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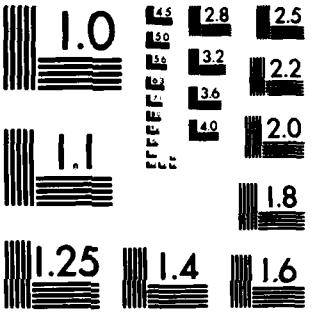

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TECHNICAL REPORT NO. 26

Bis(Bipyrazine)Ruthenium(II) Complexes: Characterisation, Spectroscopy and Electrochemistry

BY

R.J. Crutchley*, A.B.P. Lever* and A. Poggi

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Contribution from the Dept. of Chemistry, York University, Downsview (Toronto), Ontario, Canada, M3J 1P3

Bis(Bipyrazine)Ruthenium(II) Complexes: Characterisation, Spectroscopy and Electrochemistry.

By R.J.Crutchley*, A.B.P.Lever* and A.Poggi

Abstract:

Bis(Bipyrazine)ruthenium(II) complexes of general formula cis-$[Ru(BPZ)_2X_2]^{n+}$ are reported where X = Cl^-, Br^-, SCN^-, NO_2^-, CO_3^{2-}, oxalate^{2-}, H_2O, OH^- and $(OH)(H_2O)^-$, and n = 0, 1, or 2. The complexes are characterised by microanalysis, electronic, vibrational and nmr spectra and conductivity. Electrochemical data are reported and interpreted in terms of the Ru(III)/Ru(II) and BPZ/BPZ^- couples. Two principal charge transfer bands in the electronic spectra of these complexes are rationalised in terms of the effective charge on the ruthenium atom as indicated by the electrochemical data and simple ideas on ligand electronegativity. The pK_a values for the species $[Ru(BPZ)_2(H_2O)_2]^{2+}$ and $[Ru(BPZ)_2(H_2O)(OH)]^+$ are reported.

Recently we have reported the synthesis of an important new photocatalyst, the ruthenium(II) tris(bipyrazine) cation1. The chemical, physical and photophysical properties of this cation have been discussed.[2,3] Moreover it has been shown to form a series of protonated species in acid media, including a hexaprotonated species in concentrated sulfuric acid.[4]

We believe that bipyrazine ruthenium(II) complexes may have an important role to play in the development of future photocatalysts and to this end wish to report the syntheses and characterisation of bis(bipyrazine)ruthenium(II) complexes, cis-$Ru(BPZ)_2X_2$ where X is Cl^-,

Br^-, I^-, SCN^-, NO_2^-, H_2O, OH^-, $CO_3^{=}$ and oxalate. The complexes are characterised by electronic, vibrational and nmr spectra, and electrochemistry.

Experimental Section

Electronic spectra were recorded with a Perkin-Elmer-Hitachi Model 340 microprocessor UV/VIS spectrometer, infrared spectra were recorded with a Beckman IR12 spectrometer, ^1H NMR spectra were obtained using a Varian EM360 60 MHz nmr spectrometer. Tetramethylsilane at 0.00 ppm or residual protons of dimethyl-d^6 sulfoxide at 2.50 ppm were used as internal references. Conductivity data were obtained with a Wayne-Kerr conductivity bridge, and electrochemical data using Princeton Applied Research equipment[5] (and cell set-up[2]) as previously described.

Preparation of complexes: $Ru(BPZ)_2Cl_2.2H_2O$ This complex was initially reported via the photoanation of $Ru(BPZ)_3Cl_2$. It may be prepared, directly, as follows.

$RuCl_3.nH_2O$ (0.35g) and BPZ (0.6g) were stirred and refluxed in DMF (50ml). After 11 h, the purple solution was filtered and ether added thereto to precipitate $Ru(BPZ)_2Cl_2$. The crude product was washed with ether and recrystallised from acetonitrile to yield black microcrystals of $Ru(BPZ)_2Cl_2.2H_2O$ (yield 0.6g, 85%).Anal. C,H,N,Cl.

The bromo and iodo complexes prepared in a similar fashion from an in situ generation of the corresponding ruthenium halides, as follows.

Preparation of in situ RuX_3, X = Br, I. To a solution of $RuCl_3.nH_2O$ (1.5g) in water (40ml) was added 10 N NaOH (2ml). The solution was boiled and filtered and the black precipitate of $RuO_{2+x}.yH_2O$ was washed with water and acetone. After drying, the oxide was placed in a beaker together with concentrated HX (30ml, X = Br or I). The mixture was digested at low temperature until evaporated almost to dryness (overheating can lead to the formation of insoluble products). The ruthenium halide was then vacuum dried. The yield is almost quantitative. The iodide should be used fresh since it becomes inert over a period of time.

$Ru(BPZ)_2Br_2.2H_2O$ was prepared as for the chloride. Anal. C,H,N,Br.

$Ru(BPZ)_2I_2$ was prepared in an analogous fashion except that the product

was thrown out of solution by adding methanol (75ml) and ether (300ml), and storing the solution in a freezer overnight. Anal. C,H,N,I.

$Ru(BPZ)_2(NO_2)_2.\ 0.5H_2O.\ 0.5CH_3CN$: $Ru(BPZ)_2Cl_2$ (0.5g) and sodium nitrite (1.0g) were refluxed in 1:1 ethanol/water (30ml) for one hour with constant stirring. Upon cooling and leaving overnight in the freezer, the orange red nitro product (0.35g, 66%) was obtained. Anal C,H,N.

$Ru(BPZ)_2(NCS)_2.\ 1.5H_2O$: This was prepared in the same fashion as the nitro derivative, but using ammonium thiocyanate (2.0g). However after 1.5 hr, additional water (10ml) was added, and the ethanol removed by azeotropic distillation. After storage overnight at room temperature, black microcrystals of the thiocyanate product (0.4g, 70%) were obtained. Anal. C,H,N.

$Ru(BPZ)_2(C_2O_4).2H_2O$: $Ru(BPZ)_2Cl_2$ (1.0g) and ammonium oxalate (2.0g) were placed in a 4:1 water/ethanol solution (50ml) and refluxed for 2hr. with constant stirring. The red solution was filtered hot and the filtrate cooled to room temperature. The black microcrystals which formed were washed with water and ethanol (Yield 0.6g, 58%). Anal. C,H,N.

$Ru(BPZ)_2(CO_3).5H_2O$: $Ru(BPZ)_2Cl_2$ (0.5g) and potassium carbonate (1.0g) were placed in 1:1 ethanol/water solution (30ml) amd refluxed for 2hrs. with constant stirring. The hot solution was filtered and placed in a freezer overnight. Black microcrystals of the carbonate species were collected and washed with water and ethanol (yield 0.4g, 74%). Anal. C,H,N. (The H analysis was slightly high). Both the oxalate and carbonate are only very sparingly soluble in organic solvents limiting the collection of data on these complexes. The complexes are soluble in water and the low conductivity of such solutions infers that little hydrolysis takes place at least at room temperature.[6]

Results and Discussion

The complexes $Ru(BPZ)_2X_2$, X = Cl^-, Br^-, I^-, SCN^- and NO_2^- are non-conducting in acetonitrile consistent with a six coordinate un-ionised pseudo octahedral formulation.

The 1H NMR spectra are fully consistent with a cis-stereochemistry, the trans form probably being inhibited because of proton-proton

repulsion between trans planar BPZ groups. The ^1H NMR spectrum of $Ru(BPZ)_2Cl_2$ has already been adequately discussed.[2] Chemical shifts for the various protons (see I) are reported in Table 1, with assignments based upon our earlier analysis.[2] Briefly, the complexes have C_2 symmetry and thus each complex contains two magnetically in-equivalent pyrazine moieties. The protons of one pyrazine ring are influenced by the anisotropic effect of a neighbouring pyrazine ring and experience chemical shifts similar to those of the tris(bipyrazine) cation.[2] Protons of the other pyrazine moiety will be shifted downfield relative to the other ring as confirmed nicely by experiment (Fig.3: ref.2, and Table 1). As shown in Table 1, the protons H_3, $H_{3'}$, H_5, $H_{5'}$ and $H_{6'}$ remain fairly constant whereas the chemical shift of H_6 varies considerably with variation of X. For $X = Cl^-$, Br^- and I^-, H_6 shifts downfield as the radius of X increases suggesting a van der Waals deshielding interaction. For $X = NO_2^-$ and SCN^-, the magnetic anisotropy of X must also be taken into account. The J values given in Table 1 are slightly dependent on the ligand. The exact nature of this dependence requires further study.

The ir spectrum of the nitro complex shows N-O stretching vibrations at 1300 and 1350 cm^{-1} consistent with N bound *nitro coordination*, rather than O bound nitrito.[7] The thiocyanate derivative shows (CN) at 2100 cm^{-1} (broad), but the (CS) frequency is apparently obscured by BPZ absorption. In parallel with $Ru(Bipy)_2(NCS)_2$,[8] it is probable that the thiocyanate is N-bound.[9] Indeed the data to be discussed below would be inconsistent with S bonding.

Infrared spectra for the carbonate and oxalate species are consistent with a coordinated anion in the solid state. The carbonate complex exhibits bands at ca 1600, 1260, 1040, 840 and 760 cm^{-1} consistent with bidentate bound carbonate.[10] The oxalate complex exhibits a broad band at 1690 cm-1, plus other absorption, consistent with bound rather than ionic oxalate.[10]

Electrochemical data are reported in Table 2. The BPZ ligands are reduced at potentials similar to that of the tris(bipyrazine) cation[2].

The first reduction potential is about 200mV less positive than for the tris(bipyrazine)ruthenium(II) cation probably because the polarising power of the ruthenium has been reduced by the relacement of a hard bipyrazine ligand by softer anions. This is reflected by the oxidation couple Ru(III)/Ru(II) which is dependent upon X. With X a halogen, the potentials are less positive than with the harder nitrogen ligands, NO_2^- and SCN^-, and much less than for the tris(bipyrazine) case with X = BPZ.

The electronic spectra of these bis(bipyrazine) complexes (Table 3) show two MLCT bands, one near 18,000 and the other near 25,000 cm^{-1}, due to transitions from $Ru(t_{2g})^6$ to the first two acceptor pi* orbitals on the coupled bipyrazine ligands (see ref.2). The uv absorptions near 32,000 and 42,000 cm^{-1} are internal pi-pi* transitions on the bipyrazine ligands. The shoulder between these two transitions may be pi-pi* or perhaps n-pi*. It is not likely to be an MLCT transition, though tentatively assigned as such in ref.2, since, unlike the other MLCT transitions, it is almost invariant in position with change in X.

The MLCT bands shift to the red in passing from the very hard BPZ to the hard nitrogen (SCN^- and NO_2^-) and oxygen ligands (carbonate etc) to the softer halides, the charge transfer frequencies being directly proportional to the Ru(III)/Ru(II) oxidation potentials. As charge is placed on the ruthenium atom, making it less positive, this facilitates both electrochemical oxidation, and charge transfer from metal to ligand.

Aquo and hydroxy species

If dilute perchloric acid is added to $Ru(BPZ)_2CO_3$, the cation $[Ru(BPZ)_2(H_2O)_2]^{2+}$ is formed. Although not isolated, this species has electronic spectra (Table 3, Fig.1) consistent with the slightly harder nature of water relative to halogen, and consistent with previous data reported for the bipyridine analog.[10] If NaOH is added to this solution, two new species may be detected (Fig.1). In strong base solution, the two MLCT charge transfer bands are shifted 2700 - 3000 cm^{-1} to the red. When an acid solution of the dihydrate complex is titrated with base, (or a basic solution is treated with acid), an intermediate is seen with spectra lying between these two species, i.e.

shifted about 1300 - 1800 cm^{-1} to the red of the dihydrate. Indeed titration of an acid solution with standard NaOH results in two successive sets of isosbestic points being observed; plotting the peak position of the lower energy MLCT band against titre, yields a double sigmoidal curve with inflection points at pH = 7.6 and pH = 9.8.

These data are entirely consistent with the hydrolysis of $[Ru(3PZ)_2(H_2O)_2]^{2+}$ with a pK_a of 7.6 to yield $[Ru(BPZ)_2(H_2O)(OH)]^+$ followed by its hydrolysis with a pK_a of 9.8 to yield $Ru(BPZ)_2(OH)_2$. Corresponding data for the bipyridine analogs do not appear to have been reported. However the pK_a value for the hydrolysis of $Ru(bipy)_2(py)(H_2O)^{2+}$ is 10.8,[12], and the consecutive values for the rhodium(III) and rhodium(II) species $Rh(bipy)_2(H_2O)_2^{3+}$ and $Rh(bipy)_2(H_2O)_2^{2+}$ are 4.8 and 6.87, and 8.6 and 11.1 respectively[13]; these results are consistent with our data.

The MLCT band positions of the hydroxy species span the halide data suggesting that hydroxide ion acts as a soft ligand towards Ruthenium(II) transferring appreciable charge density to the metal.

Further photochemical studies of these species are in hand. We note that the hydroxy species may be useful starting materials towards the generation of Ru(IV) oxo species which would parallel those formed with bipyridine[12,14] but would be much stronger oxidising agents. Indeed the procedures outlined here provide new synthetic routes into bis(bipyrazine) Ruthenium(II) chemistry and later may allow the generation of bis(bipyrazine)osmium(II) complexes whose bipyridine analogs are of especial photocatalytic interest.[15]

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Table 1. ^{1}H NMR Spectra of $Ru(BPZ)_2X_2$ Species[a]

Complex	H_3	H_5	H_6	$H_{3'}$	$H_{5'}$	$H_{6'}$	$J_{3,6}$	$J_{3',6'}$	$J_{5,6}$	$J_{5',6'}$
$Ru(BPZ)_2(NO_2)_2$	10.02	9.03	9.63	9.93	8.44	7.88	1.0	1.0	3.2	3.2
$Ru(BPZ)_2(NCS)_2$	10.02	9.08	9.23	9.85	8.38	7.89	0.9	0.9	3.2	3.4
$Ru(BPZ)_2Cl_2$	10.03	8.98	9.92	9.86	8.28	7.88	0.8	0.8	3.3	3.3
$Ru(BPZ)_2Br_2$	10.03	9.00	10.11	9.86	8.32	7.92	0.9	0.9	3.5	3.3
$Ru(BPZ)_2I_2$	10.00	8.99	10.33	9.84	8.33	7.92	0.9	0.9	3.3	3.3

a) Recorded in d^6-dmso. * from tetramethylsilane in ppm; J in Hz. H_3, H_5, and H_6, are in the ring trans to coordinated ligands other than bipyrazine.

Table 2 Electrochemical Data in Acetonitrile, versus sce[a]

Complex	Ru(III)/Ru(II)	BPZ/BPZ^-	$BPZ^-/BPZ^=$
$Ru(BPZ)_3^{2+}$ [b]	1.86	-0.80	-0.98, -1.24
$Ru(BPZ)_2(NO_2)_2$	1.18[c]		
$Ru(BPZ)_2(NCS)_2$	0.94[d]	-0.93	-1.18[c]
$Ru(BPZ)_2Cl_2$	0.80	-1.04[c]	-1.27[c]
$Ru(BPZ)_2Br_2$	0.79	-1.09[c]	-1.22[c]
$Ru(BPZ)_2I_2$	0.80[d]	-1.05[c]	-1.18[c]

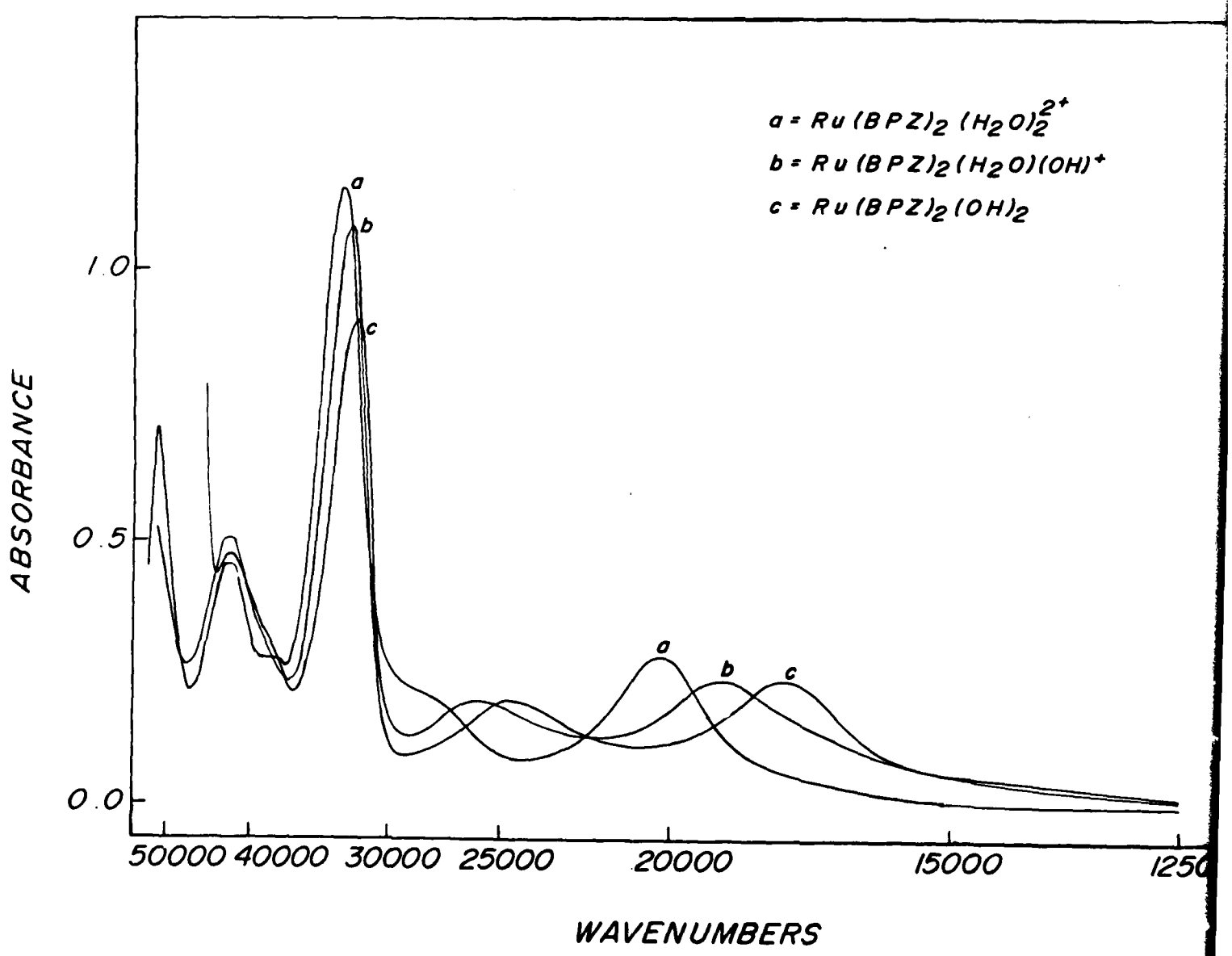
a) 0.1M Tetraethylammonium hexafluorophosphate. All data are averages of anodic and cathodic peaks at 100 mV/s scan rate. The waves are reversible except for those indicated otherwise. b) data from ref.2. c) partially reversible. d) irreversible.

Table 3 Electronic Spectra of $Ru(BPZ)_2X_2$ Species[a]

Complex	Ruthenium to Diimine MLCT		pi-pi* Bipyrazine	
$Ru(BPZ)_3^{2+}$	22,575(4.18)	29,155(4.27)	33,900(4.79)	37,455(4.34)
			41,495(4.37)	
$Ru(BPZ)_2(NO_2)_2$	20,660(3.94)	28,735(3.97)	32,365(4.57)	37,735sh
		37,455(4.34)	42,020(4.29)	
$Ru(BPZ)_2(NCS)_2$	19,010(3.96)	26,740(3.95)	32,155(4.59)	37,455sh
			42,200(4.41)	
$Ru(BPZ)_2Cl_2$	18,020(4.03)	25,315(3.94)	32,050(4.54)	-
			41,325(4.31)	
$Ru(BPZ)_2Br_2$	18,250(3.99)	25,510(3.91)	31,950(4.53)	38,170sh
			42,020(4.36)	
$Ru(BPZ)_2I_2$	18,115(3.90)	25,510(3.89)	31,450(4.46)	-
			42,735(4.43)	
$Ru(BPZ)_2(Ox)^{b,c}$	19,380(4.08)	26,740(3.97)	32,360(4.70)	37,455sh
			41,495(4.30)	
$Ru(BPZ)_2CO_3^{c}$	20,080(3.93)	26,320sh	32,360(4.59)	37,595sh
			41,840(4.22)	
$Ru(BPZ)_2(H_2O)_2^{2+c,d}$	20,240(4.11)	27,780sh	32,680(4.74)	37,595sh
			42,195(4.33)	
$Ru(BPZ)_2(H_2O)(OH)^{+c,e}$	18,870(4.04)	26,040(3.96)	32,260(4.71)	38,460sh
			42,020(4.37)	
$Ru(BPZ)_2(OH)_2^{c,f}$	17,480(4.05)	24,690(3.97)	31,550(4.65)	38,460sh
			42,195(4.36)	

a) Data in wavenumbers, log e in parentheses: all data in acetonitrile except where noted. Data for the tris(bipyrazine) complex from ref.2. b) oxalate. c) in water. d) pH = 3. e) pH = ca 8.5. f) pH = 14.

Legend: The electronic spectra of a) $Ru(BPZ)_2(H_2O)_2^{2+}$ in water at pH 3; b) $Ru(BPZ)_2(H_2O)(OH)^+$ in water at pH 8.5; c) $Ru(BPZ)_2(OH)_2$ in water at pH 14.


a = Ru(BPZ)2(H2O)2 2+
b = Ru(BPZ)2(H2O)(OH)+
c = Ru(BPZ)2(OH)2
ABSORBANCE
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0.5
0.0
a
b
c
a
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