraction patterns and the theoretical radial distribution curves. The expected diffraction pattern for one substance, CuCl₂.2pyridine has been calculated and compared with the photograph.

e) Compounds involving the complex ions of the form MX₆³⁻ and M₂X₉³⁻. Several compounds which presumably contain the complex ions MX₆³⁻ and M₂X₉³⁻ where M is Cr, Mo or W and X is Cl or Br have been prepared by Mr. F.W. Smith. The

compounds for which powder diffraction photographs are available are shown in Table 2.

Table 2. The compounds containing MX_6^{3-} or $M_2X_9^{3-}$ for which powder photographs are available.

Compound	prepared by
$K_3Mo_2F_9$	PWS
$(Et_4N)_3Cr_2Cl_9$	D. Machin
$(Ph_3MeAs)_2(H_3O)Mo_2Cl_9$	PWS
$(Ph_4As)_2H_3OMo_2Br_9$	PWS
$(Ph_4As)_2H_3OMo_2Cl_9 \cdot nH_2O$	PWS
$(Et_4N)_3Mo_2Cl_9$	PWS
$(Et_4N)_2H_3OMo_2Cl_9$	PWS
$(Me_3H_3N)_3Mo_2Cl_9$	PWS
$Cs_3Mo_2Cl_9$	PWS
$K_3W_2Cl_9$	PWS
$Cs_3W_2Cl_9$	PWS
$(Ph_4As)_2H_3OW_2Cl_9$	PWS
K_3MoCl_6	PWS
Cs_3MoCl_6	PWS
$(CH_3H_3N)_3MoCl_6$	PWS
Cs_3MoBr_6	PWS
The potassium hexachloro salts of Rh, Os, Re,	
Pt, Ti and Pb	PWS

Me = methyl Et = ethyl Ph = phenyl

PWS prepared by Peter W. Smith

The structure of $K_3W_2Cl_9$ and of many similar compounds is

known,⁸ and consists of two octahedra of halogen atoms each with a metal atom in the centre sharing one face. The structure of the MoCl_6^{3-} ion is unknown but presumably is an octahedral arrangement of Cl atoms. We have measured photographs and calculated the RDC function⁹

$$rD(r) = I \frac{\sin^2(2\theta)}{1+\cos^2(2\theta)} e^{-\delta s^2} \sin(4\pi r s)$$

where I is a measured intensity and $s = \frac{\sin\theta}{\lambda}$ for the compounds $(\text{CH}_3\text{H}_3\text{N})_3\text{MoCl}_6$, K_3MoCl_6 , $(\text{CH}_3\text{H}_3\text{N})_3\text{Mo}_2\text{Cl}_9$ and $(\text{PH}_4\text{As})_2\text{H}_3\text{O}\text{Mo}_2\text{Cl}_9$. These RDC's are shown in figure 2, and it is seen that it is quite possible with reasonable conviction to separate the four curves into two groups, those containing the complex ion MoCl_6^{3-} and those containing the complex ion $\text{Mo}_2\text{Cl}_9^{3-}$. We have not interpreted these curves in terms of the atomic interactions involved nor calculated the theoretical RDC's from either the known structure of $\text{K}_3\text{Mo}_2\text{Cl}_9$ or from hypothetical complex ion models. Nonetheless, the separation of these curves has given us encouragement that these RDC methods will be applicable and valuable in our study of the stereochemistry of coordination compounds.

d) Eight-coordinated compounds of the form $\text{MX}_4 \cdot 2\text{Diarsine}$, including the single crystal structure analysis of $\text{TiCl}_4 \cdot 2\text{Diarsine}$. Dr. Robin Clark in this laboratory has prepared the compounds $\text{TiCl}_4 \cdot 2\text{Diarsine}$, $\text{ZrCl}_4 \cdot 2\text{Diarsine}$, $\text{HfCl}_4 \cdot 2\text{Diarsine}$, $\text{VCl}_4 \cdot 2\text{Diarsine}$ and $\text{TiBr}_4 \cdot 2\text{Diarsine}$.¹⁰ We have taken x-ray powder photographs of them and shown that the five substances are isostructural. The powder pictures appeared

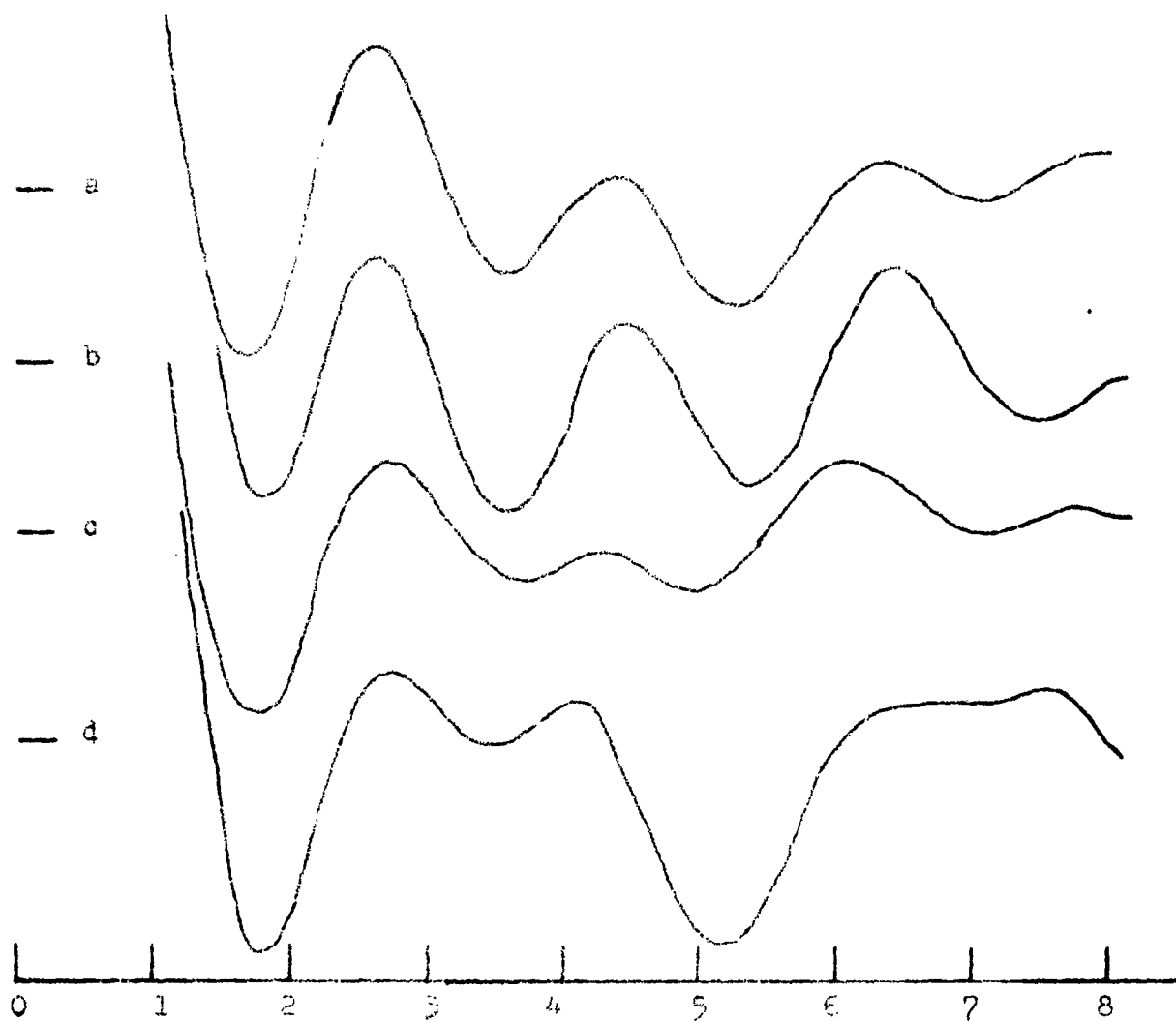


FIGURE 2. ADP's calculated from observed diffraction data for the compounds a) $(\text{CH}_3\text{I})_2\text{MoCl}_5$; b) $(\text{Th}_2\text{O}_5)_2\text{H}_2\text{O} \cdot \text{Mo}_2\text{Cl}_5$; c) K_2MoCl_5 ; d) $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{MoCl}_5$.

fairly simple (had rather few lines) and Dr. Clark was able to grow some single crystals of $\text{TiCl}_4 \cdot 2\text{Diarsine}$ from nitrobenzene solution. Therefore we decided that the structure might easily by single crystal methods be analyzed. We were able to take Weissenberg and precession camera single crystal diffraction photographs of the (100) and (001) zones of the crystal.

The compound is tetragonal, space group $I\bar{4}2m$
 $a_0 = 9.26 \text{ \AA}$, $c_0 = 16.32 \text{ \AA}$, $\rho_{\text{observed}} = 1.80 \text{ g/cc}$, 2.00 molecules per unit cell. The sharpened Patterson function¹¹ for these two zones was calculated and interpreted in terms of the Ti, Cl and As atoms. The carbon atoms of the ring and the methyl groups were placed according to stereochemically accepted values of the bond angles and bond lengths. Most of the atoms are in special positions, of space group $I\bar{4}2m$, the Ti atoms in 2 a $\bar{4}2m$ at $000 + B C$, the As, Cl and 3 independent C atoms of the ring in 8 i m x, x, z ; \bar{x}, \bar{x}, z ; x, \bar{x}, \bar{z} ; $\bar{x}, x, \bar{z} + B C$, and the methyl groups in the general positions 16 j l x, y, z ; \bar{x}, \bar{y}, z ; \bar{x}, y, \bar{z} ; x, \bar{y}, \bar{z} ; \bar{y}, x, \bar{z} ; y, \bar{x}, \bar{z} ; \bar{y}, \bar{x}, z ; and $y, x, z + B C$, 13 positional parameters. The structure was refined with the (100) data (the (001) data is not a function of the z coordinates) with the structure factor least squares computer programme written by J.S. Rollett. After eight rounds of least squares refinement the R factor for the 45 observed planes of the (100) zone dropped from 18.4% to 6.8% and that for the 57 planes of the (001) zone from 25.6% to 10.5%.

The atomic coordinates at this stage in the refinement are given in Table 4.

Table 4. The atomic coordinates of $\text{TiCl}_4 \cdot 2\text{Diarsine}$

atom	x	y	z	B
Ti	0	0	0	2.5
Cl	0.1794	0.1794	0.04487	2.72
As	0.1225	0.1225	0.1337	2.31
Cl	0.0533	0.0533	0.2415	3.0
C 2	0.1153	0.1153	0.3118	3.1
C 3	0.0513	0.0513	0.3851	3.1
C 4	0.3275	0.1115	0.1415	3.7

A perspective drawing and views from several directions of the molecule are shown in figure 3. It is seen that the Ti atom is eight coordinate, the first example of an eight coordinated atom in the first long period of the periodic table.

The coordination polyhedron around the titanium atom is a dodecahedron with eight vertices consisting of four equivalent arsenic atoms and four equivalent chlorine atoms. The arsenic atoms are $2.71 \pm 0.02 \text{ \AA}$ from the titanium atom and are at an angle of 36° to the tetragonal axis. The chlorine atoms are $2.46 \pm 0.02 \text{ \AA}$ from the titanium atom and are at an angle of 73° to the tetragonal axis.

The molecular symmetry of these compounds is the same as that reported for the complex ion $\text{Mo}(\text{CN})_8^{4-}$ ¹². For this symmetry a set of hybrid bond orbitals determined by Racah¹³ from d^4sp^3 orbitals has one group of four with maximum strength 2.968 at an angle of $72^\circ 47'$ to the tetragonal axis and another

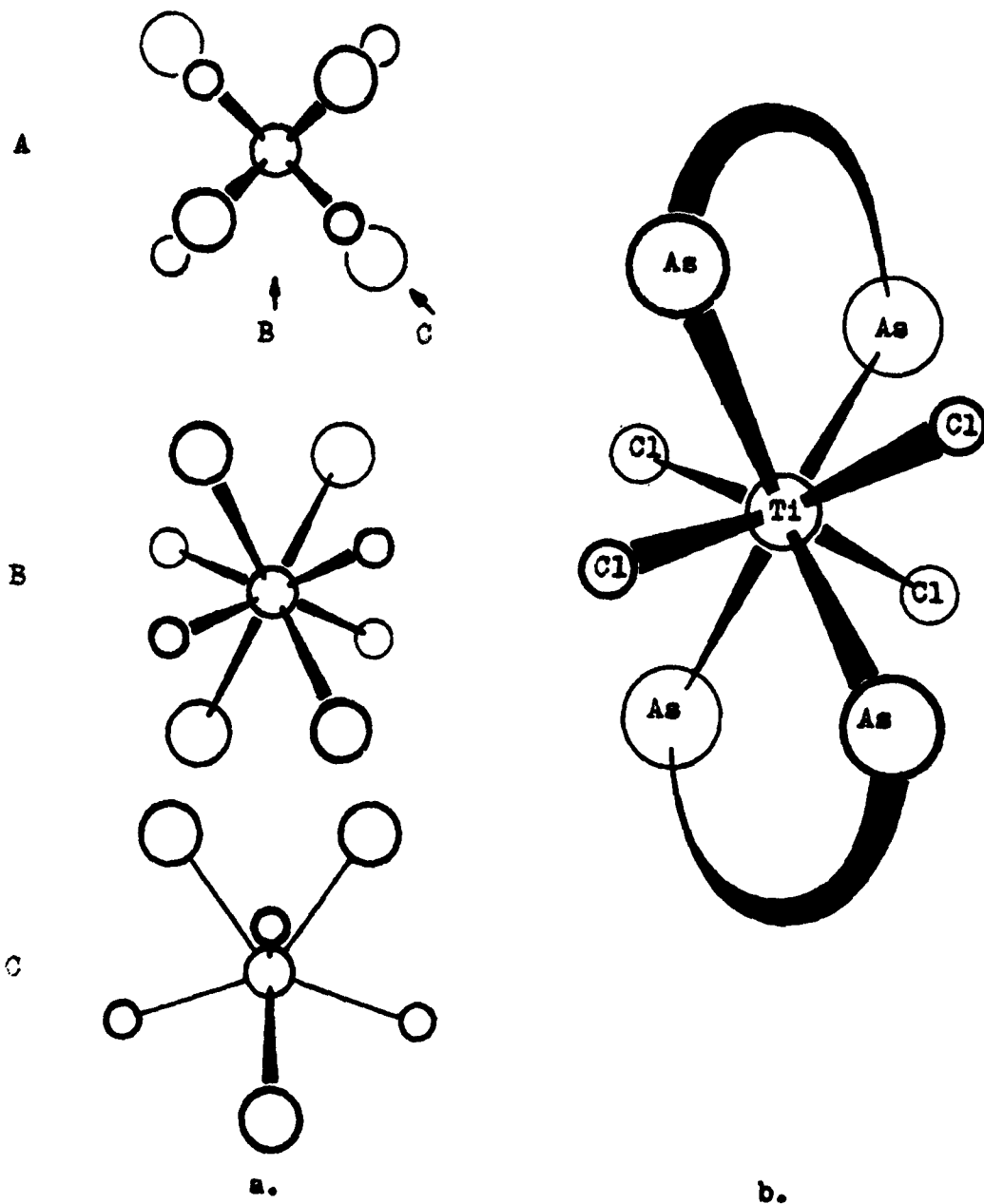


Figure 3. a. three views of the coordination group of $TiCl_4 \cdot 2Diarsine$. b. a perspective drawing of the molecule $TiCl_4 \cdot 2Diarsine$. The carbon rings are represented diagrammatically and the CH_3 groups are not shown.

group of four with maximum strength 2.995 at an angle of $34^{\circ} 33'$ to the tetragonal axis.

The direction of the titanium-chlorine bond coincides with that of the first group of these hybrid bond orbitals. The angle between the direction of the titanium-arsenic bond and the tetragonal axis (36°), however, is 2° larger than that of the corresponding maximum strength hybrid orbital, while the neighbouring carbon'-carbon-arsenic angle (117°) is 3° smaller than the ideal trigonal angle of 120° . While barely significant, this suggests that the stability of the molecule is sensitive to the titanium-arsenic distance, and that the angular distortion necessary to obtain this distance is correspondingly distributed between these two angles.

Precession camera single crystal pictures covering about 80% of the total available data within the copper sphere have been taken and this data is being measured and processed for a complete three dimensional refinement of the crystal structure. A refinement programme (the treatment of atoms in special positions causes complications in the least squares matrices) has been provided by J.S. Rollett as a modification to his general programme.

e) Five coordinated compounds including the single crystal analysis of $KPt(acac)_2Cl$. In the course of our work on compounds with unusual coordination numbers and in our attempt to determine something about the stereochemistry by ADC methods, we decided that we could not determine the

structure of five coordinate complexes without being sure of such a structure. Consequently we undertook the analysis of the structure of $\text{KPt}(\text{acac})_2\text{Cl}$ where acac is acetylacetonate, prepared by Dr. Ron Long. We collected single crystal diffraction data from the three major zones of the crystal.

The crystal has space group $I2/c$, $a_0 = 25.97 \text{ \AA}$, $b_0 = 13.73 \text{ \AA}$, $c_0 = 7.70 \text{ \AA}$, $\beta = 92.0^\circ$, 8 molecules per unit cell. The molecules are in general positions. The Patterson functions for the three zones were calculated and the platinum atom coordinates determined from them. The observed structure factors phased on the platinum atom were used to calculate the three Fourier projections. It was possible to place all the other atoms in the molecule from these Fouriers, and these atomic coordinates were used in a least squares refinement of the structure. At this stage of refinement the value of R is 15.34% for 443 observed planes in the three projections considered together. The atomic coordinates of the platinum, chlorine, potassium and oxygen atoms are listed in Table 5.

Table 5. The coordinates of the platinum, chlorine, potassium and oxygen atoms of the compound $\text{KPt}(\text{acac})_2\text{Cl}$ as determined from the projections

Atom	x	y	z
Pt	0.106	0.171	0.152
Cl	0.023	0.184	0.003
K	0.008	0.409	0.752
O 1	0.179	0.164	0.303
O 2	0.092	0.013	0.145
O 3	0.118	0.338	0.178
O 4	0.093	0.163	0.383

The molecular geometry of the platinum atom is that of a tetragonal pyramid with a square base formed by atoms O1, O2, O3 and Cl. The interatomic distances and angles for this group of atoms are given in Table 6.

Table 6. Interatomic distances and angles for the coordination group of $\text{KPt}(\text{acac})_2\text{Cl}$

Pt - Cl	2.22 Å	O4 - Pt - O1	80°
Pt - O1	2.00	O4 - Pt - O2	84°
Pt - O2	2.20	O4 - Pt - O3	91°
Pt - O3	2.32	O1 - Pt - O2	96°
Pt - O4	1.93	O1 - Pt - O3	85°
Cl - Pt - O1	175°	Cl - Pt - O2	85°
O2 - Pt - O3	175°	Cl - Pt - O3	93°
		O4 - Pt - Cl	95°

We consider that this structure is probably correct though inaccurate at this stage and in order to ensure its correctness and to obtain accurate values of the interatomic distances and angles we have collected fairly complete three dimensional data out to the copper limit using copper radiation and the Weissenberg camera and molybdenum radiation and the precession camera. This data includes the planes HKO to HK3, OKL to 3KL, $HH_{\pm} 1L$ to $HH_{\pm} 3L$ and H1L to H5L. We expect to have available about 3500 independent planes for the accurate analysis of this structure. We are measuring these films, the Weissenberg by eye and the precession photographs on the Joyce-Loebl recording densitometer. This structure analysis is being done in collaboration with Dr. R. Mason of Imperial College, University of London.

f) The partial structure analyses of Ph_3PAuCH_3 . Dr. E. Coffee has made some interesting compounds (cf. part 1 d)) of which the compound Ph_3PAuCH_3 was thought to be $(Ph_3PAu)_2$ with a Au-Au metal-metal bond. This compound would be very suitable to treatment by the RDC method if Au-Au bonds were present because of the high atomic number of Au. Powder diffraction photographs were taken but it was decided to see if single crystal techniques would not more quickly give more accurate information. Single crystal pictures were taken and the space group was determined as $P2_12_12_1$, $a_0=12.5$ A, $b_0=10.1$, $c_0=13.2$ with four molecular units of Ph_3PAuCH_3 per unit cell. Since the general position of the non-centrosymmetric space group $P2_12_12_1$ is fourfold, there is no way in which two Au atoms could be closer to each other than one half of the shortest axis, or 5 A, and consequently it was proved that the compound did not

have a Au-Au bond.

The material from a second preparation of what is now known to be $\text{Ph}_3\text{PAuCH}_3$ was studied by powder and single crystal diffraction techniques. This substance had a different crystal structure, space group $P2_1/c$, $a_0=8.6$ A, $b_0=11.3$ A, $c_0=16$ A, $\beta=115^\circ$, four molecular units of $\text{Ph}_3\text{PAuCH}_3$ per unit cell. This space group is centrosymmetric with fourfold general position. Consequently, it would be perfectly possible for a centrosymmetric dimeric molecule with a metal-metal bond to exist in this crystal symmetry. The (100) and (010) zones of data were collected from a single crystal and the sharpened ¹¹ Patterson functions calculated for these zones. The Patterson functions were interpreted in terms of the Au and P positions and these are listed in Table 7. The Au-Au distance is about 5.2 A, clearly larger than could be considered a Au-Au metal-metal bond. The compound $(\text{Ph}_3\text{PAu})_2$ has yet to be prepared.

Table 7. Rough coordinates of the Au and P atoms in the $P2_1/c$ form of $\text{Ph}_3\text{PAuCH}_3$ as determined from the Patterson function

Atom	x	y	z
Au	0.32	0.06	0.10
P	0.42	?	0.07

4. Discussions, papers, meetings

A preliminary paper announcing the preparation and structure analysis of the compound $\text{TiCl}_4 \cdot 2\text{Diarsine}$ and its isomorphs entitled "Eight-co-ordinate Diarsine Complexes of Quadrivalent Metal Halides" by R.J.H. Clark, Jack Lewis, R.S. Nyholm, Peter Pauling and G.B. Robertson which gives the crystal structure of

the compound in somewhat less detail than is given in this report has been published in Nature, 192, 222 (1961).

Dr. Peter Pauling travelled to the United States in July and August to attend the annual meeting of the American Crystallographic Association in Boulder, Colorado July 31 to August 4 and to visit various laboratories. Transportation on the North Atlantic was arranged by the European Research Office of the United States Department of the Army.

Dr. Pauling gave two papers at the ACA meeting; the first entitled "The Use of Radial Distribution Curves in the Stereochemical Study of Coordination Compounds" by Jean Dollimore, Peter Pauling and G.B. Robertson stated the problem and the mode of attack by the RDC method and announced the structure analyses as presented in this report of the compounds $TiCl_4 \cdot 2Diarsine$ and $KPt(acac)_2Cl$.

The second paper was entitled "The Design of a Versatile Instrument for the Automatic Collection of Three Dimensional Single Crystal Diffraction Data" by Peter Pauling in which he proposed the use of a small stored programme digital computer as the control box in a system for the measurement of three dimensional single crystal diffraction data. The use of a computer for such a purpose, the design of such systems, and the present and future costs of such a system were presented in an attempt to get the many people actively interested in this problem to seriously consider the very great advantages of the proposal.

Dr. Pauling visited the Ordnance Materials Research Laboratory, Watertown, Massachusetts. The work there by Dr. R.J. Weiss on determining the radial distribution of electron density of elements by measuring the diffraction pattern parallels our own work though on a different level. His results and the results of selfconsistent field calculations of wave functions of elements by Drs. A.J. Freeman and R.E. Watson are and will be used by us (and all other crystallographers) in our treatment of one-dimensional diffraction data and in calculated structure factors and IDC's.

Dr. Pauling visited Dr. Norman W. Gregory at the University of Washington, Seattle. Dr. Gregory is using one-dimensional diffraction techniques in his study of phase transitions in materials but uses more straightforward crystallographic techniques than the RDC.

Professor G.A. Jeffrey, of the University of Pittsburgh, whom Dr. Pauling visited, wishes to apply one-dimensional diffraction methods to his study of hydrates. This was discussed.

5. Administration including expenses

The experimental work has been directed by Professor R.S. Nyholm and Dr. Peter Pauling. The crystallographic work has been done by Mr. G.B. Robertson who has worked on the Contract full-time, and the programmes for the computer have been written

by Mrs. J. Dollimore, who has spent about 80% of her time on the Contract work since 1 February 1961.

A summary of the expenditure of Contract funds is shown below. There has been no expenditure on important property.

Expenditure

G.B. Robertson	at 900 p.a. 1.11.60.-31.10.61.	900. 0.0.
	Superannuation	90. 0.0.
	National Insurance	30. 0.0.
Mrs. J. Dollimore	at 58 p.m. 1.2.61.-30.9.61.	464. 0.0.
	at 450 p.a. Oct. 1961	37.10.0.
Overheads		100. 0.0.
Materials		206. 0.0.
Computing		314.16.8.
		<hr/>
		2142. 6.8.
		<hr/> <hr/>

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Appendix I. Programme RDC 1

Calculation. The function

$$I = \frac{S_{\max}}{S_{\min}} \frac{2\sin(2\theta)\sin\theta}{1+\cos^2(2\theta)} \frac{e^{Bs}}{\text{atoms}} \frac{\sin(4\pi rs)}{(f(s^2))^2}$$

where $s = (\sin\theta)/\lambda$ is calculated for each of the values $r = 0$ by Δr to r_{\max} in A where E and B are preset constants and $f(s^2)$ are atomic scattering factors

Input

- n the number of atomic scattering factor tables to be read up to a maximum of 14
- A f₁ f₂ the scattering factor tables, each tabulated at the points 0(1)16(2)32(4)60/64 in $\sin^2\theta$ for the wavelength used and each preceded by a letter pair
- Δr the interval in r in A desired
- r_{max} the maximum value of r desired
- L number of answers printed per line
- C a constant, unused at present
- B the exponential term constant
- a a scale factor
- title for the following data terminated by two figure shifts
- M the number of heavy atom types for data following
- a A the number of each type of atom in the structure separated by two spaces from the letter pair indicating the atom type
- X Y F where X/F is θ in degrees for the first value of the data following and Y/F is the interval in θ in degrees for subsequent values of data
- I₁ I₂ I₃ not more than 218 observed intensities terminated by an asterisk on a line of its own.

Running Procedure

Autocode in, programme in, Halt hoot.

Data in TR, press key 9

To restart reading TITLE and data, ITB keys 9 and 1, put up key 2, drop key 9.

Appendix II. Programme One-Dimensional

Calculation. This programme generates values of the Miller indices (hkl) and for each plane calculates the value of s^2 where $s = (\sin\theta)/\lambda$ according to the given crystal system and cell constants. The minimum and maximum values of s^2 to be considered may be given. The values of s^2 and their corresponding indices are sorted into order of increasing magnitude in s^2 and are punched out with the indices and some further functions of s^2 as desired. If a crystal structure is given, structure factors and functions thereof are calculated and produced as desired.

Input. Each item of input is one of a group which is introduced by a DIRECTIVE on a line of its own and terminated by an asterisk on a line of its own. The directive is one of the following words:

TITLE, GROUP, LIMITS, CALCULATE, STRUCTURE, SYMMETRY, CENTRO-SYMMETRIC, POSITIONS, FORMFACTORS.

The information given with each directive is as follows:

TITLE any title

GROUP (compulsory) followed by one of the words

CUBIC, HEXAGONAL, TRIGONAL, TETRAGONAL, ORTHORHOMBIC, MONOCLINIC or TRICLINIC on a line of its own followed by one of the letters

F, F, I, A, B, C on a line of its own for the Bravais lattice

symbol followed by those necessary for the system of

a b c α β γ the cell constants in A and degrees.

LIMITS (may appear twice) followed by one or more of

S_{MIN}, S_{MAX} each followed by a number being the value of s for the

minimum and maximum value of s to be considered (will be 0 and 1 respectively if not given).

CALCULATE (compulsory, may appear twice) followed by one or more of the following each on a separate line

D calculate the interplanar spacings in a

1/D calculates the reciprocal of the interplanar spacings

D2 calculates the square of the interplanar spacings

1/D2 calculates the reciprocal of the square of the interplanar spacings

S calculates $\sin\theta$

S2 calculates $(\sin\theta)^2$

S/X calculates $(\sin\theta)/\lambda$

S2/X2 calculates $(\sin\theta)^2/\lambda^2$

T calculates θ in degrees

2T calculates 2θ in degrees

The letters S, S2, T and 2T must be followed by sp sp and the value of λ , CR LF.

STRUCTURE to be followed by the value of λ on a line of its own

CENTROSYMMETRIC (omit if not centrosymmetric)

POSITIONS (must occur if STRUCTURE occurs) followed by a list of atoms and coordinates in the order

AB sp sp X_i sp sp Y_i sp sp Z_i sp sp B_i sp sp C_i CR LF

AB is a letter or letter pair describing atom type

X_i , Y_i and Z_i are atomic coordinates

B_i is thermal factor in $e^{-B_i s^2}$

C_i is multiplicity factor for atoms in special positions

CALCULATE (must occur if STRUCTURE occurs) followed by one or more of the following items each on a separate line

F calculates the structure factor

I calculates the square of the structure factor

ILP calculates the square of the structure factor times the Lorentz and polarization factors for Debye-Scherrer cameras.
The item ILP must be followed by sp sp λ CR LF.

SYMMETRY followed by X,Y,Z, and items of the form R, -R, A+R, and A-R each three on a line of its own, where R is X,Y or Z and A is a number either in the form of a fraction (3/4) or a decimal (0.75).

FORMFACTORS followed by the f tables tabulated at C(1)16(2)32(4)60/64 in $\sin^2\theta$ and each preceded by a letter or letter pair. This list need only be read in once, before the first set of data, but it must include all atoms mentioned in POSITIONS. If a new set of data includes new atoms, further f tables must be read in before this data.

LIMITS followed on a line of its own by CR LF.

FMIN, IMIN or ILFMIN followed by sp sp the value of the limit, CR LF.
If the calculated F, I or ILP is smaller than the limiting value, the plane is not punched

Operating Procedure Fig F in

Programme in with ITB no keys; ends on a rather horrid hoot.

Data in TR, press key 9; after a successful calculation, warbles six times on a variable note and comes to control hoot.

To re-enter programme, ITB key 8, Tap keys 1,2,8; to start fresh press key 9; to read more f tables and new data, press key 8.

Spurious characters on tape

Will copy next 10 characters on tape and print B registers and accumulator and hoot. Restart necessary