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Complexes of 2,2′-Bipyrimidine and 3,6-Di(2-pyridyl)tetrazine

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Abstract

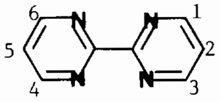
The synthesis, characterisation and cyclic voltammetric behaviour of new complexes of 2,2′-bipyrimidine (bpm) with the metals rhodium, osmium, platinum, palladium and mercury and 3,6-di(2-pyridyl)-1,2,4,6-*sym*-tetrazine (dpt) with nickel and ruthenium are described.

Introduction

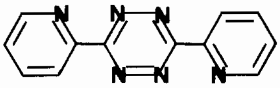
The unusual properties of the luminescent trisbipyridine ruthenium(II) ion, $[Ru(bpy)_3]^{2+}$, as a sensitiser for the photochemical cleavage of H_2O and solar energy conversion (for example, see ref. 1) has led to a vast investigation of its luminescence and redox behaviour [1–6] as well as the synthetic behaviour of the ligand (for example, refs. 7–14). Furthermore, and in an attempt to emulate its behaviour, diimine ligands such as bipyrazine (bpz) [14–19] and bipyrimidine (bpm) [19–37] have been investigated. In the case of bipyrimidine, its complexes with Fe(II), Ni(II), Cu(II), Co(II) were prepared by Westcott [32] and Ruminski *et al.* [37]. Carbonyl–bipyrimidine complexes with Cr, Mo, W, Pt(II) and Pt(IV) and Pt–alkyl complexes [22, 27, 28] have also been reported and investigated. Bailar *et al.* were able to isolate several Co(II) and Co(III) complexes [30] including $[Co(bpm)_3]^{2+}$, which as the perchlorate salt was later found to possess highly favourable Co(II)–Co(III) oxidation, compared to the bpy complex, thus making it a potential candidate for use in a storage battery [33]. The first bipyrimidine–ruthenium complex was prepared by Dose *et al.* [20] and Hunziker *et al.* [21]. The redox and luminescent properties of new mixed and single ligand (bpy, bpm, bpz) ruthenium complexes were extensively studied by Rillema *et al.* [19].

Bipyrimidine has an added advantage over bipyridine or bipyrazine due to its ability to act as a bridging ligand. Various Pt, W, Mo and Cr complexes of this nature have been reported [22–27]. The bridging behaviour of bpm has also been established in Cu(II) and Ag(I) complexes [29]. The resulting bimetallic species led to interesting studies on mixed valence compounds that can be generated chemically and electrochemically. Thus ruthenium complexes of the formulae $[Ru(bpy)_2(bpm)Ru(bpy)_2](PF_6)_4$ [20, 21] and $[(NH_3)_4Ru(bpm)Ru(NH_3)_4](ClO_4)_4$ [34] have been prepared and their multistep redox behaviour has been studied [20, 21, 34, 35]. Among other bridging ligands, bipyrimidine was also used to prepare Ru and Os mixed valence compounds [36]. The cyclic voltammograms and the low lying intervalence bands of these compounds lead to valuable information on the intramolecular electron transfer between two metallic sites of different valency [36].

To the best of our knowledge, the complexing behaviour of 3,6-di-(2-pyridyl)-1,2,4,5-s-tetrazine (dpt) has been reported only by Gustav *et al.* [38] and Kaim *et al.* [39]. We report in this paper the synthesis of new complexes of bpm and dpt. IR, electronic spectra and cyclic voltammetry of these complexes are presented and discussed.



bpm



dpt

Experimental

Materials

All solvents were AR grade. bpm was purchased from Lancaster Synthesis, Ltd., and crystallized from benzene. dpt was prepared by the method of Gildard and Lions [40] and crystallised from a 1:1 mixture of chloroform and ethanol. Metal salts were of Fluka, BDH or Laborat manufacture, and were used without purification. *cis*-Dichloro-bis-(benzonitrile) palladium(II) was prepared by the method of Kharash *et al.* [41], while *trans*-dibromo-bis-(benzonitrile)platinum(II) was prepared according to Church *et al.* [42]. *cis*-$Ru(bpy)_2Cl_2$ was prepared by the method of Sullivan *et al.* [43].

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TABLE I. Elemental Analyses of the Metal Complexes

Compound	Analysis, calculated (found)			
	%C	%H	%N	%X^a
$[Hg_2(bpm)Cl_4]$	13.70	0.86	7.99	20.22
	(13.81)	(0.89)	(8.13)	(21.00)
$[Hg_2(bpm)Br_4]$	10.93	0.69	6.37	36.36
	(11.03)	(0.72)	(6.50)	(41.30)
$[Hg_2(bpm)I_4]$	9.00	0.57	5.25	47.60
	(8.89)	(0.65)	(5.41)	(48.10)
cis-$[Rh(bpm)_2Cl_2]Cl \cdot 2H_2O$	34.22	2.87	19.95	18.32
	(34.10)	(2.90)	(19.90)	(18.60)
$[Rh_2(bpm)_3Cl_6] \cdot 3H_2O$	30.43	2.55	17.75	22.46
	(29.89)	(2.44)	(17.60)	(23.10)
$[Rh(bpm)H_2OCl_3] \cdot 2H_2O$	22.80	2.87	13.29	25.24
	(24.68)	(2.75)	(12.49)	(25.18)
$Rh(bpm)_2Br_3 \cdot 2H_2O$	28.39	2.08	16.55	35.41
	(29.90)	(2.10)	(17.38)	(35.10)
$[Os(bpm)_3](ClO_4)_2 \cdot 2H_2O$	31.97	2.49	18.64	7.86
	(32.00)	(2.19)	(17.62)	(8.81)
$[Os(bpm)_2Cl_2]Cl \cdot 2H_2O$	29.61	2.48	17.27	16.39
	(29.23)	(2.74)	(16.92)	(17.04)
$[Pd(bpm)Cl_2] \cdot H_2O$	27.15	2.29	15.85	20.06
	(27.61)	(1.91)	(15.70)	(21.30)
$[Pt(bpm)Br_2] \cdot H_2O$	18.09	1.51	10.55	30.09
	(19.43)	(1.62)	(11.06)	(31.56)
$Ni(dpt)_2Cl_2 \cdot H_2O$	46.49	2.93	27.10	11.43
	(47.04)	(2.96)	(26.77)	(12.28)
$[\{(bpy)_2Ru\}_2dpt](PF_6)_4 \cdot 2H_2O$	37.22	2.64	11.68	27.17
	(37.65)	(2.85)	(11.70)	(28.56)

^{a}X = Cl Br, I.

Elemental Analyses

These were done by Pascher Microanalysis (F.R.G.), MEW (Phoenix, Arizona) and Butterworths (U.K.) Laboratories. Table I shows the results.

Instrumental

KBr disk IR spectra were taken on a Pye Unican SP3-300 spectrophotometer. An SP8-100 of the same company was used for UV–Vis spectra. Conductivity measurements on 10^{-3} M solutions were made using a Harris conductivity meter. NMR spectra were obtained using a Bruker WP 80Y instrument, while cyclic voltammograms were performed using a Hi-Tech potentiostat and waveform generator.

Preparation of the Complexes

(i) cis-Dichlorobis-(2,2′-bipyrimidine)rhodium(III) chloride dihydrate, cis-$[Rh(bpm)_2Cl_2]Cl \cdot 2H_2O$

A solution of $RhCl_3 \cdot 3H_2O$ (0.60 g, 2.28 mmol) in 40 ml of hot ethanol was added to a solution of 2,2′-bipyrimidine (0.72 g, 4.56 mmol) in 40 ml of hot ethanol. A yellow–ochre precipitate appeared. The reaction mixture was refluxed for 18 h and filtered while hot. The isolated solid (1.09 g) was refluxed in chloroform to remove any excess ligand. It was filtered, and then dissolved in water and reprecipitated with a mixture of acetone and ether. The yield was 0.60 g (37%). The complex decomposes at 235 °C.

(ii) Hexachlorotris-(2,2′-bipyrimidine)dirhodium(III) dihydrate, $[Rh_2(bpm)_3Cl_6] \cdot 2H_2O$

To a stirred solution of $RhCl_3 \cdot 3H_2O$ (0.20 g, 0.76 mmol) in 10 ml ethanol was added a solution of bipyrimidine (0.30 g, 1.9 mmol) in 10 ml ethanol. The brick-red precipitate that was formed became yellow after boiling for 30 min. The yellow precipitate was filtered, washed with water, crystallized from DMF and washed with ethanol and ether to yield 0.24 g (67%).

(iii) Trichloroaquo-(2,2′-bipyrimidine)rhodium(III) dihydrate, $[Rh(bpm)H_2OCl_3] \cdot 2H_2O$

A water–acetone mixture (25:20 ml) of $RhCl_3 \cdot 3H_2O$ (0.26 g, 1 mmol) and bipyrimidine (0.16 g, 1 mmol) was refluxed. A red–orange colour formed immediately; it turned deep-red after one hour of reflux. A brown precipitate formed after 17 h of reflux. The mixture was allowed to cool. It was filtered and washed with acetone and ether, and then refluxed in 20 ml chloroform to remove excess ligand. The product was dried under vacuum at 40 °C. The yield was 0.13 g (31%). The complex decomposes at 215 °C.

(iv) Dibromobis-(2,2′-bipyrimidine)rhodium(III) bromide dihydrate, [Rh(bpm)$_2$Br$_2$]Br·2H$_2$O

A solution of $RhCl_3 \cdot 3H_2O$ (0.26 g, 1 mmol) and KBr (1.0 g in water (15 ml) was boiled for 3 min giving a red–brown solution of $RhBr_6^{3-}$ [8]. An ethanolic solution (15 ml) of bipyrimidine (0.32 g, 2.0 mmol) was then added. The red–brown colour became red and then turned to orange on heating for 7 min. Heating was continued for another 25 min. After cooling, the dirty-orange precipitate that formed was filtered, washed with water, acetone (three times) and ether, and dried under vacuum at 40 °C. The yield was 0.48 g (65%). The compound does not decompose or melt below 360 °C.

(v) Tris-(2,2′-bipyrimidine)osmium(II)perchlorate dihydrate, [Os(bpm)$_3$](ClO$_4$)$_2$·2H$_2$O

A modification of the procedure of Liu *et al.* [44] for $[Os(bpy)_3](ClO_4)_2$ was used. A solution of K_2OsCl_6 (0.48 g, 1 mmol) and excess sodium (+)tartrate (1.48) in 30 ml of water was refluxed until the colour changed to yellowish-green. After 4.5 h bipyrimidine (0.51 g, 3.2 mmol) was added and the mixture was refluxed for two more hours. Few drops of concentrated $HClO_4$ were added when a dark precipitate appeared. The mixture was cooled and filtered. The solid was washed twice with cold dilute $HClO_4$, acetone and ether, and then dried by suction. The dark green product obtained was recrystallized from water. The yield was 0.13 g (14%).

(vi) Dichlorobis-(2,2′-bipyrimidine)osmium(III) chloride dihydrate, [Os(bpm)$_2$Cl$_2$]Cl·2H$_2$O

A mixture of 2,2′-bipyrimidine (0.80 g, 5.0 mmol) and K_2OsCl_6 (0.46 g, 1 mmol) in a test tube was stirred with a glass rod at 160 °C in an oil bath for 3 h. The mixture solidified upon raising the temperature to 200 °C. The solid was then refluxed in chloroform for 10 min, and then filtered and washed several times with chloroform and ethanol to remove any excess ligand. The solid was dissolved in about 25 ml of methanol and filtered. The filtrate was evaporated to about 3 ml; diethyl ether was then added, and the brown precipitate formed was washed with ether and dried by suction. The yield was 0.48 g (74%).

(vii) Dichloro(2,2′-bipyrimidine)palladium(II) monohydrate, [Pd(bpm)Cl$_2$]·H$_2$O

To a stirred solution of *cis*-$Pd(PhCN)_2Cl_2$ (0.39 g, 1 mmol) in 25 ml of acetone was added a solution of bipyrimidine (0.16 g, 1 mmol) in acetone (25 ml). A yellow precipitate appeared immediately. The mixture was stirred for 30 min. The solid formed was filtered and washed with acetone and ether. The yield was 0.39 g (90%). The complex changed to yellow–ochre at 260 °C with no further change up to 360 °C.

(viii) cis-Dibromo(2,2′-bipyrimidine)platinum(II) monohydrate, [Pt(bpm)Br$_2$]·H$_2$O

To a stirred solution of bipyrimidine (0.08 g, 0.5 mmol) in 25 ml acetone was added a solution of $Pt(PhCN)_2Br_2$ (0.28 g, 0.5 mmol) in acetone (45 ml). The mixture was refluxed for 20 h. The orange precipitate formed was filtered, washed with acetone and ether and dried by suction. The yield was 0.10 g (39%). The complex does not melt or decompose up to 300 °C.

(ix) Tetrachloro-μ-(2,2′-bipyrimidine)dimercury-(II), [Hg$_2$(bpm)Cl$_4$]

This compound was prepared by us before it was reported by Lanza [24]. To a stirred solution of $HgCl_2$ (0.55 g, 2.0 mmol) in 20 ml of H_2O was added a solution of bipyrimidine (0.16 g, 1 mmol) in water (15 ml). A white precipitate appeared immediately. The reaction mixture was stirred for 15 min. The product was filtered, washed with water, acetone and ether and dried under vacuum at 40 °C. The yield was 89%. The complex sublimes at 320 °C.

(x) Tetrabromo-μ-(2,2′-bipyrimidine)dimercury-(II), [Hg$_2$(bpm)Br$_4$]

This complex was prepared by a procedure similar to that reported in (i) above. Mercuric bromide, $HgBr_2$ was used instead of $HgCl_2$. The yield was 75%. The complex does not melt or decompose up to 360 °C.

(xi) Tetraiodo-μ-(2,2′-bipyrimidine)dimercury(II), [Hg$_2$(bpm)I$_4$]

This complex was prepared by a procedure similar to that reported in (i) above. However, mercuric iodide, HgI_2, was used instead of $HgCl_2$ and acetone was used as a solvent. The yield was 80%. The complex melts at 233 °C with decomposition.

(xii) Bis-(3,6-di(2-pyridyl)1,2,4,5-s-tetrazine)-nickel(II) chloride monohydrate, [Ni(dpt)$_2$]Cl$_2$·H$_2$O

A solution of $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) in ethanol (20 ml) was added dropwise over a period of 15 min to a stirred solution of dpt (0.49 g, 2 mmol) in 60 ml of hot ethanol. The mixture was boiled for another hour. The brick-red solid formed was filtered, washed with hot ethanol and ether, and then dried by suction. The yield was 0.51 g (82%). The complex decomposes at 310 °C.

(xiii) Tetrakis-(2,2′-bipyridine)-μ-{3,6-di(2-pyridyl)1,2,4,5-s-tetrazine}diruthenium(II)hexafluorophosphate trihydrate, [(bpy)$_2$Ru(dpt)Ru(bpy)$_2$]-(PF$_6$)$_4$·3H$_2$O

This product was reported recently after we had prepared it [39]. A solution of the ligand dpt (0.24 g, 1 mmol) in 50 ml of hot ethanol was added dropwise over a period of 80 min to a stirred solution of Ru-(bipy)$_2$Cl$_2$ (1.2 g, 2.1 mmol) in hot ethanol (120 ml). The colour became deep-blue. The reaction mixture was refluxed for 24 h. The solvent was evaporated to dryness on a rotatory evaporator. The residue was dissolved in water. An aqueous saturated solution of NaPF$_6$ was added dropwise. The blue precipitate formed was filtered and dried under vacuum at 40 °C. The yield was 60%.

Results

Elemental analysis results are shown in Table I. The conductivity results in DMF, H_2O or nitromethane are included in Table II. Unfortunately, for some of the complexes, their insolubility in most common solvents has prevented us from doing conductivity, UV–Vis, NMR and cyclic voltammetry measurements. The UV–Vis results are shown in Table III. NMR and IR results are shown in Tables IV and V respectively, The halfwave potentials *vs.* SCE obtained on a Pt working electrode are shown in Table VI. Figures 1 and 2 show cyclic voltammograms for [Os(bpm)$_3$](ClO$_4$)$_2$ and Hg$_2$-(bpm)Cl$_4$, respectively. Table VI, however, does not include results for the Pt, Pd and Rh complexes since these proved to be very reactive, leaving dark deposits on the Pt electrode and rendering the resulting curves impossible to analyse.

Discussion

Conductivity

Conductivity results in Table I show that Hg(II), Pt(II) and Pd(II) are not ionic; this is consistent with

TABLE II. Conductivity Measurements of Metal Complexes[a]

Complex	Λm (ohm^{-1} cm^2 mol^{-1})	Solvent
Hg$_2$(bpm)Cl$_4$	5.0	DMF
Hg$_2$(bpm)Br$_4$	4.0	DMF
Hg$_2$(bpm)I$_4$	3.0	DMF
cis-[Rh(bpm)$_2$Cl$_2$]Cl·2H$_2$O	112.0	H_2O
[Rh(bpm)H$_2$OCl$_3$]·2H$_2$O	11.0	DMF
[Rh$_2$(bpm)$_3$Cl$_6$]·3H$_2$O	36.0	DMF
[Os(bpm)$_3$](ClO$_4$)$_2$·2H$_2$O	187.0	CH_3NO_2
[Os(bpm)$_2$Cl$_2$]Cl·2H$_2$O	115.0	H_2
[Pd(bpm)Cl$_2$]·H$_2$O	2.0	DMF
[Pt(bpm)Br$_2$]·H$_2$O	1.0	DMF
[{(bpy)$_2$Ru}$_2$dpt](PF$_6$)$_4$·3H$_2$O	327.0	CH_3NO_2

[a]Results were compared with reported values in ref. 52.

TABLE III. UV–Vis Spectra of the Metal Complexes

Compound	λ$_{max}$ (nm)	ε × 10^{-3} (l mol^{-1} cm^{-1})
2,2′-bipyrimidine[a]	288	0.99
	268	2.38
Hg$_2$(bpm)Cl$_4$[a]	289(sh)	2.16
	266	4.99
Hg$_2$(bpm)Br$_4$[a]	267	22.8
Hg$_2$(bpm)I$_4$[a]	296	32.2
	267	37.6
cis-[Rh(bpm)$_2$Cl$_2$]Cl·2H$_2$O[b]	390(sh)	0.127
	289	3.26
[Rh$_2$(bpm)$_3$Cl$_6$]·3H$_2$O	399(sh)	1.62
	271	28.28
[Rh(bpm)H$_2$OCl$_3$]·2H$_2$O[a]	440(br)	1.03
	274	2.45
[Os(bpm)$_3$](ClO$_4$)$_2$·2H$_2$O[a]	586	2.41
	479	11.2
	389	15.7
	345	16.6
	269	39.9
[Os(bpm)$_2$Cl$_2$]Cl·2H$_2$O[b]	520(sh)	0.35
	316	7.94
	274	27.1
[Pd(bpm)Cl$_2$]·H$_2$O[a]	389(sh)	0.38
	284	5.36
[Pt(bpm)Br$_2$]·H$_2$O[a]	408(br)	2.38
	380	2.38
	268	11.50
[{(bpy)$_2$Ru}$_2$dpt](PF$_6$)$_4$·2H$_2$O[a]	683	12.1
	577	4.96
	463	3.45
	411	7.54
	291	31.2

[a]In DMF. [b]In H_2O. sh = shoulder; br = broad.

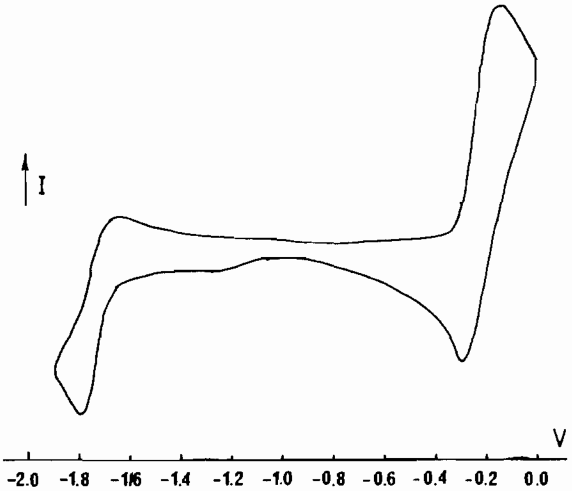


Fig. 1. Cyclic voltammogram of Cl$_2$Hg(bpm)HgCl$_2$ in DMF at a Pt electrode *vs.* SCE.

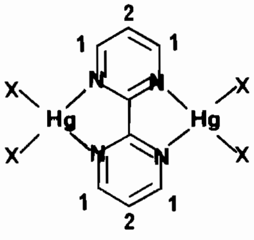
TABLE IV. NMR Results

Compound	NMR band shift (ppm)
Proton NMR	
2,2'-bipyrimidine	D: 9.10, 9.04 (2) T: 7.76, 7.7, 7.64 (1)
$Hg_2(bpm)Br_4$[a]	D: 9.23, 9.17 (2) T: 8.01, 7.95, 7.89 (1)
$Hg_2(bpm)I_4$	D: 9.23, 9.17 (2) T: 7.99, 7.93, 7.87 (1)
cis-$[Rh(bpm)_2Cl_2]Cl$[b]	DD: 9.94 (1), 9.45 (1), 9.18 (1) M: 8.24 (2) T: 7.71 (1)
$[Os(bpm)_3](ClO_4)_2$[c]	DD: 9.08, 9.02 (1) DD: 8.35, 8.29 (1) T: 7.72, 7.66, 7.60 (1)
C^{13} NMR	
2,2'-bipyrimidine[d]	161.25 (NS); 158.87 (SD), 123.30 (SD)
cis-$[Rh(bpm)_2Cl_2]$ Cl[d]	162.96 (SD); 162.34 (SD); 161.51 (NS); 160.41 (SD); 159.79 (SD); 127.35 (SD); 126.83 (SD)
$Hg_2(bpm)\cdot Br_4$	158.86 (NS); 156.91 (NS); 124.08 (SD)

[a] $Hg_2(bpm)Cl_4$ was reported by Lanza [24] [b] In D_2O. [c] In D_2O with DSS as reference. [d] In D_2O with deuterated dioxane as reference; all other samples were measured in d_6-DMSO. D = doublet; DD = doublet of doublet; M = multiplet; T = triplet; NS = line not split in off-resonance conditions; SD = off-resonance splitting into a doublet by one proton. Numbers in brackets refer to integrated area.

structures I and II (square planar coordination [22]. Structure I (tetrahedral) was suggested by Lanza [24] for $Cl_2Hg(bpm)HgCl_2$. Similarly, the low conductivity (11) of $Rh(bpm)Cl_3\cdot H_2O$ suggests that all the chlorines are coordinated to Rh. The results for *cis*-$Rh(bpm)_2Cl_3\cdot 2H_2O$, $Os(bpm)_3(ClO_4)_2$ and $Os(bpm)_2Cl_3\cdot 2H_2O$ indicate a 2:1 charge ratio (+2 to −1) consistent with metallic oxidation states of +3, +2 and +3, respectively. The dpt–ruthenium complex shows a 4:1 charge ratio consistent with the structure III suggested with a bridging dpt.

The result for $Rh_2(bpm)_3Cl_6\cdot 3H_2O$ is more difficult to reconcile. The molecule shows a conductivity (36) which is too high for a non-ionic compound and too low for a 1:1 electrolyte (or higher). Thus the structure IV (2:1 electrolyte) is not consistent with the result. Nor is the structure $[Rh(bpm)_2Cl]^+$, $[Rh(bpm)Cl_4]^-$ (V) (1:1 electrolyte) which was suggested for $[Rh_2(bpy)_3Cl_6]$ by Gidney *et al.* [7]. Furthermore, the structure VI leads to no conductivity at all.



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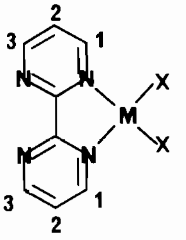
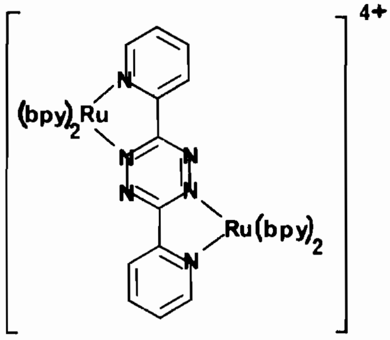
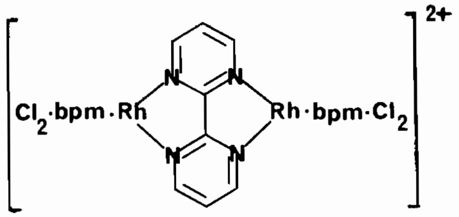


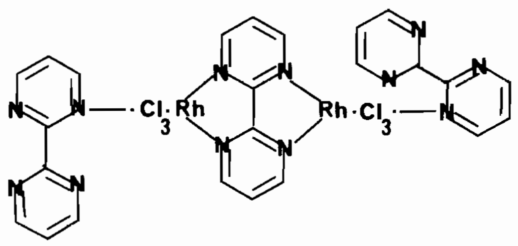
II (M = Pt, Pd)



III



IV



VI

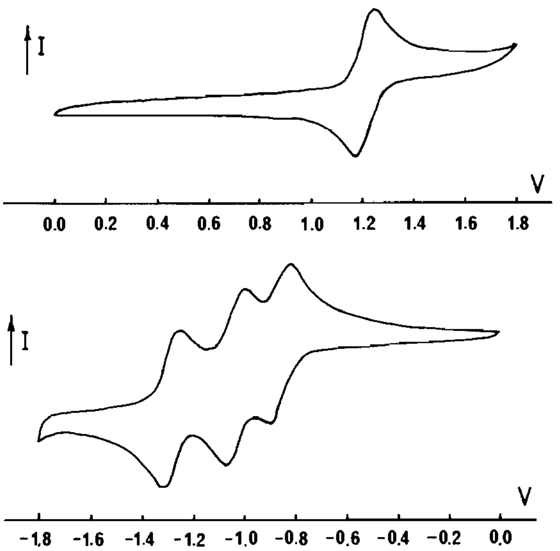


Fig. 2. Cyclic voltammograms of $[Os(bpm)_3](ClO_4)_2$ in acetonitrile at a Pt electrode *vs.* SCE.

Since the preparation of *cis*-$[Rh(bpm)_2Cl_2]Cl$ and $Rh_2(bpm)_3Cl_6$ are similar except that a higher concentration of $RhCl_3$ and bpm are needed for the latter, it is not impossible that an equilibrium between structures **IV**, **V**, **VI** or just between **V** and **VI** (**V** $\rightleftharpoons$ **IV**) exists. Unfortunately, little evidence can be obtained from other types of measurements employed here. The unreported NMR spectrum of this complex in deuterated DMF gives six broad structureless peaks in the range (8.0–10.2 ppm). While this is not inconsistent with the equilibrium suggested here, it does not provide conclusive evidence.

Electronic Spectra

The UV–Vis spectrum for bipyrimidine exhibits a sharp peak at 266 nm and a broader one at 288 nm. Theoretical and PES results [45] show that the HOMO in bipyrimidines is a non-bonding orbital. Thus an n,π^* assignment for the low energy band and a π,π^* assignment for the higher one are quite reasonable. From Table III the mercury bridged complexes still show a ligand n, π^* band which becomes a shoulder to the more intense ligand π,π^* transition. This effect has to do with the involvement of all the non-bonding electrons of the bridging ligand in σ-donation. All rhodium complexes exhibit a high energy ligand band (π,π^*) and a new shoulder (390 and 399 nm for the *cis* complex and dinuclear complex) and a broad peak (440 nm). By comparison to *cis*-$[Rh(bpy)_2Cl_2]Cl$ [46], which shows a similar peak, these are assigned as ligand field transitions (d–d). In the Pt and Pd complexes high energy (π,π^*) bands are observed, while MLCT bands (shoulder for Pd) appear at lower energy. The two broad bands (MLCT) for $Pt(bpm)Br_2$ correspond to those obtained for the chloro complex [22].

Theoretical considerations predict the existence of three closely lying MLCT states in $Ru(bpy)_3^{2+}$ [6]. This is supported by the three MLCT bands observed in the electronic spectrum (451, 345, 323 nm) [16]. In $Ru(bpm)_3^{2+}$ the corresponding bands are (454, 418, 362 nm) [19]. Since bpm is expected to have lower LUMO π^* orbitals, the lower transitions in its complex are not surprising [34]. Several MLCT bands are observed in $Os(bpy)_3^{2+}$ (640, 580, 478, 447, 436, 385, 368 nm) [3, 10]. Our results for $Os(bpm)_3^{2+}$ show at least four MLCT (345–586) transitions in DMF, although there could be more which are hidden by the broad features of the spectrum. The band at 269 nm is expected to be a ligand π,π^* transition. It might be added in passing that $[Os(bpm)_3](PF_6)_2$ did not exhibit any emission at room temperature. This is contrary to the well-known emission of the analogous bipyridine complexes of Ru and Os [1]. A broad MLCT feature and a π,π^* transition (269 nm) are also observed in our results for $[Os(bpm)_3Cl_2]Cl$.

Finally, four MLCT peaks and one π,π^* (291 nm) are observed for the bridged ruthenium–dpt complex. Since $d\pi \rightarrow \pi^*$ transitions to bipyridine orbitals are expected to appear at less than 450 nm [35] (see above for $Ru(bpy)_3^{2+}$), the low energy MLCT bands (683, 577 nm) in our complex (as well as in complexes prepared by Rillema *et al.* [35]) are expected to involve the π^* orbitals of the bridging ligand (dpt).

NMR Spectra

As mentioned earlier, solubility problems limited severely the use of NMR. In Table IV proton and ^{13}C results for the successful attempts are reported. The mercury complexes in d_6-DMSO exhibit a proton spectrum similar to bipyrimidine. This confirms the bridged structure with 4 equivalent protons on the carbons nearest to the complexed nitrogens, thus preserving the local symmetry of the bipyrimidine. The ^{13}C NMR for $Br_2Hg(bpm)HgBr_2$ confirms this by showing 3 lines (as does bipyrimidine). In both the ligand and the complex, the peaks that are not split by protons (at 161.25 and 156.91 ppm, respectively) belong to the connective carbons in the ligand. The carbon peaks nearest to the nitrogen (position 1) occur at 158.87 and 158.86 ppm, while the other carbons exhibit peaks at 123.30 and 124.08 ppm, respectively. In $Os(bpm)_3^{2+}$ two doublets of doublets and a triplet are obtained. Following the numbering scheme of structure **II**, the triplet is due to H_2 and the doublets arise in H_1 and H_3, which are split by H_2. A further smaller splitting takes into account a weak coupling between H_1 and H_3. Naturally, retention of D_3 symmetry in solution is obvious from the results.

TABLE V. Infra-red Spcctra of bpm and dpt and their Complexes[a]

	ν(O–H)	ν(C=N)	ν(C=C)	ring stretching	β(C–H)	ring breathing	γ(C–H)	ring bending	γ(H- O–H)	Unassigned
2,2'bipyrimidine		1558(s)	1547(s)	1403(s)	1140(m)	1029(m)	823(m), 765(w)	637(w)		3012(w) 3038(w) 3072(s) 1115(w), 1107(m) 788(w) 683(w)
$Hg_2(bpm)I_4$		1557(s)		1403(s)	1080(w)	1007(w)	825(m), 755(s)	652(m), 642(s)		3080(w), 3040(w) 1410(s) 1240(w) 995(w) 678(m)
$Hg_2(bpm)Br_4$		1558(s)		1412(s)	1098(m)	1010(m)	810(m), 754(s)	660(m)		3082(w), 3055(w) 687(w)
cis-$[Rh(bpm)_2Cl_2]Cl \cdot 2H_2O$	3400(m,b)	1573(s)	1547(m)	1405(s)		1025(w)	820(m), 745(s)	670(m)	1622(w)	3055(w) 1445(w), 1215(w), 690(m) 345(m)
$[Rh_2(bpm)_3Cl_6] \cdot 3H_2O$	3100(b)	1575(s)	1547(m)	1410(s)	1132(w)	1030(s)	820(s), 740(s)	670(m)	1625(w)	3090(m) 1450(m), 1340(m), 1248(m), 1212(m), 1104(w), 690(m) 340(m)
$[Rh(bpm)H_2OCl_3] \cdot 2H_2O$	3250(m,b)	1585(s)	1559(sh)	1410(s)	1135(w)	1045(w)	815(w), 725(m)		1610(sh) 1690(w,b)	3070(m), 1210(m), 794(w), 710(w), 330(m)
$[Os(bpm)_3](ClO_4)_2 \cdot 2H_2O$	3200(m,b)	1579(m)	1538(w)	1402(s)		1015(m)	820(m), 747(s)	660(w)	1620(w)	3090(w) 3045(w), 1135 - 1070(s,b) 788(w), 620(s) 520(w), 395(w)
$[Os(bpm)_2Cl_2]Cl \cdot 2H_2O$	3360(b)	1578(m)	1540(w)	1403(s)		1022(w)	818(w), 743(s)		1615(w)	3075(w)
$[Rh(bpm)_2Br_2]Br \cdot 2H_2O$	3250(m,b)	1578(s)	1555(m)	1400(s)	1137(m)	1027(m)	827(m), 752(s)	672(s)	1622(w)	3070(w), 3040(w) 3025(w), 1440(m) 1322(w) 1283(w), 1218(w) 1098(m) 834(m), 694(m) 511(w), 335(w)

(continued overleaf)

TABLE V. *(continued)*

	ν(O–H)	ν(C=N)	ν(C=C)	ring stretching	β(C–H)	ring breathing	γ(C–H)	ring bending	γ(H–O–H)	Unassigned
[Pd(bpm)Cl_2]·H_2O	3300(w,b)	1577(s)	1550(m)	1410(s)	1134(w)	1028(m)	822(m), 745(s)	678(s)	1625(w)	3070(m), 3048(w) 1460(w) 1210(m) 692(w) 357(m)
[Pt(bpm)Br_2]·H_2O	3280(w,b)	1582(s)	1555(m)	1407(s)	1138(w)	1022(m)	810(m), 735(s)	670(m)	1620(w)	3060(m), 3030(w) 1235(w) 1210(w), 1085(w) 1070(w) 830(w) 787(w)
(dpt)		1582(s)	1568(m)		1131(s)		749(s) 733(s)			3095(w), 3060(w) 1479(w), 1443(m) 1392(s), 1352(w) 1260(w), 1240(w) 1157(w), 1092(m) 1065(w), 1041(w) 955(s), 923(s), 801(s) 621(m), 600(s), 450(w) 409(m), 371(w)
Ni(dpt)$_2$$Cl_2$·$H_2O$	3150(w,b)	1590(w)	1578(w)		1138(s)		745(m), 750(m)			3080(w) 3045(w), 1440(w) 139(s), 1256(m) 1154(m), 1010(w) 989(w), 947(s) 796(s), 598(s), 440(w)

[a] Assignments based on ref. 50.

TABLE VI. Half Wave Potentials *vs.* SCE[a]

	$E_{1/2}$ (1)	$E_{1/2}$ (2)	$E_{1/2}$ (3)	$E_{1/2}$ (4)	$E_{1/2}$ (5)	$E_{1/2}$ (6)	Potential difference for anodic and cathodic peaks
$Cl_2Hg(bpm)HgCl_2$[b]	−1.71	−0.22					160 mV
$I_2Hg(bpm)HgI_2$[b]	−1.72	−0.25					160 mV
$Br_2Hg(bpm)HgBr_2$[b]	−1.71	−0.21					160 mV
$[Os(bpm)_3](ClO_4)_2$[c]	−1.29	−1.04	−0.86	+1.20			70 mV (−) region; 60 mV (+) region
$[Os(bpm)_2Cl_2]PF_6$[c]	−1.53	−1.30[d]	−1.23	−1.08[d]	0.27	1.64	80 mV
$[(bpy)_2Ru(dpt)Ru(bpy)_2](PF_6)_4$[b]	−1.78	−1.52	−0.92	0.00	1.58	2.10	160 mV (−); 110 mV (+)

[a] At room temperature. Solutions were all degassed with N_2 for half an hour. Scan at 0.1 V/s. All values are in volts. [b] 10^{-2} M in 0.1 M tetrabutylammonium hexafluorophosphate in DMF. [c] 10^{-2} M in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. [d] Large uncertainty due to overlap of peaks.

The results for *cis*-$[Rh(bpm)_2Cl_2]Cl$ are less straightforward. If C_2 symmetry is assumed (C_2 bisecting the Cl–Rh–Cl angle), the proton spectrum is expected to show six peaks each corresponding to two equivalent hydrogens. H_2 and H_5 should give triplets and the rest should be doublets. The recorded spectrum shows only five groups of peaks (area 1:1:1:2:1). A multiplet appears at 8.24 ppm (area 2) and a triplet at 7.71 ppm (H_2 and H_5). The three doublets exhibit the weaker doublet splitting shown in $Os(bpm)_3^{2+}$ (coupling H_1 and H_3 as well as H_4 and H_6). An accidental coincidence of a doublet and triplet seems to lead to the multiplet. A similar effect is observed in the ^{13}C spectrum; of the eight peaks expected in C_2 symmetry, only seven are observed (with accidental degeneracy for two peaks). The off-resonance spectrum exhibits well-defined doublet splitting of the peaks at 127.35 and 126.83 ppm. The other five peaks are split to seven peaks of the same central position.

IR Spectrum

The effect of complexation on the ligand IR bands has been discussed in several references. The ring breathing mode in (1030 cm^{-1}) pyridine was found to increase on complexation. The effect was explained by an increase in electron density on the ring (mostly CN) due to strong π-back donation from the metal [47] Since π-back donation places metal electrons in π* ring orbitals, this explanation seems doubtful. In bipyridine and phenanthroline complexes, the ring stretching bands (1560 1505 and 1558, respectively), which are dominated by CN stretching, increase most on protonation and to a lesser extent by complexation; hence polarization of the ring charge by the complexing cation was used to explain the effect [48]. A similar study on 4-picoline complexes establishes a correlation between the effects of polarization and π-donation, with each playing a role of varying importance [49]. Both protonation and metal σ-bonding reduce the negative charge on the nitrogen and polarize the ring π-charge density, thus increasing the CN bond strength and raising the frequency [50]. π-Back donation has the opposite effect, since the occupation of π* ring orbitals should weaken the ring bonds including CN. Except for the mercury complexes, all bipyrimidine complexes (Table V) show an increase (15–27 cm^{-1}) in the ring stretching frequency involving CN at (1558) [24, 49]. The anomalous behaviour for Hg(II) was observed with 4-picoline as well [49]. This effect is probably due to the weak σ-donation (polarising effect) of Hg(II). $[Rh(bpm)H_2OCl_3]$ has a higher frequency than the other rhodium complexes due to lowered π-back donation caused by an additional electron-withdrawing chlorine bonded to the metal. Both $Os(bpm)_3^{2+}$ and $[Os(bpm)_2Cl_2]Cl$ exhibit the same frequency. An easy explanation for this is not possible, but it is not unlikely that the expected strong σ-bond in the Os(III) complex is compensated for by π-donation. The π-donation is stronger in the Os(III) complex than in the Os(II) complex because the latter has a larger number of ligands over which π-donation is distributed.

Table V also shows that ν(C–C) and ring stretching are unaffected by complexation, except in bridging cases where they disappear altogether [24]. β(CH) and ring breathing bands show dramatic decreases for the bridged mercury complexes only. Of the two γ-CH frequencies, only the one at 765 cm^{-1} suffers a decrease (for comparison see refs. 22 and 27).

A band at 710 cm^{-1} in $[Rh(bpm)H_2OCl_3]$ and non-existent in other complexes points to coordinated water [51]. Comparison of M–X and M–N frequencies for pyridine and bipyridine complexes [50, 51] indicates that a medium band at 330 cm^{-1}

should be assigned as ν(Rh–Cl) for this same complex. In *cis*-[Rh(bpm)$_2$Cl$_2$]Cl the broad medium band (doublet) at 345 cm^{-1}, also assigned as ν(Rh–Cl) frequency, confirms the NMR result. The more symmetric *trans* complex would not lead to splitting of this band.

In Pd(bpm)Cl$_2$ a band at 357 cm^{-1} is assigned as Pd–Cl. M–N bands and M–Cl bands were difficult to distinguish from the KBr background. M–I and M–Br bands are expected but are outside the range of our instrument.

The IR spectrum for the bridged Ru–dpt complex yields broad bands (due to the large number of ligands) and is not reported here.

Cyclic Voltammetry

The results in Table VI for the voltammetric measurements show that the structure for the mercury complexes shows only two irreversible reduction steps consistent with a bimetallic bridged complex. The corresponding reductions would be Hg(II)–Hg(II) → Hg(II)–Hg(I) → Hg(I)–Hg(I). Variation of the halogen has little or no effect on the half-wave potentials.

In Os(bpm)$_3^{2+}$ one reversible oxidation step with $E_{1/2}$ equal to 1.20 V and three quasi-reversible reductions are observed. The results are consistent with Ru(bpy)$_3^{2+}$ (1.27, –1.31, –1.50, –1.77 V) and Ru(bpm)$_3^{2+}$ (1.69, –0.91, –1.08, –1.28 V) [19]. The metal naturally exhibits a large effect on the oxidation potentials (M(II) → M(III)), being much larger in the ruthenium complex. The half-wave reduction potentials, however, show much smaller variation and are expected to involve the ligand orbitals as the reduction site. The oxidation potential of Os(bpm)$_3^{2+}$ is higher than that of the corresponding bipyridine complex (0.82 V *vs.* H$_2$ electrode(1g)), which shows the same trend as in the ruthenium complexes.

In [Os(bpm)$_2$Cl$_2$]$^+$ there are two well-defined oxidation steps, while the reduction region involves overlapping peaks.

The dpt-bridged complex shows features similar to other bridged ruthenium compounds [35, 37]. Two well-defined oxidation peaks are observed and are expected to be Ru(II)–Ru(II) + Ru(III)–Ru(II) → Ru(III)–Ru(III). By comparison with results on complexes in which dpt is replaced by bpm or other bridging ligands [35, 37], it is expected that reductions with the more negative potentials are due to the bridging ligand.

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References

1 (a) W. J. Dressick, T. J. Meyer, B. Durham and D. P. Rillema, *Inorg. Chem., 21,* 3451 (1982); (b) S. F. Chan, M. Chou, C. Creutz, T. Matsubara and N. Sutin, *J. Am. Chem. Soc., 103,* 369 (1981); (c) T. J. Meyer, *Acc. Chem. Res., 11,* 94 (1978); (d) V. Balzani, F. Bolletta, M. T. Gandolfi and M. Maestri, *Top. Curr. Chem., 75,* 1 (1978). (e) D. G. Whitten, *Acc. Chem. Res., 13,* 83 (1980); (f) N. Sutin and C. Creutz, *Adv. Chem. Ser., No. 168,* 1 (1978); (g) J. Van Houten and R. J. Watts, *J. Am. Chem. Soc., 98,* 4853 (1975); (h) J. S. Conally (ed.), 'Photochemical Conversion and Storage of Solar Energy', Academic Press, New York, 1981; (i) M. Gratzel. *Acc. Chem. Res., 14,* 376 (1981); (j) K. Kalyanasundaram, *Coord. Chem. Rev., 46,* 159 (1982).

2 D. M. Klassen and G. A. Crosby, *Chem. Phys. Lett., 1,* 127 (1967); (b) F. Zuloga and M. Kasha, *Photochem. Photobiol., 7,* 549 (1986); (c) J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc., 26,* 72 (1968); (d) G. A. Crosby, K. W. Hipps and W. H. Elfring, Jr., *J. Am. Chem. Soc., 96,* 629 (1974); (e) T. J. Meyer, *Prog. Inorg. Chem., 30,* 389 (1983); (f) M. K. DeArmond and C. M. Carlin, *Coord. Chem. Rev., 36,* 325 (1981).

3 E. M. Kober, B. P. Sullivan and T. J. Meyer, *Inorg. Chem., 23,* 2098 (1984).

4 E. M. Kober and T. J. Meyer, *Inorg. Chem., 22,* 1614 (1983).

5 G. A. Crosby and W. H. Elfring, Jr., *J. Phys. Chem., 80,* 2206 (1976).

6 E. M. Kober and T. J. Meyer, *Inorg. Chem., 23,* 3877 (1984).

7 P. M. Gidney, R. D. Gillard and B. T. Heaton, *J. Chem. Soc., Dalton Trans.,* 2621 (1972).

8 R. D. Gillard, J. A. Osborn and G. Wilkinson, *J. Chem. Soc.,* 1951 (1965).

9 D. A. Buckingham, F. P. Dwyer, H. A. Goodwin and A. M. Sargeson, *Aust. J. Chem., 17,* 325 (1964).

10 G. M. Bryant, J. E. Fergusson and H. K. J. Powell, *Aust. J. Chem., 24,* 257 (1971).

11 J. V. Kingston, F. T. Mahmoud and G. R. Scollary, *J. Inorg. Nucl. Chem., 34,* 3197 (1972).

12 E. Bielli, P. M. Gidney, R. D. Gillard and B. T. Heaton, *J. Chem. Soc., Dalton Trans.,* 2133 (1974).

13 C. M. Harris and E. D. McKenzie, *J. Inorg. Nucl. Chem., 25,* 171 (1963).

14 W. A. Little and R. Lorentz, *Inorg. Chim. Acta, 18,* 273 (1976).

15 R. J. Crutchley, A. B. P. Lever and A. Poggi, *Inorg. Chem., 22,* 2647 (1983).

16 R. J. Crutchley and A. B. P. Lever, *Inorg. Chem., 21,* 2276 (1982).

17 R. J. Crutchley and A. B. P. Lever, *J. Am. Chem. Soc., 102,* 7129 (1980).

18 J. Gonzales-Velasco, I. Rubinstein, R. J Crutchley and A. B. P. Lever, *Inorg. Chem., 22,* 822 (1983).

19 D. P. Rillema, G. Allen, T. J. Meyer and D. Conrad, *Inorg. Chem., 22,* 1617 (1983).

20 E. V. Dose and L. J. Wilson, *Inorg. Chem., 17,* 2660 (1978).

21 M.Hunziker and A. Ludi, *J. Am. Chem. Soc., 99,* 7370 (1977).

22 P. M. Kiernan and A. Ludi, *J. Chem. Soc., Dalton Trans., 9,* 1127 (1978).

23 K. J. Moore and J. D. Petersen, *Polyhedron, 2,* 279 (1983).

24 S. Lanza, *Inorg. Chim. Acta, 75,* 131 (1983).

25 C. Overton and J. A. Connor, *Polyhedron, 1,* 53 (1982).
26 W. Kaim, *Inorg. Chem., 23,* 3365 (1984).
27 V. F. Sutcliffe and G. B. Young, *Polyhedron, 3,* 87 (1984).
28 D. C. Griffiths and G. B. Young, *Polyhedron, 2,* 1095 (1983).
29 A. Teuerstein, B. A. Feit and G. Navon, *Inorg. Nucl. Chem., 36,* 1055 (1974).
30 J. C. Bailar, Jr., D. J. Baker and R. A. Bauer, *U.S. NTIS Adv. Rep., AD-AO, 15508,* 1975.
31 J. Watanable, T. Saji and S. Aoyagui, *Bull. Chem. Soc. Jpn., 55,* 327 (1982).
32 P. A. Westcott, *Ph.D. Thesis,* Colorado State Univ., 1971.
33 R. R. Ruminski and J. D. Peterson, *Inorg. Chim. Acta, 88,* 63 (1984).
34 R. R. Ruminski and J. D. Petersen, *Inorg. Chem., 21,* 3706 (1982).
35 D. P. Rillema and K. B. Mack, *Inorg. Chem., 21,* 3849 (1982).
36 K. A. Goldsby and T. J. Meyer, *Inorg. Chem., 23,* 3002 (1984).
37 R. R. Ruminski and J. D. Peterson, *Inorg. Chim. Acta, 97,* 129 (1985).
38 K. Gustav and J. Schmidt, *Z. Chem., 9,* 32 (1969).
39 W. Kaim, S. Ernst, S. Kohlmann and P. Welkerling, *Chem. Phys. Lett., 118,* 431 (1985).
40 J. F. Geldard and F. Lions, *J. Org. Chem., 30,* 318 (1965).
41 M. S. Karash, R. C. Seyler and F. R. Mayo, *J. Am. Chem. Soc., 60,* 882 (1938).
42 M. J. Church and M. J. Mays, *J. Inorg. Nucl. Chem., 33,* 253 (1971).
43 B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem., 17,* 3334 (1978).
44 C. F. Liu, N. C. Liu and J. C. Bailar, Jr., *Inorg. Chem., 3,* 1085 (1964).
45 V. Barone, C. Cauletti, F. Lelj, M. N. Piancastelli and N. Russo, *J. Am. Chem. Soc., 104,* 4571 (1982).
46 M. Nishizawa, T. M. Suzuki, S. Sprouse, R. J. Watts and P. C. Ford, *Inorg. Chem., 23,* 1837 (1984).
47 P. T. T. Wong and D. G. Brewer, *Can. J. Chem., 46,* 131 (1968).
48 A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem., 9,* 211 (1959).
49 D. Cook, *Can. J. Chem., 42,* 1964 (1964).
50 A. R. Katritzky and P. J. Taylor, in A. R. Katritzky (ed.), 'Physical Methods in Heterocyclic Chemistry', Vol. IV, Academic Press, New York, 1971.
51 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 3rd edn., Wiley, New York, 1978, p. 227.
52 R. J. Angelici, 'Synthesis and Technique in Inorganic Chemistry', 2nd edn., Saunders, Philadelphia, 1977.