Complexes of 2-(2′-Pyridyl)quinoline and 3,6-Di(4′-pyridyl)-S-tetrazine

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(Received March 16, 1989)

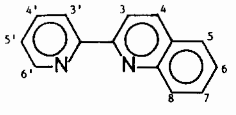
Abstract

The reactions of 2-(2′-pyridyl)quinoline (pq) with $RhCl_3 \cdot 3H_2O$, K_3RhBr_6 (prepared *in situ*), $[Rh(CO)_2Cl]_2$ and $M(PhCN)_2X_2$ (M = Pd, Pt; X = Cl, Br, I) and 3,6-di(4′-pyridyl)-1,2,4,5-S-tetrazine (s-dpt) with $[Ru(bpy)_2ClNO](PF_6)_2$ have been investigated. The new complexes *cis*-$[Rh(pq)_2Cl_2](PF_6)$, *cis*-$[Rh(pq)_2Br_2]Br$, *cis*-$[Rh(pq)_2Cl_2][Rh(CO)_2Cl_2] \cdot H_2O$, *cis*-$Pd(pq)X_2$ (X = Cl, Br), *cis*-$Pt(pq)X_2$ (X = Cl, Br, I) and $[\{(bpy)_2ClRu\}_2\text{s-dpt}](PF_6)_2 \cdot 3H_2O$ have been characterized by elemental analyses, conductivity and cyclic voltammetric measurements, infrared, electronic absorption and ^1H NMR data.

Introduction

Recently, there has been some interest in the spectral properties of complexes of Rh(III) and in their potential as electron transfer agents in the storage of radiant energy (for example, see ref. 1). Moreover, cationic complexes of Rh(III) of the type $[Rh(N\text{-}N)_2X_2]X \cdot nH_2O$ (N-N = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) or 2,2′-biquinoline (biq); X = Cl, Br or I) have been synthesized [2] and those with *cis* configuration have received considerable attention because of the possibility of their use as hydrogenation catalysts and as antibacterial and antitumor agents [2c, 3]. Furthermore, Rh(I) and Rh(III) carbonyl complexes with these and other related N-heterocyclic ligands have been prepared [4] and have been reported to exhibit a great deal of biological activity [4b, c]. A survey of chemical literature showed that no analogous complexes of Rh(III) or Rh(I) with 2-(2′-pyridyl)quinoline (pq, **I**) have been reported.

The compound pq seems to be a suitable chelating agent for Pd(II) and Pt(II) ions which show preference for N-donors and for square planar geometry. Although the complexes $[M(N\text{-}N)X_2]$ (M = Pd, Pt; N-N = phen or bpy; X = Cl, Br or I) [5], $Pd(biq)Cl_2$ [6] and $Pt(biq)Cl_2$ [7] are known, to our knowledge no Pd(II) or Pt(II) complexes with pq have been isolated. Complexes of these ions having *cis* configuration are of importance due to their potential anticancer or antitumor activity [for example, see ref. 8].



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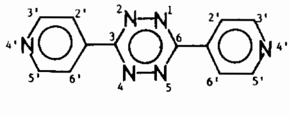

II

Although a few complexes of 3,6-di(2′-pyridyl)-1,2,4,5-S-tetrazine are known [1c], no complexes with the other symmetrical tetrazine namely 3,6-di(4′-pyridyl)-1,2,4,5-S-tetrazine (s-dpt, **II**) have been reported. The latter tetrazine seems promising as a bridging ligand through the two nitrogens of the pyridyl groups. Complexes of Ru(II) with bridging diimine ligands have been extensively studied in recent years because of the information they give about the processes of electron transfer in bimolecular redox reactions [for example, see refs. 1c, 7, 9a, 10].

All these considerations prompted us to further investigate the reactions of pq with Rh(III), Rh(I), Pd(II) and Pt(II) and of s-dpt with Ru(II). In an earlier paper we reported some complexes of biq and pq with Ru(III), Ru(II), Rh(III), Ir(III) and Pt(II) [7]. We now report the isolation and characterization of new complexes of pq and s-dpt.

Experimental

Materials

All solvents used were AR grade. The pq ligand was obtained from Laborat and was recrystallized from methanol. The s-dpt ligand was prepared by the method of Libman and Slack [11] and was recrystallized from nitromethane. Metal salts were purchased from Fluka, Laborat or Aldrich and were used without further purification. *μ*-Dichlorotetracarbonyldirhodium(I) [12], *cis*-dichlorobis(benzonitrile)palladium(II) [13], *trans*-dibromobis(benzonitrile)palladium(II), *cis*-dichloro- and -dibromobis(benzonitrile)platinum(II) [14], *trans*-diiodobis(benzonitrile)platinum(II) [15] and *cis*-chlorobis(2,2′-bipyridine)nitrosylruthenium(II) hexafluoro-

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phosphate [16] were prepared as described in the literature.

Physical Measurements

Infrared absorption spectra (KBr and CsI pellets) were recorded on a Pye-Unicam SP3-300 spectrophotometer. Ultraviolet–Vis spectra were measured using a Pye-Unicam SP8-100 spectrometer. Proton NMR spectra were determined with a Bruker WP 80SY instrument in DMSO-d_6 using TMS as internal standard. Conductivity measurements were carried out on a Harris conductivity bridge. Cyclic voltammograms were performed using a Hi-Tek potentiostat and waveform generator. Measurements were made under argon for 10^{-3} M solutions with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte and on a Pt working electrode and a saturated calomel reference electrode (SCE). The half-wave potentials ($E_{1/2}$) were calculated from the average of the anodic and cathodic peak potentials. The peak separation (ΔE_p) was calculated from the difference in potential between the anodic and cathodic peak currents. Elemental analyses for all complexes were performed by M-H-W Laboratories, Phoenix, AZ, U.S.A.. Melting points were not corrected.

Preparation of the Complexes

cis-Dichlorobis(2-(2′-pyridyl)quinoline)rhodium(III) hexafluorophosphate, cis-$[Rh(pq)_2Cl_2]PF_6$

To a stirred solution of $RhCl_3 \cdot 3H_2O$ (0.132 g, 0.50 mmol) in hot water (7 ml) was added a solution of pq (0.210 g, 1.02 mmol) in hot ethanol (12 ml). After 20 min of heating (60 °C), the color of the solution changed from red to orange–red. After 40 min, hydrazinium dihydrochloride (0.062 g) was added [2a, b]. The reaction mixture was refluxed for 30 min until a clear yellow solution was obtained. The mixture was allowed to cool and then treated with an excess aqueous solution of NH_4PF_6. The bright yellow precipitate which appeared was filtered, washed with water, ethanol and diethyl ether, and dried under vacuum at 40 °C.

cis-Dibromobis(2-(2′-pyridyl)quinoline)rhodium(III) bromide, cis-$[Rh(pq)_2Br_2]Br$

A mixture of $RhCl_3 \cdot 3H_2O$ (0.132 g, 0.50 mmol) and KBr (0.50 g) in water (10 ml) was boiled for a few minutes until a red–brown solution of $RhBr_6^{3-}$ was obtained [2a, b]. A solution of pq (0.210 g, 1.02 mmol) in hot ethanol (10 ml) was then added. An orange color was formed immediately. Hydrazinium dihydrochloride (0.01 g) was added. The reaction mixture was refluxed for a few minutes and filtered. The filtrate was kept overnight in a refrigerator. The orange crystals obtained were filtered, washed with ethanol, acetone and diethyl ether, and then vacuum dried at 40 °C.

cis-Dichlorobis(2-(2′-pyridyl)quinoline)rhodium(III)cis-dichlorodicarbonylrhodate(I) monohydrate, cis-$[Rh(pq)_2Cl_2][Rh(CO)_2Cl_2] \cdot H_2O$

A solution of pq (0.210 g, 1.02 mmol) in chloroform (15 ml) was added slowly to a solution of $[Rh(CO)_2Cl]_2$ (0.193 g, 0.50 mmol) in chloroform (20 ml). The color of the solution changed immediately from yellow to red followed by the formation of a small amount of a violet–red precipitate. The reaction mixture was refluxed for 5 h, allowed to cool and filtered. Excess diethyl ether was added to the filtrate. The resulting yellow product was filtered, washed several times with diethyl ether and dried under vacuum at 40 °C.

cis-Dichloro(2-(2′-pyridyl)quinoline)palladium(II), cis-$Pd(pq)Cl_2$

To a stirred solution of *cis*-$Pd(PhCN)_2Cl_2$ (0.384 g, 1.0 mmol) in acetone (40 ml) was added a solution of pq (0.210 g, 1.02 mmol) in acetone (20 ml). A small amount of a yellow precipitate appeared immediately. The mixture was refluxed for 45 min, allowed to cool and filtered. The yellow product was washed well with acetone and diethyl ether, and vacuum dried at 40 °C.

cis-Dibromo(2-(2′-pyridyl)quinoline)palladium(II), cis-$Pd(pq)Br_2$

A solution of pq (0.104 g, 0.50 mmol) in chloroform (8 ml) was added slowly to a stirred suspension of *trans*-$Pd(PhCN)_2Br_2$ (0.236 g, 0.50 mmol) in chloroform (30 ml). After 5 min, the color of the solution changed from dark brown to light brown. The mixture was refluxed for 15 h, allowed to cool and filtered. The resulting orange product was washed well with chloroform and diethyl ether, and then dried under vacuum at 40 °C.

cis-Dichloro(2-(2′-pyridyl)quinoline)platinum(II), cis-$Pt(pq)Cl_2$

A solution of pq (0.106 g, 0.51 mmol) in chloroform (6 ml) was added dropwise to a stirred solution of *cis*-$Pt(PhCN)_2Cl_2$ (0.236 g, 0.50 mmol) in chloroform (12 ml). No immediate change was observed. The mixture was refluxed for 12 h and then allowed to cool. Most of the solvent was removed under reduced pressure and an excess of diethyl ether was then added. The orange–yellow product which appeared was filtered, washed well with diethyl ether, and dried under vacuum at 40 °C.

cis-Dibromo(2-(2′-pyridyl)quinoline)platinum(II), cis-$Pt(pq)Br_2$

To a stirred suspension of *cis*-$Pt(PhCN)_2Br_2$ (0.561 g, 1.0 mmol) in hot acetone (30 ml) was added a solution of pq (0.210 g, 1.02 mmol) in acetone (15 ml). After a few minutes, the color changed from brown to yellow. The mixture was refluxed for 11 h and allowed to cool. The solution was concentrated under reduced pressure. The orange solid formed was washed well with diethyl ether, and dried under vacuum at 40 °C.

cis-Diiodo(2-(2'-pyridyl)quinoline)platinum(II), cis-Pt(pq)I$_2$

To a stirred solution of *trans*-$Pt(PhCN)_2I_2$ (0.327 g, 0.50 mmol) in chloroform (20 ml) was added a solution of pq (0.110 g, 0.53 mmol) in chloroform (10 ml). No immediate change was observed. The mixture was stirred at room temperature for 2 days and then filtered. The wine-red precipitate obtained was washed well with chloroform and diethyl ether, and vacuum dried at 40 °C.

Dichlorotetrakis(2,2'-bipyridine)-µ-{3,6-di(4'-pyridyl)-1,2,4,5-S-tetrazine}diruthenium(II) hexafluorophosphate trihydrate, [{(bpy)$_2$ClRu}$_2$s-dpt](PF$_6$)$_2$·3H$_2$O

The complex was prepared under nitrogen atmosphere and in the absence of light. A solution of NaN_3 (0.017 g, 0.26 mmol) in methanol (5 ml) was added dropwise to a solution of $[Ru(bpy)_2(NO)Cl](PF_6)_2$ (0.20 g, 0.26 mmol) in acetone (30 ml). The resulting solution was stirred for 15 min at room temperature then warmed up to 40 °C. To this solution, a solution of s-dpt (0.0307 g, 0.13 mmol) in boiling acetone (30 ml) was then added dropwise. The mixture was stirred for 1 h at 50–60 °C then refluxed for 1 h and cooled. The mixture was filtered and the brown filtrate was treated with excess diethyl ether. The brown product was filtered, washed with ether and dried under vacuum at 40 °C.

Results

Elemental analyses and conductivity measurements for the complexes are shown in Table 1. The IR spectral data (KBr and CsI pellets) are presented in Table 2. Figure 1 shows the IR spectrum of *cis*-$[Rh(pq)_2Cl_2][Rh(CO)_2Cl_2]\cdot H_2O$ in the carbonyl and the low frequency regions. The difficulties encountered in the preparation of some complexes and/or their insufficient solubility in common organic solvents have hindered their study. Therefore, not all same measurements were carried out for all complexes. The electronic and ^1H NMR spectra of some pq complexes were measured in DMSO and DMSO-d_6 and the results are given in Tables

TABLE 1. Elemental analyses and conductivity measurements of metal complexes

Complex	Analysis: calculated (found) (%)				Decomposition temperature (°C)	Yield (%)	Λ_M[b] (ohm^{-1} cm^2 mol^{-1})
	C	H	N	X[a]			
cis-$[Rh(pq)_2Cl_2]PF_6$	45.99 (45.69)	2.76 (2.98)	7.66 (7.72)	9.70 (10.14)	303	42	84.0[c]
cis-$[Rh(pq)_2Br_2]Br$	44.53 (44.51)	2.67 (2.65)	7.42 (7.39)	31.75 (31.92)	274	80	88.0[d]
cis-$[Rh(pq)_2Cl_2][Rh(CO)_2Cl_2]\cdot H_2O$	43.19 (43.63)	2.66 (2.95)	6.72 (6.90)	17.00 (17.53)	135	40	52.0[e]
cis-$[Pd(pq)Cl_2]$	43.84 (43.78)	2.63 (2.76)	7.31 (7.28)	18.49 (18.03)	330	75	1.0[e]
cis-$[Pd(pq)Br_2]$	35.59 (35.37)	2.13 (2.64)	5.93 (5.82)	33.82 (33.68)	308	85	2.0[e]
cis-$[Pt(pq)Cl_2]$	35.60 (35.82)	2.13 (2.21)	5.93 (6.11)	15.02 (14.91)	213	40	2.0[e]
cis-$[Pt(pq)Br_2]$	29.96 (30.20)	1.80 (1.23)	4.99 (5.02)	28.48 (28.38)	202	60	2.0[e]
cis-$[Pt(pq)I_2]$	25.67 (25.60)	1.54 (1.77)	4.28 (4.19)	38.74 (39.42)	249	50	1.0[f]
$[\{(bpy)_2ClRu\}_2s\text{-}dpt](PF_6)_2\cdot 3H_2O$[g]	42.26 (42.25)	3.14 (3.17)	13.27 (13.25)	4.80 (4.41)	281	70	163[c]

[a] X = Cl, Br, I. [b] Molar conductance for 10^{-3} M solutions at 25 °C in [c] nitromethane, [d] methanol, [e] DMF and [f] nitrobenzene. [g] P: calculated 4.19, found 3.98%.

TABLE 2. Some important infrared bands of pq and its complexes (KBr pellets; cm^{-1})

Compound	νC=C and νC=N	γC–H	νM–X[a]
2-(2′-pyridyl)quinoline(pq)	1590(s), 1543(m), 1495(w)	842(vs), 796(s) 775(vs), 740(s)	
cis-$[\mathrm{Rh(pq)_2Cl_2}]\mathrm{PF_6}$[b]	1595(m, b), 1515(w), 1480(s)	790(s), 768(s) 738(s)	360(m), 347(m) (split)
cis-$[\mathrm{Rh(pq)_2Br_2}]\mathrm{Br}$	1590(m), 1510(w), 1475(s)	820(s), 790(s) 760(s)	c
cis-$[\mathrm{Rh(pq)_2Cl_2}][\mathrm{Rh(CO)_2Cl_2}]\cdot\mathrm{H_2O}$[d]	1595(s, b), 1510(w), 1480(s)	825(m), 790(s) 770(vs), 735(m)	365(m), 350(m), (split), 308(w), 280(vw)
cis-$\mathrm{Pd(pq)Cl_2}$	1580(m, b), 1510(m), 1475(m)	823(s), 785(s) 770(sh), 730(m)	375(s), 366(s, sh)
cis-$\mathrm{Pd(pq)Br_2}$	1590(m), 1510(w), 1480(s)	830(s), 785(s) 768(vs), 743(s)	282(m), 270(m, sh)
cis-$\mathrm{Pt(pq)Cl_2}$	1584(m, b), 1510(m), 1480(m)	823(w), 785(s), 770(vs), 730(w)	337(s), 305(m)
cis-$\mathrm{Pt(pq)Br_2}$	1590(m), 1510(vw), 1480(m)	820(w), 785(w) 770(m), 750(vs)	257(s), 240(m)
cis-$\mathrm{Pt(pq)I_2}$	1592(m, b), 1510(w), 1470(m)	830(s), 785(s), 762(vs)	e

[a] $\mathrm{C_sI}$ pellets; X = Cl, Br, I. [b] νP–F: 835(vs, b), 555(s). [c] νRh–Br not clearly seen due to the presence of other weak bands. [d] νC≡O: 2060(vs), 1983(vs); ν(O–H): 3470(m, b). [e] Not observed. vs = very strong; s = strong; m = medium; w = weak; b = broad; sh = shoulder.

3 and 4, respectively. The cyclic voltammograms of $[\{\mathrm{(bpy)_2ClRu}\}_2\mathrm{s\text{-}dpt}](\mathrm{PF_6})_2\cdot3\mathrm{H_2O}$ are shown in Fig. 2. The structures III–VI for these complexes are proposed on the basis of all these data.

TABLE 3. Electronic absorption spectra of pq complexes[a]

Compound	λ_{max} (nm)	$\epsilon \times 10^{-3}$ (1 mol^{-1} cm^{-1})
cis-$[\mathrm{Rh(pq)_2Cl_2}](\mathrm{PF_6})$	269 349(br) 440(sh) 460(sh)	44.8 29.1 0.23 0.13
cis-$[\mathrm{Rh(pq)_2Br_2}]\mathrm{Br}$	265 351(br) 440(sh) 465(sh)	45.8 26.6 0.37 0.27
cis-$\mathrm{Pd(pq)Cl_2}$	355(br)	19.2
cis-$\mathrm{Pd(pq)Br_2}$	352 336(sh)	13.8 6.6
cis-$\mathrm{Pt(pq)Cl_2}$	426(br) 359 344(sh) 305	3.58 11.6 10.02 3.05
cis-$\mathrm{Pt(pq)Br_2}$	436(br) 358 346(sh) 308	5.46 19.8 18.6 12.1

[a] In DMSO. br = broad; sh = shoulder.

TABLE 4. ^{1}H NMR data for pq complexes[a]

Compound	NMR band shift: δ (ppm) (*J* (Hz))
cis-$[\mathrm{Rh(pq)_2Cl_2}]\mathrm{PF_6}$	9.86(d, 1H; *J* = 6.5); 9.72(d, 1H; *J* = 5.4); 9.22–8.49(m, 6H); 8.49–7.86(m, 6H); 7.22–7.82(2t, 4H); 6.97(d, 2H).
cis-$[\mathrm{Rh(pq)_2Br_2}]\mathrm{Br}$	10.18(d, 1H; *J* = 5.5); 10.06(d, 1H; *J* = 5.7); 9.21–7.88(m, 12H); 7.88–6.79(m, 6H).
cis-$\mathrm{Pt(pq)Cl_2}$	8.72(d, 1H; *J* = 8.9); 8.51(d, 1H; *J* = 7.8); 8.45(d, 1H; *J* = 6.4); 7.99–7.5(m, 7H).
cis-$\mathrm{Pt(pq)I_2}$	9.43(d, 1H; *J* = 5.6); 8.74(d, 1H; *J* = 7.8); 8.53(d, 1H; *J* = 4.5); 8.38-(d, 1H; *J* = 5.6); 8.26–7.75(m, 4H); 7.75–7.34(m, 2H).

[a] In DMSO-d$_6$ with TMS as internal standard, at 80 MHz. d = doublet, m = multiplet, 2t = two triplets.

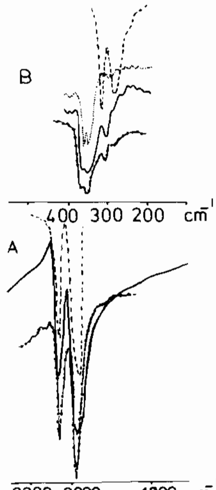


Fig. 1. The IR spectrum of *cis*-$[Rh(pq)_2Cl_2][Rh(CO)_2Cl_2] \cdot H_2O$: (A) in the carbonyl region (KBr pellet) —— (– · – for the product of the reaction of *cis*-$[Rh(pq)_2Cl_2](PF_6)$ and $[Bu_4N][Rh(CO)_2Cl_2]$; ---- for $[Bu_4N][Rh(CO)_2Cl_2]$ and (B) in the low frequency region (CsI pellet) —— (······ for *cis*-$[Rh(pq)_2Cl_2](PF_6)$; others, same sign as in (A)).

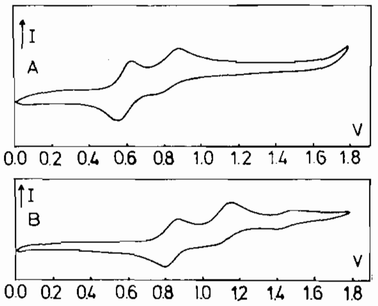
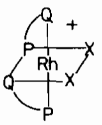


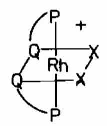
Fig. 2. Cyclic voltammograms of $[\{(bpy)_2ClRu\}_2s\text{-}dpt](PF_6)_2 \cdot 3H_2O$: (A) oxidation and (B) reduction in acetonitrile at a Pt electrode vs. SCE.

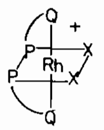
Discussion

Conductivity

The molar conductance values for 10^{-3} M solutions for the complexes (Table 1) were compared and are in good agreement with those reported for similar complexes [17]. The Rh(III) compounds *cis*-$[Rh(pq)_2Cl_2]PF_6$ and *cis*-$[Rh(pq)_2Br_2]Br$ behave as 1:1 electrolytes in nitromethane and methanol, respectively. These results are consistent with the octahedral structure **III** proposed for these cationic species. However, it is important to mention that for these complexes *cis*-$[Rh(pq)_2X_2]^+$ (X = Cl, Br), with the unsymmetrical pq ligand, three geometrical isomers are possible **IIIa**–**IIIc**, each of which can give a pair of enantiomers (see NMR section for further details).





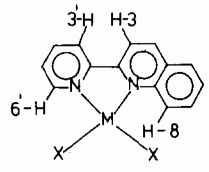


(P⌒Q = pq ; X=Cl, Br)

IIIa **IIIb** **IIIc**

Moreover, the rhodium carbonyl halide complex *cis*-$[Rh(pq)_2Cl_2][Rh(CO)_2Cl_2] \cdot H_2O$ gives a molar conductance of 52.0 ohm^{-1} cm^2 mol^{-1} in DMF. This value is in good agreement with data reported for 1:1 electrolytes containing large cations and anions [17a] and also of analogous complexes containing the anion $[Rh(CO)_2Cl_2]^-$ [4b, c]. Attempts to isolate any of these species from DMF solution (in which the complex is soluble) are so far unsuccessful because of the high solubility of all reactants and products in this solvent. However, to our luck, the constituent ions of this complex are known species, so it was possible to verify its structure by reacting *cis*-$[Rh(pq)_2Cl_2](PF_6)$ (prepared by us) with $[Bu_4N][Rh(CO)_2Cl_2]$ [18] in acetone (see IR section for details).

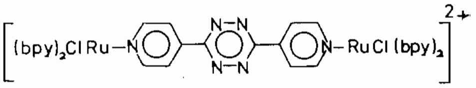
The Pd(II) and Pt(II) complexes all behave as non-electrolytes in DMF or nitrobenzene, thus supporting the square planar structure **IV**.



(M = Pd, Pt ; X = Cl, Br, I)

IV

The bridged binuclear Ru(II)–Ru(II) complex $[\{(bpy)_2ClRu\}_2s\text{-}dpt](PF_6)_2 \cdot 3H_2O$ shows a molar conductance of 163 ohm^{-1} cm^2 mol^{-1} in nitromethane which is in good agreement with that reported for 1:2 electrolytes in nitromethane [17]; this is consistent with structure **V**.



V

Infrared Spectra

IR spectra of pq complexes

The IR bands (Table 2) are assigned on the basis of earlier studies made on similar diimine ligands and their complexes [2c, 4, 6a, 7, 19–21]. However, a detailed comparison cannot be made with reference to uncoordinated pq. In the free ligand the nitrogen donor atoms are *trans* [22] but upon complexation they adopt a *cis* conformation as has been shown by X-ray structural studies as well as other physical measurements [for example, see ref. 23]. The latter conformation (pq, I) is expected to be the least stable due to steric repulsion of the H3,3′ protons. In our spectra, the main regions that were undergoing appreciable changes upon coordination are 1595–1470 cm^{-1} (νC=C and νC=N vibrations) and 842–730 cm^{-1} (C–H out of plane deformations). The spectra were also examined in the low frequency region (CsI pellets) where νM–X appears (Table 2). It was difficult, however, to assign νM–N empirically since several ligand vibrations also appear in the same frequency region [24a]. The main points are given below.

(i) The bands appearing at 835 and 555 cm^{-1} in the IR spectrum of *cis*-[Rh(pq)$_2$Cl$_2$]PF$_6$, which are assigned to νP–F vibrations, indicate the presence of ionic PF$_6^-$ groups [24b]. The IR spectrum of *cis*-[Rh(pq)$_2$Cl$_2$]PF$_6$ shows the presence of two νRh–Cl bands at 360 and 347 cm^{-1} (split, see Fig. 1). Comparison of this result with those reported for analogous octahedral systems [2c, 7, 24c] suggests a *cis* configuration for our complex. The νRh–Br bands for *cis*-[Rh(pq)$_2$Br$_2$]Br could not be easily seen among other weak bands in the region 200–300 cm^{-1}. However, the method of synthesis of both complexes using hydrazinium chloride as a catalyst [2b] further supports their *cis* configuration along with other physical measurements (see NMR section).

(ii) The IR spectrum of *cis*-[Rh(pq)$_2$Cl$_2$][Rh(CO)$_2$Cl$_2$]·H$_2$O (Table 2) is almost the sum of the spectra of *cis*-[Rh(pq)$_2$Cl$_2$](PF$_6$), except for PF$_6^-$ absorptions, and the anion [Rh(CO)$_2$Cl$_2$]$^-$. It exhibits two very strong absorption bands in the terminal carbonyl region at 2060 and 1983 cm^{-1} which are characteristic of the *cis*-[Rh(CO)$_2$Cl$_2$]$^-$ ion [4b, 25] as shown in Fig. 1. The IR spectrum in the low frequency region suggests the presence of *cis* terminal chlorine atoms bound to rhodium. The split band at 365 and 350 cm^{-1} (Fig. 1) is assigned to νRh–Cl in the cation *cis*-[Rh(pq)$_2$Cl$_2$]$^+$ as compared to that of *cis*-[Rh(pq)$_2$Cl$_2$](PF$_6$). The other two bands at 308 and 280 cm^{-1}, which are assigned to νRh–Cl in *cis*-Rh(CO)$_2$Cl$_2^-$ [4b, 25c], also support a *cis*-chlorine arrangement in this anion. As mentioned earlier, the structure of this complex was further confirmed by reacting a 1:1 molar mixture of our complex *cis*-[Rh(pq)$_2$Cl$_2$](PF$_6$) with [Bu$_4$N][Rh(CO)$_2$Cl$_2$] [18] in acetone, followed by precipitation with n-hexane. The IR of the resulting product is almost identical with that of *cis*[Rh(pq)$_2$Cl$_2$][Rh(CO)$_2$Cl$_2$], as shown in Fig. 1 for the carbonyl and the low frequency regions. The mechanism for the formation of this complex will be the subject of a coming paper.

(iii) The presence of two νPd–Cl bands at 366 and 375 cm^{-1} for Pd(pq)Cl$_2$; two νPd–Br bands at 270 and 282 cm^{-1} for Pd(pq)Br$_2$; two νPt–Cl bands at 337 and 305 cm^{-1} for Pt(pq)Cl$_2$ and two νPt–Br bands at 257 and 240 cm^{-1} for Pt(pq)Br$_2$ suggests a *cis* configuration [7, 24d] for the four-coordinate square planar complexes (**IV**).

IR spectrum of s-dpt complex

The IR spectrum of [{(bpy)$_2$ClRu}$_2$s-dpt](PF$_6$)$_2$·3H$_2$O (KBr disc) shows the following main bands characteristic of the species present: 3440 mb (νO–H); 3110, 3090w (νC–H aromatic); 1610m, 1470m, 1440s (νC=C and νC=N of pyridine rings); 1425m, 1395s (ring stretching band characteristic of the tetrazine ring [21b]); 840vsb (νP–F); 765s, 730s, 605s (γC–H) and 560s (νP–F) cm^{-1}. The band at 970–880 cm^{-1} which is characteristic of S-tetrazine (ring bend in plane) [21b] is masked by the strong absorption of the PF$_6^-$ ionic group. In general, the spectrum of this complex has a small number of bands, as compared to the free uncoordinated ligands. This result may suggest that the complex itself is highly symmetric with s-dpt acting as a bridging ligand, thus supporting structure V.

Cyclic Voltammetry

The cyclic voltammogram of the s-dpt-bridged complex [{(bpy)$_2$ClRu}$_2$s-dpt](PF$_6$)$_2$·3H$_2$O shows a two-wave oxidation pattern (Fig. 2A) typical of bimetallic systems with bridging diimine ligands [1c, 7, 10], at half-wave potentials ($E_{1/2}$) of 0.84 and 0.59 V and peak separations (ΔE_p) of 90 and 70 mV, respectively. This result confirms structure V of this complex. The oxidation potentials are expected to be due to the processes Ru(II)–Ru(II) → Ru(III)–Ru(II) → Ru(III)–Ru(III). The reduction voltammogram (Fig. 2B) shows three waves at $E_{1/2}$ values of −0.84, −1.12 and −1.46 V with ΔE_p of 70, 80 and 60 mV, respectively. Although more reduction waves are expected, they may occur at more negative values. However, some similar bimetallic complexes have also shown only three reduction waves [1c, 7, 10e].

Electronic Spectra

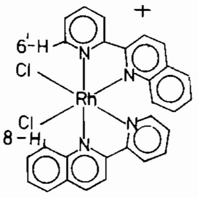
The electronic absorption spectrum of free 2-(2′-pyridyl)quinoline has been reported [26]. However, the spectra of its complexes cannot be compared with it since the ligand in both cases has different conformations (see IR section). Recently, it has been shown that, upon addition of H$^+$, pq is converted into the *cis* conformation and its UV–Vis spectrum is found to exhibit two main π–π^* transitions at 32×10^3 and 37×10^3 cm^{-1} [22]. The dominant features of the electronic absorption spectra of the pq complexes prepared in this study (Table 3) are the strong bands which occur at frequencies corresponding to π–π^* transitions of the ligand along with some ligand field and MLCT bands.

For the Rh(III) *cis*-$[Rh(pq)_2X_2]^+$ (X = Cl, Br) ions, two $\pi-\pi^*$ transitions are observed (at 349, 269 nm and 351, 265 nm for the dichloro and dibromo complexes, respectively). However, for Rh(III) octahedral complexes with the d^6 low spin state, d–d transitions of high energy (due to high Δ) are expected towards the blue end of the visible [9b, 27]. This is found to be true for *cis*-$[Rh(N\text{-}N)_2Cl_2]^+$ ions with N-N = 2,2′-bipyridine and 3,3′-dimethyl-2,2′-bipyridine [1b], 2,2′-bipyrimidine [1c] and 2,2′-biquinoline [2c]. The latter complex exhibits, in addition, MLCT transitions at 365 nm. Both types of bands (d–d and MLCT) in this region are responsible for the characteristic orange, red, yellow or brown colors of Rh(III) compounds [9b]. The *cis*-$[Rh(pq)_2Cl_2]PF_6$ complex is yellow while *cis*-$[Rh(pq)_2Br_2]Br$ is orange and both, therefore, are expected to show similar absorptions in these regions. Thus the weak shoulders at 440, 460 nm for the chloro and 440, 465 nm for the bromo compounds are assigned to ligand field (d–d) transitions. The broadness of the lower energy bands (349 nm for the chloro and 351 nm for the bromo complexes) may indicate the presence of MLCT bands underlying the $\pi-\pi^*$ ligand transitions. In *cis*-$Pd(pq)Cl_2$, the strong broad band at 355 nm which is assigned to $\pi-\pi^*$ transitions may possibly be mixed with a MLCT transition. The bands appearing at 352 and 336(sh) nm for *cis*-$Pd(pq)Br_2$ are assigned to $\pi-\pi^*$ ligand and MLCT transitions, respectively. In the Pt(II) complexes, the low energy bands at 426 nm for the chloro and 436 nm for the bromo are assigned to MLCT transitions while the other bands (Table 3) are assigned to $\pi-\pi^*$ transitions. These results are in good agreement with what has been reported for analogous Pt(II) and Pd(II) complexes with 2,2′-bipyrimidine [1c, 28].

^{1}H NMR Spectra

The ^{1}H NMR spectra of some pq complexes are presented in Table 4. Unfortunately, the insolubility of other complexes or the complexity of their spectra has hindered their study. The peak assignments were made with the aid of earlier ^{1}H NMR studies of coordinated bpy, phen, biq and other related diimine ligands [2b, 7, 19, 29]. As mentioned earlier, a detailed comparison cannot be made with reference to uncoordinated pq since this has a *trans* conformation [22] while a *cis* conformation is adopted by a coordinated ligand [for example, see ref. 23]. In the *cis* conformation, the H3,3′ protons are forced together, giving rise to a van der Waals deshielding interaction; the inductive effect of the metal deshields ring protons and the diamagnetic anisotropic effect of the aromatic ring of the adjacent ligand shields ring protons, particularly H8,6′ protons. Moreover, in the halo complexes, the protons which are directed towards a halide ion (H8,6′) are expected to be highly deshielded [2b, 7, 29a].

The spectra clearly indicate that these complexes have the *cis* configuration, as was also shown by IR data. For *cis*-$[Rh(pq)_2Cl_2](PF_6)$, the presence of two doublets centered at 9.86 (area 1H) and 9.72 ppm (area 1H) with coupling constants (*J*) of 6.5 and 5.4 Hz, respectively, suggests that the two protons (H8,6′) which are directed toward the halide ions are non-equivalent. This result is consistent with structure **VI** (equivalent to **IIIa** but here showing the numbering system). Structures **IIIb** and **IIIc** are expected to show one doublet for the equivalent 2H6′ or the equivalent 2H8 protons, respectively, or two doublets each with the same coupling constant. The spectrum of *cis*-$[Rh(pq)_2Br_2]Br$ exhibits two doublets for highly deshielded protons (2H8 or 2H6′) at 10.18 and 10.06 ppm but with relatively the same *J* values of 5.5 and 5.7 Hz, respectively. This result agrees well with structures **IIIb** or **IIIc** (the observed doublets are assigned to either 2H8 or 2H6′ protons since no NMR data for pq complexes have been reported). However, if steric factors are to be considered then structure **IIIb** would have less repulsion between the large bromide ions and the bulky quinoline parts (Q) of the ligand than **IIIc**.



VI

The spectrum of *cis*-$Pt(pq)Cl_2$ supports structure **IV** proposed for this complex. It exhibits two doublets at 8.72 ppm (area 1H; *J* = 8.9 Hz) and 8.51 ppm (area 1H; *J* = 7.8 Hz) that are assigned to the most deshielded protons H8 and H6′. Moreover, the spectrum of *cis*-$Pt(pq)I_2$ confirms with a *cis* configuration for this complex. It exhibits two doublets at 9.43 ppm (area 1H; *J* = 5.6 Hz) and 8.74 ppm (area 1H; *J* = 7.8 Hz) which are assigned to the most deshielded protons in the complex H8 and H6′ as shown in structure **IV**. The two doublets at 8.53 ppm (area 1H; *J* = 4.5 Hz) and 8.38 ppm (area 1H; *J* = 5.6 Hz) are assigned to the two non-equivalent H3,3′ protons. The wine-red color of this complex further confirms the platinum–iodine bonding [5].

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