Pergamon

0277-5387(94)00350-5

Polyhedron Vol. 14, No. 8, pp. 1011 1019, 1995
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0277-5387/95 $9.50+0.00

SUBSTITUTION REACTIONS OF *CIS*-DICHLOROBIS (2,2′-BIQUINOLINE)RHODIUM(III) CHLORIDE

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(*Received* 3 *March* 1994; *accepted* 30 *August* 1994)

Abstract—The substitution reactions of the 2,2′-biquinoline (biq) complex *cis*-[Rh(biq)$_2$Cl$_2$]Cl with Br$^-$, I$^-$, OH$^-$, NH$_3$, pyridine (py), CN$^-$, NO$_2^-$, SCN$^-$, ethylenediamine (en), 2,2′-bipyridine (bipy) and dimethylglyoxime (dmgmH$_2$) have been investigated. The new complexes *cis*-[Rh(biq)$_2$ICl]I, *cis*-[Rh(biq)$_2$(OH)$_2$]PF$_6$·3H$_2$O, *cis*-[Rh(biq)$_2$(NH$_3$)Cl](PF$_6$)$_2$·2H$_2$O, *cis*-[Rh(biq)$_2$(py)Cl]Cl$_2$, [Rh(biq)(CN)$_3$]$_n$ ($n > 1$), [Rh(biq)(NO$_2$)(H$_2$O)Cl$_2$], *cis*-[Rh(biq)$_2$(SCN)$_2$]SCN·2.5H$_2$O and [Rh(biq)$_2$(dmgm)]Cl·3H$_2$O have been characterized by elemental analysis, conductivity measurements, IR, electronic absorption and ^{1}H NMR spectra. However, the reactions of *cis*-[Rh(biq)$_2$Cl$_2$]Cl with Br$^-$, en and bipy afforded the known complexes *cis*-[Rh(biq)$_2$Br$_2$]Br, *cis*-[Rh(en)$_2$Cl$_2$]Cl and *cis*-[Rh(bipy)$_2$Cl$_2$]Cl, respectively.

Complexes of rhodium(III) with N-heterocyclic ligands have received special interest for their potential use as electron transfer agents in the storage of radiant energy.[1] Moreover, cationic complexes of rhodium(III) of the type *cis*-[Rh(NN)$_2$X$_2$]X [NN = 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) or 2,2′-biquinoline (biq); X = Cl, Br or I] have received considerable attention because of the possibility of their use as hydrogenation catalysts and as antibacterial and antitumour agents.[2]

Although substitution reactions of *cis*-[Rh(NN)$_2$Cl$_2$]Cl (NN = bipy, phen) have been investigated and various derivatives have been isolated,[3] no similar reactions have been made on analogous complexes of the structurally related but more sterically hindered 2,2′-biquinoline (biq) ligand.

Recently, a new method for the preparation of *cis*-[Rh(biq)$_2$X$_2$]X (X = Cl, Br) was reported,[4] but no other bis(biq)rhodium(III) complexes have been described.

All these considerations prompted us to study the behaviour of *cis*-[Rh(biq)$_2$Cl$_2$]Cl towards substitution. We now report the isolation of some rhodium(III)–biq complexes via substitution reactions.

EXPERIMENTAL

Materials

All solvents used were AR grade. The ligands and metal salts were obtained from Aldrich, Fluka, BDH or Laborat. The ligand biq was further recrystallized from PhMe. The *cis*-[Rh(biq)$_2$Cl$_2$]Cl starting complex (hereafter referred to as complex A) was prepared according to the literature.[4]

Physical measurements

Elemental analyses for all complexes were performed by M-H-W Laboratories, Phoenix, AZ, U.S.A. Conductivity measurements were carried out on a Jeneway 4010 digital conductivity meter at 25°C for 10^{-3} M solutions in dimethylformamide (DMF), dimethyl sulphoxide (DMSO), nitromethane and acetonitrile. The IR spectra (KBr and

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CsI pellets) were recorded on a Pye-Unicam SP3-300 spectrophotometer. Electronic absorption spectra were measured on a CARY 2390 spectrophotometer in DMF, DMSO, CH_3CN and CH_3NO_2. ^1H NMR spectra were determined with a Bruker WP 80SY instrument in DMSO-d_6 using TMS as internal standard.

Preparation of the complexes

All of the products were dried under vacuum at 30°C.

cis - *Dibromobis*(2,2′ - *biquinoline*)*rhodium*(III) *bromide*, cis-$[Rh(biq)_2Br_2]Br$. A mixture of complex **A** (0.23 g; 0.32 mmol) and excess potassium bromide (0.25 g; 2.1 mmol) in water (30 cm^3) was refluxed for 30 min. The orange solid formed was filtered off and washed well with water and ethanol (yield 83%).

cis - *Chloroiodobis*(2,2′ - *biquinoline*)*rhodium*(III) *iodide*, cis-$[Rh(biq)_2ICl]I$. A mixture of complex **A** (0.15 g; 0.21 mmol) and excess potassium iodide (1.0 g; 6.0 mmol) in aqueous ethanol (1 : 1 ; 40 cm^3) was refluxed for 1 h. The resulting brown solution was concentrated under reduced pressure to about 20 cm^3 and allowed to cool, whereupon a light brown precipitate was obtained. The product was filtered off and washed well with water and ethanol.

cis - *Dihydroxobis*(2,2′ - *biquinoline*)*rhodium*(III) *hexafluorophosphate trihydrate*, cis-$[Rh(biq)_2(OH)_2]PF_6 \cdot 3H_2O$. To a hot mixture of complex **A** (0.12 g; 0.16 mmol) and excess sodium hydroxide (0.10 g; 2.5 mmol) in water (15 cm^3) was added a small amount of hydrazine dihydrochloride (0.001 g). The mixture was boiled for 3 min. The resulting yellow solution was allowed to cool and then treated with an excess aqueous solution of NH_4PF_6. The yellow product was filtered off and washed well with warm water.

cis - *Amminechlorobis*(2,2′ - *biquinoline*)*rhodium* (III) *hexafluorophosphate dihydrate*, cis-$[Rh(biq)_2(NH_3)Cl](PF_6)_2 \cdot 2H_2O$. To a hot solution of complex **A** (0.12 g; 0.16 mmol) in water (10 cm^3) was added a solution of 1.5 cm^3 of concentrated ammonium hydroxide in water (10 cm^3). The mixture was boiled for 25 min, allowed to cool and filtered. The filtrate was treated with an excess aqueous solution of NH_4PF_6. The yellow product was filtered off and washed well with warm water.

cis - *Chloropyridinebis*(2,2′ - *biquinoline*)*rhodium* (III) *chloride*, cis-$[Rh(biq)_2(py)Cl]Cl_2$. To a hot (~60°C) solution of complex **A** (0.15 g; 0.21 mmol) in water (25 cm^3) was added excess pyridine (py; 0.13 g; 1.66 mmol). A light brown colour was formed immediately. The reaction mixture was boiled for 20 min and then allowed to cool. Most of the solvent was removed under reduced pressure. On cooling, a yellow solid was obtained. It was filtered off and washed well with warm water and then diethyl ether.

$[Rh(biq)(CN)_3]_n$ (*see IR section*). A mixture of complex **A** (0.12 g; 0.17 mmol) and excess potassium cyanide (0.19 g; 2.9 mmol) in water (20 cm^3) was boiled for 15 min and then allowed to cool. The resulting yellow solution was treated with concentrated HCl (3 cm^3) and boiled for another 4 min to remove HCN. On cooling, a yellow precipitate was obtained which was filtered off and washed with warm water.

Dichloroaquonitro(2,2′-*biquinoline*)*rhodium*(III), $[Rh(biq)(NO_2)(H_2O)Cl_2]$. A mixture of complex **A** (0.12 g; 0.16 mmol) and excess sodium nitrite (0.15 g; 2.2 mmol) in water (15 cm^3) was boiled for 5 min. Concentrated HCl (3 cm^3) was added to the resulting hot yellow solution. The mixture was then boiled for further 5 min to expel nitrogen dioxide. The yellow precipitate which was formed upon cooling was filtered off and washed well with warm water, ethanol and diethyl ether.

cis - *Dithiocyanatobis*(2,2′ - *biquinoline*)*rhodium* (III) *thiocyanate hydrate*, cis-$[Rh(biq)_2(SCN)_2]SCN \cdot 2.5H_2O$. A mixture of complex **A** (0.18 g; 0.25 mmol) and excess potassium thiocyanate (0.09 g; 0.92 mmol) in water (20 cm^3) was boiled for 5 min. An orange precipitate was formed upon cooling. It was filtered off and washed well with warm water.

cis-*Dichlorobis*(*ethylenediamine*)*rhodium*(III) *chloride*, cis-$[Rh(en)_2Cl_2]Cl$. To a hot solution of complex **A** (0.18 g; 0.25 mmol) in water (50 cm^3) was added excess ethylenediamine (en; 0.16 g; 2.6 mmol). The solution was refluxed for 1 h. The mixture was then allowed to cool and filtered yielding a white solid (identified as biq) and a light yellow filtrate. The filtrate was concentrated under reduced pressure to about 20 cm^3. On cooling, a light yellow precipitate was obtained. It was filtered off and washed well with warm water (yield 33%).

cis-*Dichlorobis*(2,2′-*bipyridine*)*rhodium*(III) *chloride*, cis-$[Rh(bipy)_2Cl_2]Cl$. A mixture of complex **A** (0.12 g; 0.16 mmol) and excess bipy (0.16 g; 1.0 mmol) in water (50 cm^3) was refluxed for 1 h, allowed to cool and filtered. A white solid (identified as biq) and a yellow filtrate were obtained. The filtrate was concentrated under reduced pressure, whereupon yellow crystals were obtained. They were filtered off and washed well with warm water and then ethanol (yield 76%).

The complex was also isolated as the hexafluorophosphate salt, *cis*-$[Rh(bipy)_2Cl_2]PF_6$, by treating the above reaction mixture with excess aqueous solution of NH_4PF_6 instead of concentrating it under reduced pressure.

Dimethylglyoximatobis(2,2′ - *biquinoline*)*rhodium* (III) *chloride trihydrate*, $[Rh(biq)_2(dmgm)]Cl \cdot 3H_2O$. A mixture of complex **A** (0.12 g; 0.16 mmol) and dimethylglyoxime ($dmgmH_2$; 0.058 g; 0.50 mmol) in aqueous ethanol (1 : 1; 60 cm^3) was refluxed for 5 h. The resulting violet–red solution was concentrated under reduced pressure to about 7 cm^3. On cooling, dark violet–red crystals were obtained which were filtered off and washed with ethanol followed by diethyl ether. The product was further purified by dissolution in acetone and reprecipitation by diethyl ether. It was filtered off and washed with diethyl ether.

RESULTS AND DISCUSSION

The starting complex (**A**) was reacted with the following ligands: Br^-, I^-, OH^-, NH_3, py, CN^-, NO_2^-, SCN^-, en, bipy and $dmgmH_2$.

It is noteworthy that when *cis*-$[Rh(biq)_2Cl_2]Cl$ was refluxed in water with an excess of KBr, bipy or en, the isolated products were the known complexes *cis*-$[Rh(biq)_2Br_2]Br$, *cis*-$[Rh(bipy)_2Cl_2]Cl$ and *cis*-$[Rh(en)_2Cl_2]Cl$, respectively. The colour, melting point, IR, electronic and NMR spectra of these complexes are identical to those obtained for samples prepared by the literature methods.[2d, 3–6] On the other hand, all the other isolated complexes have never been reported.

The elemental analyses of the new complexes are listed in Table 1. The complexes were obtained in fair to good yields (Table 1). They are all coloured solids, stable in air and insoluble to slightly soluble in common organic solvents while all are soluble in DMF and DMSO.

It seems that the steric requirements of the biquinoline ligand play an important role in determining the nature of the product. Attempts to obtain the di-iodo complex *cis*-$[Rh(biq)_2I_2]^+$ were unsuccessful and instead the chloro–iodo complex *cis*-$[Rh(biq)_2ICl]I$ was formed upon reflux of complex **A** with excess KI for 1 h in aqueous ethanol.

The reaction of *cis*-$[Rh(biq)_2Cl_2]Cl$ with a vigorously boiling aqueous solution of ammonia for 25 min gave the monosubstituted derivative *cis*-$[Rh(biq)_2(NH_3)Cl]^{2+}$, which was isolated as the hexafluorophosphate salt upon addition of NH_4PF_6.

Similarly, the reaction of *cis*-$[Rh(biq)_2Cl_2]^+$ with aqueous solution containing pyridine gave, upon reflux for 20 min, the monosubstituted derivative $[Rh(biq)_2(py)Cl]Cl_2$. We noticed that if the temperature during the addition is ~40°C and the reflux time is 10 min or less, a light green solid is obtained which gives the yellow pyridine complex upon dissolution in diethyl ether. All attempts to isolate what could possibly be a superoxide[7, 8] of rhodium from these green compounds have been unsuccessful. However, the similarities between the physical measurements of both solids (the light green and yellow pyridine complexes) may indicate that they are dimorphous varieties of the same chemical entity. A similar observation was reported for the palladium(III) complex with biq.[4]

We found that base hydrolysis of complex **A** is very much dependent upon reaction conditions. Boiling the reaction mixture for 3 min in the presence of hydrazine dihydrochloride (which is known to act as a catalyst for the synthesis of *cis*-dihalo and *cis*-dihydroxo complexes[3, 4, 9]) resulted in the formation of the dihydroxo complex, which was isolated upon addition of NH_4PF_6 as *cis*-$[Rh(biq)_2(OH)_2]PF_6 \cdot 3H_2O$. However, when the reaction was carried out in the absence of hydrazine dihydrochloride, dimeric species resulted, which are now under investigation.

The reaction of *cis*-$[Rh(biq)_2Cl_2]^+$ with a vigorously boiling aqueous solution containing potassium thiocyanate for 5 min gave *cis*-$[Rh(biq)_2(SCN)_2]SCN \cdot 2.5H_2O$ as expected, while the reactions with sodium nitrite did not proceed as predicted and the complex $[Rh(biq)(NO)_2(H_2O)Cl_2]$ was isolated. However, on boiling with aqueous potassium cyanide, a compound with the empirical formula $Rh(biq)(CN)_3$ was formed (see IR section).

Furthermore, the reaction of *cis*-$[Rh(biq)_2Cl_2]Cl$ with $dmgmH_2$ in aqueous ethanol and upon reflux for 5 h gave a tris-mixed-ligand complex $[Rh(biq)_2(dmgm)]Cl \cdot 3H_2O$.

Conductivity

The molar conductance values for 10^{-3} M solutions for the complexes (Table 1) are in good agreement with those reported for similar complexes.[10] The complex $[Rh(biq)(NO_2)(H_2O)Cl_2]$ behaves as a neutral non-electrolyte in DMSO. The slight conductance observed may be due to some dissociation of the complex. The compounds *cis*-$[Rh(biq)_2ICl]I$, *cis*-$[Rh(biq)_2(OH)_2]PF_6 \cdot 3H_2O$, *cis*-$[Rh(biq)_2(SCN)_2]SCN \cdot 2.5H_2O$ and $[Rh(biq)_2(dmgm)]Cl \cdot 3H_2O$ behave as 1 : 1 electrolytes, while *cis*-$[Rh(biq)_2(NH_3)Cl](PF_6)_2 \cdot 2H_2O$ and *cis*-$[Rh(biq)_2(py)Cl]Cl_2$ act as 1 : 2 electrolytes in the solvents indicated in Table 1.

Table 1. Analytical and physical data for the complexes

Complex	Calculated (found), %				M.p. (°C)	Yield (%)	Λ_M[b] (Ω cm^2 mol^{-1})
	C	H	N	X			
cis-$[Rh(biq)_2ICl]I$	47.8	2.7	6.2	28.1 (I)	257	74	65.4[c]
	(48.0)	(3.2)	(6.1)	(28.0) (I)			
cis-$[Rh(biq)_2(OH)_2]PF_6 \cdot 3H_2O$	51.0	3.8	6.6		230	55	77.7[d]
	(50.0)	(3.2)	(6.5)				
cis-$[Rh(biq)_2(NH_3)Cl](PF_6)_2 \cdot 2H_2O$	43.5	3.1	7.1		165	57	138.7[c]
	(43.4)	(3.2)	(6.8)				
cis-$[Rh(biq)_2(py)Cl]Cl_2$	61.5	3.7	8.7		210[a]	60	120.0[c]
	(61.9)	(3.6)	(8.1)				
$[Rh(biq)(CN)_3]$[e]	57.7	2.8	16.0		308	57	17.2[f]
	(57.6)	(2.8)	(16.0)				
$[Rh(biq)(NO_2)(H_2O)Cl_2]$	43.8	2.9	8.5		237[a]	39	15.4[f]
	(44.2)	(2.9)	(8.8)				
cis-$[Rh(biq)_2(SCN)_2]SCN \cdot 2.5H_2O$	56.1	3.5	11.8	11.5 (S)	183	67	66.1[c]
	(56.1)	(3.1)	(11.8)	10.9 (S)			
$[Rh(biq)_2(dmgm)]Cl \cdot 3H_2O$	58.7	4.4	10.3	4.3 (Cl)	214[a]	68	132.2[g]
	(59.1)	(4.3)	(10.6)	(4.2)(Cl)			

[a] Compound melts with decomposition.

[b] Molar conductance for 10^{-3} M solutions at 25°C.

[c] In DMF.

[d] In CH_3NO_2.

[e] For empirical formula, see text.

[f] In DMSO.

[g] In CH_3CN.

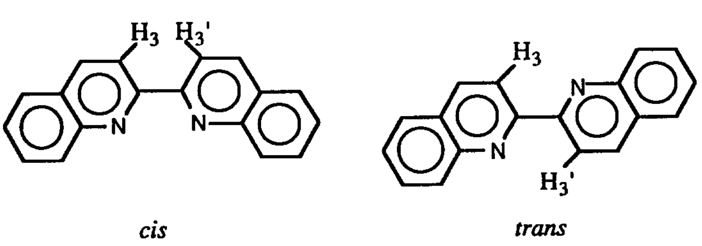
IR spectra

The IR bands (Table 2) of coordinated biq were assigned on the basis of earlier studies made on biq[11] and the starting complex **A**.[2d,4]

As has already been reported,[4] a detailed comparison with the uncoordinated biq ligand cannot be made. In the free ligand the nitrogen donor atoms are *trans*[12] in order to minimize steric repulsion between the H(3,3′) protons, but upon coordination they adopt a *cis* conformation.[2d,4]

The IR bands of coordinated biq in the new complexes (Table 2) seem to be similar to those of the starting complex **A**. The spectra were also examined in the low frequency region (CsI pellets) where ν(M—Cl) appears (Table 2). The main points are given below:

(i) The strong absorption bands appearing in the range 830–840 and 550–560 cm^{-1} in the IR spectra of the complexes *cis*-$[Rh(biq)_2(OH)_2]PF_6 \cdot 3H_2O$ and *cis*-$[Rh(biq)_2(NH_3)Cl](PF_6)_2 \cdot 2H_2O$, which are



biq

Table 2. Important IR frequencies for the complexes (KBr pellets; cm^{-1})

Compound	ν(C=C), ν(C=N)	ν(C—H)	ν(Rh—Cl)[a]
cis-$[Rh(biq)_2Cl_2]Cl$[b]	1575s, 1510m, sh,1500m, 1463w, 1453w	820vs, 770s, 730s	349s, 334s
cis-$[Rh(biq)_2ICl]I$[c]	1580s, 1510w, sh,1505m, 1465w	820vs, 775s, 735s	335m
cis-$[Rh(biq)_2(OH)_2]PF_6 \cdot 3H_2O$[d]	1590s, 1510s,1500m, sh, 1435m	820vs, 780s, 750s	
cis-$[Rh(biq)_2(NH_3)Cl](PF_6)_2 \cdot 2H_2O$[e]	1590s, 1515s,1505w, sh, 1475w, sh,1440m	820vs, 780s, 755s	330w
cis-$[Rh(biq)_2(py)Cl]Cl_2$[f]	1590s, 1510w, 1500m, 1470w, sh, 1435w, sh	825vs, 780, 760m	325w
$[Rh(biq)(CN)_3]_n$[g]	1585s, 1525m, sh, 1510s, 1465w, 1555w	830vs, 785s, 750s	
$[Rh(biq)(NO_2)(H_2O)Cl_2]$[h]	1510m, 1480w, sh 1450w	820s, 770s, 754s	350m, 330w, sh
cis-$[Rh(biq)_2(SCN)_2]SCN \cdot 2.5H_2O$[i]	1605s, 1580vs, 1510s, 1500w, sh, 1460w, 1430s	820vs, 775s, 745s	
$[Rh(biq)_2(dmgm)]Cl \cdot 3H_2O$[j]	1565m, sh, 1520m, sh, 1495w, sh, 1450w, 1430s	820vs, 775s, 750s	

[a] CsI pellets.

[b] Refs 2d and 4.

[c] ν(Rh—I) not observed.

[d] ν(O—H): 3450 m,b; γ(HOH): 1620 w; γ(RhO—H): 1150 m, 1160 m,sh; ν(P—F): 830 vs, 550 s.

[e] ν(O—H) and ν(N—H): 3440 m,b; γ(HOH) and δ(HNH): 1615 m; ρ(NH_3): 885s,sh; ν(P—F): 840 vs, 560 s.

[f] β(py): 625 m; γ(py): 430 m; ν[Rh—N(py)]: 275 w.

[g] ν(C≡N): 2140 vs, 2230 s, 2240 s.

[h] ν(O—H): 3440 m,b; γ(HOH): 1610sh; ρ(H_2O): 690 m; ν(—NO_2): 1415 s, 1315 s; δ(ONO): 825 m, sh.

[i] ν(O—H): 3460 m, b; γ(HOH): 1625w; ν(CN): 2100 vs, 2120 vs (split); ν(CS): 705 s; SCN^-: 2060 vs; ν(Rh—SCN): weak bands near 420.

[j] ν(O—H): 3460 s, b; γ(HOH): 1610 w; coordinated dmgm: 1520 vs [ν(NO)], 1430 w, 1255 w, 1140 m, 1100 s.

vs, very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder.

assigned to ν(P—F) vibrations, indicate the presence of ionic PF_6^- groups.[6]

(ii) The complex $[Rh(biq)(NO_2)(H_2O)Cl_2]$ shows two ν(Rh—Cl) peaks at 350 and 330 cm^{-1}. Comparison of this result with those reported for complex **A** (Table 2), *cis*-$[Rh(bipy)_2Cl_2]Cl$ [ν(Rh—Cl) at 330 and 355 cm^{-1}]† and other related systems[6] suggests a *cis*-chlorine arrangement in this complex. The IR spectra of the complexes *cis*-$[Rh(biq)_2ICl]I$, *cis*-$[Rh(biq)_2(NH_3)Cl](PF_6)_2 \cdot 2H_2O$ and *cis*-$[Rh(biq)_2(py)Cl]Cl_2$ show bands at 335, 330 and 325 cm^{-1}, respectively, which may be attributed to ν(Rh—Cl).[6]

(iii) The appearance of medium broad absorptions in the range 3460–3440 cm^{-1}, together with other bands in the range 1610–1625 cm^{-1}, supports the presence of water molecules in the hydrated complexes. In addition, the IR spectrum of *cis*-$[Rh(biq)(NO_2)(H_2O)Cl_2]$ shows a band at 690 cm^{-1} that is absent in the free biq ligand and the other complexes, which confirms the involvement of water in coordination,[6] in a similar manner to analogous biq and 2-(2′-pyridyl)quinoline (pq) complexes, namely $[Rh(biq)Cl_3(H_2O)]$ and $[Rh(pq)Cl_3(H_2O)]$.[4]

(iv) The IR spectrum of *cis*-$[Rh(biq)_2(OH)_2]PF_6 \cdot 3H_2O$ exhibits two bands at 1150 and 1160 cm^{-1}, which may be attributed to the bonded O—H (RhO—H) bending modes,[6] thus suggesting a *cis* configuration for our complex.

(v) The IR band at 885 cm^{-1} [ρ(NH_3)] for *cis*-

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† CsI pellets; measured for a sample prepared by the literature method.[5]

$[Rh(biq)_2(NH_3)Cl](PF_6)_2 \cdot 2H_2O$ characterizes the presence of coordinated NH_3 in our complex.[6]

(vi) The IR spectrum of *cis*-$[Rh(biq)_2(py)Cl]Cl_2$ shows bands at 625 cm^{-1} (in-plane py ring deformation) and at 430 cm^{-1} (out-of-plane py ring deformation) that indicate the presence of coordinated pyridine in the complex. The band appearing in the low frequency region at 275 cm^{-1} may be assigned to ν[Rh—N(py)].[6]

(vii) The IR spectrum of the compound with the empirical formula $Rh(biq)(CN)_3$ reveals that it contains both terminal ($\nu = 2140$ cm^{-1}) and bridging ($\nu = 2230$ and 2240 cm^{-1}) cyanide groups. These values are in good agreement with the reported data for similar systems.[5, 6] For example, the IR spectrum of $Rh(py)_2(CN)_2Cl \cdot 2H_2O$ has been reported to show bands at 2152 and 2201 cm^{-1} that were assigned to terminal and bridging cyanide groups, respectively.[5] Based on these data and its insolubility in water and common organic solvents (except DMF and DMSO), our complex is probably polymeric and formulated as $[Rh(biq)(CN)_3]_n$, where $n > 1$.

(viii) The appearance of strong bands at 1415, 1315 and 825 cm^{-1} for $[Rh(biq)(NO_2)(H_2O)Cl_2]$ indicates the presence of a coordinated nitro (—NO_2) rather than a nitrito (—ONO) group.[3, 6]

(ix) The IR spectrum of *cis*-$[Rh(biq)_2(SCN)_2]SCN \cdot 2.5H_2O$ exhibits two bands at 2120 and 2100 cm^{-1}, which can be attributed to C—N stretching frequencies in a *cis*-octahedral geometry.[6, 13] From these values one may conclude that the —SCN groups are bonded through sulphur rather than the nitrogen atom. The C—N stretching frequencies are generally lower in nitrogen-bonded complexes (near and below 2050 cm^{-1}) than in sulphur-bonded complexes (near 2100 cm^{-1}). The spectrum also shows an absorption band at 705 cm^{-1}, which on the basis of the reported studies,[6, 13] may be assigned to C—S stretching frequency. It has been reported that the C—S stretching frequencies fall in the range 860–780 cm^{-1} for nitrogen-bonded, and 720–690 cm^{-1} for sulphur-bonded —SCN complexes.[6, 13] Moreover, the presence of weak bands near 420 cm^{-1} supports sulphur-bonded thiocyanato groups. In addition, the IR spectrum shows a band at 2060 cm^{-1}, indicating the presence of ionic SCN^- groups.

(x) The IR spectrum of $[Rh(biq)(dmgm)]Cl \cdot 3H_2O$ shows bands that are characteristic of coordinated dimethylglyoximate anion[5] at 1520 cm^{-1}, which may be assigned to ν(NO), and at 1430, 1255, 1140 and 1100 cm^{-1}.

Electronic spectra

The electronic absorption spectrum of biq has been reported.[14] However, it cannot be compared directly with those of the complexes because of the differences in conformation upon coordination discussed earlier. Recently, it has been shown that upon addition of H^+, biq is converted into the *cis* conformation and its UV–vis spectrum exhibits two main ligand centred (LC) or $\Pi \rightarrow \Pi^*$ transitions at ~268 and 372 nm.[12a] Moreover, the electronic spectrum of the starting complex **A** has been reported and it shows two LC bands at 271 and 370 nm and a metal–ligand charge transfer band (MLCT) at 352 nm.[2d]

The electronic spectra of the biq complexes prepared in this study are characterized by the presence of strong LC bands, along with some MLCT and ligand-field (*d*–*d*) bands (Table 3). The latter types of transitions (MLCT and *d*–*d*) are responsible for the characteristic orange, yellow or brown colours of rhodium(III) compounds.[15] Our rhodium(III) complexes, prepared in this study, all have colours in this range.

The complexes *cis*-$[Rh(biq)_2XY]^{n+}$ (X = Cl, Y = I, NH_3 or py; X = Y = SCN or OH) exhibit, in addition to LC bands, bands in the range 316–357 nm, which may be assigned to MLCT transitions. The strong band at 294 nm in the spectrum of *cis*-$[Rh(biq)_2(py)Cl]Cl_2$ may by assigned to $\Pi \rightarrow \Pi^*$ transitions of the pyridine ligand,[5] as well as an MLCT.

We have noticed that all the above octahedral *cis*-$[Rh(biq)_2XY]^{n+}$ complexes have absorption bands in almost the same regions and are in good agreement with those reported for the starting complex **A**.

Therefore, and based upon similar results found for previously reported compounds[3, 16] and on the basis of the steric requirements of the biq ligand,† we conclude that all these complexes have *cis* configurations, as shown in structure **I**. That is, substitution reactions of the rhodium(III) complex *cis*-$[Rh(biq)_2Cl_2]^+$ occur with retention of configuration. Similarly, substitution reactions of *cis*-$[Rh(NN)_2Cl_2]^+$ (NN = bipy, phen) with many of the same ligands used in this study (I^-, H_2O, OH^-, CN^-, NO_2^-, SCN^- and py) have been found to occur with retention of configuration.[3]

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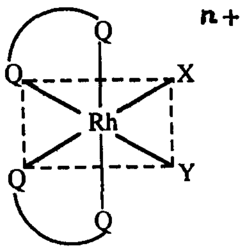
† Four-coordinate complexes with the biq ligand are found to adopt a non-planar arrangement, e.g. $Cu(biq)X_2$ (X = Cl, Br and NO_3), $Fe(biq)X_2$, $Fe(biq)_2^{2+}$ and $Ni(biq)X_2$ (X = Br, I) have a pseudo-tetrahedral arrangement.[17] Moreover, no *trans*-bis-biquinoline complexes of the type $[M(biq)_2X_2]^{n+}$ have been reported.



I


= biq

$X = Cl$; $Y = I, NH_3$, py.

$X = Y = OH$, SCN.

Table 3. Electronic absorption spectra of the complexes

Metal complexes (2.0×10^{-5} M solutions)	λ_{max} (nm)	$\varepsilon \times 10^{-3}$ ($l\ mol^{-1}\ cm^{-1}$)	Assignment
cis-$[Rh(biq)_2ICl]I$[a]	271	60.9	LC
	352 br,sh	23.0	MLCT
	370	29.0	LC
cis-$[Rh(biq)_2(OH)_2]PF_6 \cdot 3H_2O$[b]	275	105.0	LC
	322 sh	28.0	MLCT
	356 br,sh	40.0	MLCT
	370	51.3	LC
cis-$[Rh(biq)_2(NH_3)Cl](PF_6)_2 \cdot 2H_2O$[a]	275	25.2	LC
	316 sh	6.9	MLCT
	357 br,sh	12.5	MLCT
	372	11.9	LC
cis-$[Rh(biq)_2(py)Cl]Cl_2$[a]	274	70.2	LC
	294 sh	35.1	LC/MLCT
	355 br,sh	12.4	MLCT
	370 br	15.6	LC
$[Rh(biq)(CN)_3]_n$[c]	272	56.8	LC
	293 sh	14.8	MLCT
	303	14.0	MLCT
	330	14.0	MLCT
	340	15.8	MLCT
	357	17.8	MLCT
	372	18.4	LC
	400	0.98	*d–d*
$[Rh(biq)(NO_2)(H_2O)Cl_2]$[c]	275	78.4	LC
	285 sh	19.0	MLCT
	372	28.0	LC
	395 sh	8.0	MLCT
cis-$[Rh(biq)_2(SCN)_2]SCN \cdot 2.5H_2O$[a]	275	78.4	LC
	322 sh	23.0	MLCT
	374	6.5	LC
$[Rh(biq)_2(dmgm)]Cl \cdot 3H_2O$[d]	272	16.0	LC
	285	33.0	MLCT
	368	43.0	LC
	391 sh	11.9	MLCT

br, broad; sh, shoulder.

[a] In DMF.

[b] In CH_3NO_2.

[c] In DMSO.

[d] In CH_3CN.

The electronic spectrum of $[Rh(biq)(NO_2)(H_2O)Cl_2]$ shows the MLCT bands as shoulders at 285 and 395 nm. The electronic absorption spectrum of the complex $[Rh(biq)_2(dmgm)]Cl \cdot 3H_2O$ exhibits bands at 285 and 391 nm that are assigned to MLCT transitions. The strong band at 285 nm may indicate the presence of an absorption band due to the dimethylglyoximate anion[5] underlying the MLCT transition.

On the other hand, the complex $[Rh(biq)(CN)_3]_n$ exhibits an almost completely different type of electronic absorption spectrum from those of the six-coordinate complexes. It shows the LC bands within the expected regions (272 and 372 nm). However, several other bands appear which may be assigned to MLCT or *d–d* transitions (Table 3).

^{1}H *NMR spectra*

The ^{1}H NMR spectra of some biq complexes are presented in Table 4. The insufficient solubility of the other complexes has hindered their study. Assignments of the peaks were made by comparison with ^{1}H NMR data reported for *cis*-$[Rh(biq)_2X_2]X \cdot nH_2O$ (X = Cl, Br),[4] *cis*-$[Rh(pq)_2Cl_2]PF_6$ and *cis*-$[Rh(pq)_2Br_2]Br$,[9] and for rhodium(III) and iridium(III) complexes with bipy and phen.[18]

As mentioned in the IR spectra section, a detailed comparison with the free biq ligand cannot be made. X-ray[12b] and ^{1}H NMR[19] studies of biq have shown that the free ligand exists mainly in the *trans* conformation, while a *cis* conformation is adopted by a coordinated ligand.[2d,4]

In the *cis*-dihalo complexes of biq, two H(8) protons are directed away from any other rings and toward a halide ion, thus experiencing a significantly different environment. These two protons are found to be highly deshielded and their presence has been used as evidence for the *cis* configuration.[4]

The spectrum of *cis*-$[Rh(biq)_2ICl]I$ exhibits two doublets for two highly deshielded protons at 10.64 and 9.93 ppm. These peaks may be assigned to the H(8) protons which are directed toward the chloride and iodide ions, respectively, since chlorine is more electronegative than iodine. The spectrum of *cis*-$[Rh(biq)_2(NH_3)(Cl)](PF_6)_2 \cdot 2H_2O$ shows only one peak for a highly deshielded proton at 9.44 ppm, as expected; the singlet at 2.51 ppm (area 3 protons) confirms the presence of bonded ammonia.[20] Moreover, the spectrum of *cis*-$[Rh(biq)_2(SCN)_2]\ SCN \cdot 2.5H_2O$ has a doublet for two highly deshielded protons at 9.89 ppm. These data clearly indicate that these complexes have a *cis* configuration.

However, no similar pattern was observed in the case of *cis*-$[Rh(biq)_2(OH)_2]PF_6 \cdot 3H_2O$ and $[Rh(biq)_2(dmgm)]Cl \cdot 3H_2O$. The spectrum of the dihydroxo complex shows, in addition to the solvent peak at 2.49 ppm, another sharp peak at 3.30 ppm (area 1 : 4, respectively) which may be assigned to bonded DMSO.[21] It appears that the two hydroxyl groups are labile and are easily displaced by DMSO. The spectrum of $[Rh(biq)_2(dmgm)]Cl \cdot 3H_2O$ shows, in addition to biq peaks, a singlet at 1.26 (area 6H) for the two methyl protons of the dimethylglyoximate anion.

Table 4. ^{1}NMR data for 2,2′-biquinoline complexes[a]

Compound	NMR band shift: δ, ppm (J, Hz)
cis-$[Rh(biq)_2ICl]1$	10.64 (d, 1H; $J = 5.92$); 9.93 (d, 1H; $J = 6.58$); 8.68–9.18 (2d, 6H); 8.55 (d, 2H; $J = 9.0$); 8.43–7.81 (m, 10H); 7.71 (d, 2H; $J = 6.57$); 6.77–7.41 (m, 2H).
cis-$[Rh(biq)_2(NH_3)Cl]PF_6 \cdot 2H_2O$	9.44 (d, 1H; $J = 5.60$); 9.09 (m, 5H); 8.34 (d, 2H; $J = 7.56$); 8.14 (d, 2H; $J = 8.40$); 7.93–7.24 (m, 12H); 7.07 (d, 2H; $J = 4.13$); 2.51 [s, 3H (3 protons of bonded NH_3)]
cis-$[Rh(biq)_2(SCN)_2]SCN \cdot 2.5H_2O$	9.89 (d, 2H; $J = 5.71$); 9.21 (d, 2H; $J = 5.70$); 9.09 (d, 2H; $J = 7.14$); 8.29–8.79 (m, 10H); 8.19 (d, 2H; $J = 7.10$); 7.73 (d, 2H; $J = 3.68$); 6.71–7.39 (m, 4H)
cis-$[Rh(biq)_2(OH)_2]PF_6 \cdot 3H_2O$	8.91–9.45 (m, 8H); 8.38 (d, 2H; $J = 8.65$); 8.17 (d, 4H; $J = 8.0$); 6.69–7.83 (m, 10H).
$[Rh(biq)_2(dmgm)]Cl \cdot 3H_2O$	9.0–9.5 (m, 9H); 8.10–8.29 (m, 4H); 7.69 (d, 1H; $J = 4.90$); 7.24 6.68 (m, 7H); 6.96 (d, 3H; $J = 3.62$); 1.26 [s, 6H (2-CH_3 protons of dmgm)].
$[Rh(biq)(CN)_3]_n$	9.30 [d, 2H, H (8, 8′); $J = 3.41$]; 8.97 [t, 4H, H (7, 7′), H (6, 6′}]; 8.72 (d, 2H; $J = 5.63$); 8.24 (d, 2H; $J = 6.4$); 8.01 (d, 2H; $J = 5.93$).

[a] In DMSO-d_6 with TMS as internal standard, at 80 MHz. d, doublet; m, multiplet; s, singlet; t, triplet.

The spectrum of $[Rh(biq)(CN)_3]_n$ is characterized by the presence of well resolved doublets and triplets. It shows a doublet for two deshielded [H(8,8′)] protons, which may be directed toward the cyanide ions. It is noteworthy that the NMR peak for the least deshielded protons appears at 8.01 ppm, whereas it is at much lower values for the complexes shown in Table 4.

Acknowledgements—We greatly appreciate the financial support from the Deanship of Research and Graduate Studies at Yarmouk University (Jordan) through projects 20/90 and 44/93.

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