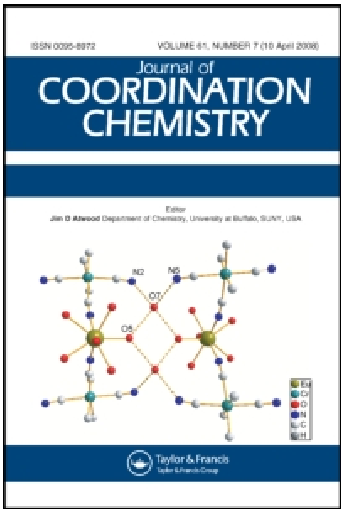

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COMPLEXES OF TECHNETIUM(V) AND RHENIUM(V) WTH 2,3-BIS(2-PYRIDYL)PYRAZINE (DPP) AND 2,3-BIS(2-PYRIDYL)QUINOXALINE (DPQ). EVIDENCE FOR SEVEN-MEMBERED CHELATE RING FORMATION IN DPQ COMPLEXES

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COMPLEXES OF TECHNETIUM(V) AND RHENIUM(V) WTH 2,3-BIS(2-PYRIDYL)PYRAZINE (DPP) AND 2,3-BIS(2-PYRIDYL)QUINOXALINE (DPQ). EVIDENCE FOR SEVEN-MEMBERED CHELATE RING FORMATION IN DPQ COMPLEXES

J.G.H. DU PREEZ, T.I.A. GERBER* and R. JACOBS

(Received February 18, 1994)

Complexes formed by the reaction of (n-Bu_4N)[$MOCl_4$] (M = Re, Tc) with the diimines 2,3-bis(2-pyridyl)pyrazine (DPP) and 2,3-bis(2-pyridyl)quinoxaline (DPQ) in ethanol were studied. With DPP as ligand, the monometallic complexes [$MOCl_2$(X)(DPP)] (M = Tc, Re; X = Cl, OEt) and the bimetallic compounds [$MOCl_2$(X)](μ-DPP) [$MOCl_2$(OEt)] (X = Cl for M = Tc; X = OEt for M = Re) were isolated. Infrared and ^{1}H NMR data suggest that coordination of DPP to the metals occurs in a bidentate manner through one pyrazine and one pyridine nitrogen atom to form a five-membered metallocycle. Only monometallic complexes of formulation [$MOCl_2$(X)(DPQ)] (X = Cl, OEt) could be isolated with DPQ as ligand, irrespective of the mol ratio of reactants. Experimental evidence suggests bidentate coordination of DPQ to the metals through the two pyridinic nitrogen atoms, with the two quinoxaline nitrogens not participating in bonding to the metals, to form a single seven-membered chelate ring.

KEYWORDS: technetium(V), rhenium(V), diimines, seven-membered chelate rings

INTRODUCTION

Ligands of the diimine type such as 2,3-bis(2-pyridyl)pyrazine (DPP) and 2,3-bis(2-pyridyl)quinoxaline (DPQ) (Figure 1) are closely related to pyrazine and 2,2'-bipyrimidine, of which dinuclear complexes have been well studied from structural and magnetic points of view.[1-4] Recently, the ligands DPP and DPQ have been used to control the properties of metal-to-ligand charge transfer excited states, principally for ruthenium-based systems.[5] However, little is known of the behaviour of these ligands towards other 4d and 5d transition metal cations, although their interaction with the 3d metals Fe(II),[1] Co(II), Ni(II) and Cu(II)[6-10] has been reasonably well studied.

The ligand DPQ has served as a model to discuss the structural ways in which these diimine compounds may act as ligands. Geary[6] pointed out the impossibility

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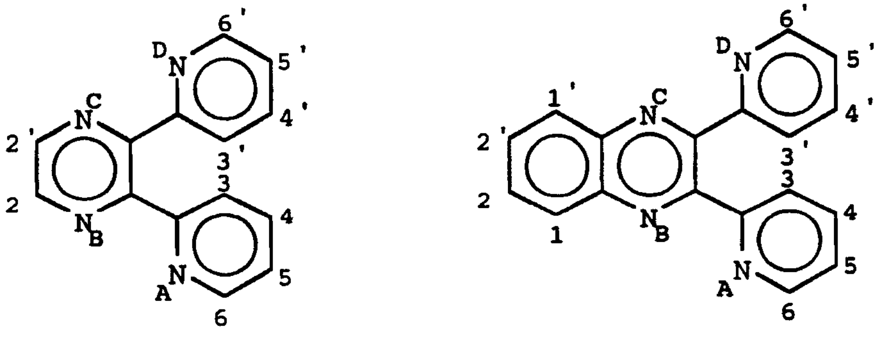

DPP DPQ

Figure 1 Ligands used in the study.

for the pyridine rings to be co-planar simultaneously with the quinoxaline system because of steric interactions between protons attached to the 3 and 3' positions (see Figure 1) of the pyridine rings. By analogy with the 2,2'-dipyridine (dipy) he considered chelate formation only through one N-pyridine and one N-pyrazine as donor atoms. This assumption has been experimentally corroborated by the structural determination[5] of $[Ru(DPQ)(dipy)_2](PF_6)_2$. Moreover, the angle between the plane of the pyrazine ring and the plane of the coordinated pyridine is 24°.

However, these diimine ligands can, in fact, also bind to metal ions by using the nitrogen atoms of the two terminal pyridine rings placed in a *cis*-conformation (Figure 1 shows them in the *trans*-conformation). This possibility, which gives a seven-membered chelate ring after coordination, was observed in the compound[11] $[Cu(DMeDPQ)(hfacac)_2]$ (DMeDPQ = 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline).

Based on the above arguments, it is therefore surprising that several dinuclear complexes with these ligands and interaction through the pyrazine have been reported.[1,12-16] The logical conclusion is that a necessary structural requirement should be imposed: from the in-plane conformation, the pyridyl groups must rotate in opposite directions with respect to the pyrazine plane to a reasonable angle, so that the steric hindrance becomes negligible but the overlap with the N-pyrazine atom will still be effective. This condition has been theoretically explored[17]: if the two pyridyls turn symmetrically the distance H_3—H_3' increases proportionally to the angle, while the distance between the N-pyridine and the N-pyrazinic atoms is practically constant. Under these conditions, it is possible to obtain dinuclear complexes with a minimum H_3-H_3' distance of 1.8Å with a torsion angle of *ca* 20°. This requirement forces the two metal centres out of the plane, one of them above and the other below, with the axis of coordination rotated with respect to the pyrazine. This torsion angle is not a requirement for the existence of mononuclear complexes in a five-membered chelate ring, because it is possible to have in the same plane the pyrazine and the pyridine ring which posses the nitrogen coordinating atoms but from structural information, the torsion angle exists: 24° in[5] $[Ru(DPQ)(dipy)_2]^{2+}$ and 14.6° and 13.4° in $[Co(BDPQ)(hfacac)_2]$ and $[Co(DMeDPQ)(hfacac)_2]$, respectively.[17]

In this study, complex formation of DPP and DPQ with rhenium(V) and technetium(V) was studied. Dinuclear complexes could only be isolated with the ligand DPP, and only mononuclear complexes were obtained with DPQ.

EXPERIMENTAL

Health Precautions

All references to technetium are to the isotope ^{99}Tc, which is a β-emitter (0.292 MeV) with a half-life of 2.12×10^5 years. Precautions have been detailed elsewhere.[18]

Materials

The compounds (n-Bu_4N)[$MOCl_4$] (M=Re, Tc) were prepared according to literature procedures.[19,20] The ligand DPP was obtained commercially (Aldrich), and DPQ was synthesized by a literature method.[21] All solvents were of analytical grade, and were purified and dried by standard methods.

Apparatus

Scientific instrumentation used in this study is the same as reported elsewhere.[22]

Syntheses of the Complexes

$[TcOCl_3(DPP)]\cdot 2H_2O$

A mixture of 24.4 mg (104 μmol) of DPP and 52 mg (104 μmol) of (n-Bu_4N)[$TcOCl_4$] in 20 cm^3 of ethanol was heated under reflux for 30 min, during which time a dark orange solid precipitated continuously from the dark red solution. After cooling to room temperature, the product was removed by filtration, washed with ethanol, acetone and diethyl ether, and dried under vacuum. The yield was 71% (based on Tc); m.p. > 300°C. It is insoluble in all the common organic solvents, slightly soluble in acetonitrile, and soluble in DMF and DMSO, in which it dissolves to give red-orange solutions, and which turn purple on standing for a few minutes. This decomposition of the product precluded its recrystallization and the obtaining of meaningful ^{1}H NMR and electronic spectra. However, the complex precipitated analytically pure from the preparative solution. Anal; calcd. for $C_{14}H_{14}N_4O_3Cl_3Tc$: C, 34.20; H, 2.87; N, 11.40; Cl, 21.63%. Found: C, 34.02; H, 2.79; N, 11.27; Cl, 21.74%. IR(KBr): ν(Tc=O) 982; ν(C=N) 1603, 1618, 1636; ν(Tc–Cl) 316, 321 cm^{-1}.

$[TcOCl_3(DPP\cdot HCl)]$

One cm^3 of a concentrated (12 M) HCl solution was added to 100 mg (200 μmol) of (n-Bu_4N)[$TcOCl_4$] in 5 cm^3 of ethanol, after which a solution of 47 mg (201 μmol) of DPP in 5 cm^3 of ethanol was added dropwise. The colour of the solution turned dark yellow, and the reaction solution was heated under reflux for one hour. After about 15 min a green precipitate started to form. After the heating was stopped, the solution was cooled to room temperature, and the product was removed by filtration, washed with ethanol and acetone, and dried under vacuum. The yield was 78% (based on Tc); m.p. > 300°C. Of all the common solvents, the product only dissolves in DMF, nitromethane (weakly), acetonitrile (weakly) and DMSO to give green solutions which turn orange-brown after a few minutes. Due to this instability, conductivity measurements, ^{1}H NMR and electronic spectra could not be obtained for this complex. Anal; calcd. for $C_{14}H_{11}N_4Cl_4OTc$: C, 34.17; H, 2.25; N, 11.39; Cl, 28.82%. Found: C, 34.29; H, 2.37; N, 11.33; Cl, 28.31%. IR(KBr): ν(Tc=O) 951; ν(C=N) 1604, 1616, 1638; $\nu(NH^+)$ 3126; ν(Tc–Cl) 318, 296 cm^{-1}.

$[TcOCl_3](\mu\text{-DPP})[TcOCl_2(OEt)]$

To 102 mg (204 μmol) of $(n\text{-}Bu_4N)TcOCl_4]$ in 5 cm^3 of ethanol was added 24 mg (102 μ mol) of DPP in 5 cm^3 of ethanol, and the mixture was heated under reflux for an hour. After 15 min of heating the colour of the solution turned dark red, and an orange-brown precipitate started to form. After heating was discontinued, the solution was cooled to room temperature, and the solid material was removed by filtration. The product was washed with ethanol and acetone (yield = 73%, based on DPP); m.p. >300°C. The compound is insoluble in common organic solvents, weakly soluble in nitromethane, and acetonitrile, and moderately soluble in DMF and DMSO. Anal; calcd. for $C_{16}H_{15}N_4Cl_5O_3Tc_2$: C, 27.99; H, 2.20; N, 8.16; Cl, 25.82%. Found: C, 27.99; H, 2.38; N, 8.44; Cl, 25.76%. IR(KBr): ν(Tc=O) 986, 936; ν(C=N) 1603, 1617; δ(OEt) 909; ν(Tc–Cl) 318, 321 cm^{-1}. ^{1}H NMR $[(CD_3)_2SO]$: $\delta(H_{2,2'})$ 8.93(s,2H), $\delta(H_{6,6'})$ 8.44(d,2H,5.1Hz), $\delta(H_{5,5'})$ 7.57(t,2H,5.6Hz), $\delta(H_{4,4'})$ 8.13(t,2H,7.3Hz), $\delta(H_{3,3'})$ 8.03(d,2H), $\delta(OCH_2)$ 3.18(q,2H), $\delta CH_3)$ 0.95(t,3H) ppm. Conductivity (10^{-3}M, DMF): 47 ohm^{-1}cm^{2}mol^{-1}. Electronic spectrum (CH_3CN, nm (ε M^{-1}cm^{-1})): 436(3600), 325(8600), 278(11500).

$[ReOCl_2(OEt)(DPP)]$

A solution of 81.1 mg (346 µmol) of DPP in 10 cm^3 of acetone was added dropwise to 99.5 mg (170 µmol) of $(n\text{-}Bu_4N)[ReOCl_4]$ in 10 cm^3 of ethanol to give an orange-brown solution. The mixture was heated under reflux for 30 min, and after cooling to room temperature, the orange precipitate that formed was removed by filtration. The filtrate was reduced in volume, and the addition of *n*-heptane gave a further crop of product, which was washed with ethanol and acetone, and dried under vacuum (yield 77%, based on Re); m.p. = 255°C. Anal; calcd. for $C_{16}H_{15}N_4O_2Cl_2Re$: C, 34.79; H, 2.74; N, 10.14; Cl, 12.83%. Found: C, 34.73; H, 2.56; N, 10.31; Cl, 12.66%. IR(KBr): ν(Re=O) 963; δ(OEt) 905; ν(C=N) 1570, 1588, 1603; ν(Re–Cl) 323 cm^{-1}. ^{1}H NMR $[(CD_3)_2SO]$: $\delta(H_2)$ 9.10(d,1H,3.3Hz), $\delta(H_6)$ 8.91(d,1H,5Hz), $\delta(H_{2'})$ 8.63(d,1H), $\delta(H_{6'})$ 8.58(d,1H), $\delta(H_5)$ 7.73(dd,1H), $\delta(H_{5'})$ 7.51(t,1H), $\delta(H_{4'})$ 8.21(td,1H), $\delta(H_4)$ 7.92(t,1H), $\delta(H_{3'})$ 8.06(d,1H), $\delta(H_3)$ 6.88(d,1H,8.3Hz), $\delta(OCH_2)$ 3.45(q,2H), $\delta(CH_3)$ 1.42(t,3H) ppm. Conductivity (10^{-3}M, CH_3CN): 24 ohm^{-1}cm^{2}mol^{-1}. Electronic spectrum (CH_3CN, nm (ε M^{-1}cm^{-1})): 508(2800), 313(11700), 272(17000).

(μ-DPP)[$ReOCl_2(OEt)]_2$

A mass of 20 mg (85 μmol) of DPP in 5 cm^3 of ethanol was added to a solution of 100 mg (171 μmol) of (n-Bu_4N)[$ReOCl_4$] in 10 cm^3 of ethanol. After heating the mixture under reflux for 1h, the purple product was removed after cooling to room temperature, washed with ethanol and acetone, and dried under vacuum. The yield was 73%, based on DPP; m.p. = 225°C. Anal; calcd. for $C_{18}H_{20}N_4O_3Cl_4Re_2$: C, 24.83; H, 2.32; N, 6.44; Cl, 16.29%. Found: C, 24.83; H, 2.32; N, 6.39; Cl, 16.51%. IR(KBr): ν(Re=O) 946; δ(OEt) 914; ν(C=N) 1577, 1603; ν(Re-Cl) 326 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: $\delta(H_{2,2'})$ 8.99(s,2H), $\delta(H_{6,6'})$ 8.53(d,2H,5.2Hz), $\delta(H_{5,5'})$ 7.69(t,2H,5.7Hz), $\delta(H_{4,4'})$ 8.24(t,2H,7.3Hz), $\delta(H_{3,3'})$ 8.12(d,2H), $\delta(OCH_2)$ obscured by d_6-DMSO peak, $\delta(CH_3)$ 1.07(t,3H), $\delta(CH_3)$ 0.95(t,3H) ppm. Conductivity (10^{-3}M, DMF): 35 $ohm^{-1}cm^2mol^{-1}$. Electronic spectrum (DMF, nm (ε $M^{-1}cm^{-1}$)): 578(3900), 310(14600), 278(17900).

[$TcOCl_2$(OEt)(DPQ)]

The addition of 58 mg (204 μmol) of DPQ in 10 cm^3 of ethanol to 100 mg (200 μmol) of (n-Bu_4N)[$TcOCl_4$] in 10 cm^3 of ethanol led to the immediate formation of a green precipitate. The solution was stirred for 30 min at room temperature, after which the solution was filtered. The green precipitate was washed with ethanol and acetone, and dried under vacuum. Due to the low solubility of the product in common organic solvents, recrystallization was not attempted. The yield was 76%, based on Tc; m.p. = 210°C (decomp). Anal; calcd. for $C_{20}H_{17}N_4O_2Cl_2Tc$: C, 46.62; H, 3.33; N, 10.87; Cl, 13.76%. Found: C, 46.48; H, 3.29; N, 10.80; Cl, 13.68%. IR(KBr): ν(Tc=O) 939; δ(OEt) 916; ν(C=N) 1561, 1601; ν(Tc-Cl) 314 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: $\delta(H_{6,6'})$ 8.45(dt,2H,5Hz), $\delta(H_{5,5'})$ 7.58(dt,2H), $\delta(H_{1,1'})$ 8.29(dd,2H,3.4Hz), $\delta(H_{2,2'})$ 8.04(dd,2H), $\delta(H_{3,3',4,4'})$ 8.14–8.18(m,4H), $\delta(OCH_2)$ 3.46(q,2H), $\delta(CH_3)$ 1.07(t,2H) ppm. Conductivity (10^{-3}M, DMF): 40 $ohm^{-1}cm^2mol^{-1}$. Electronic spectrum (CH_3CN, nm ($\varepsilon M^{-1}cm^{-1}$)): 453(900), 306(6400), 272(11300). The formation of this product is independent of the molar ratio of reactants, and it was isolated even with a tenfold molar excess of [$TcOCl_4^-$].

[$TcOCl_3$(DPQ)]

This complex was prepared by adding 1 cm^3 of a 12M HCl solution to 103 mg (206 μmol) of (n-Bu_4N)[$TcOCl_4$] in 10 cm^3 of EtOH, followed by the addition of 59 mg (208 μmol) of DPQ in 10 cm^3 of ethanol. Heating under reflux for 90 min gave a yellow solution, from which a yellow precipitate formed. After removal by filtration, the yellow product was washed with ethanol and acetone, and dried under vacuum at 40°C. The dry product was green in colour. Yield = 72%; m.p. = 242°C (decomp). Anal; calcd. for $C_{18}H_{12}N_4OCl_3Tc$: C, 42.75; H, 2.39; N, 11.08; Cl, 21.03%. Found: C, 42.46; H, 2.30; N, 10.97; Cl, 21.64%. IR(KBr): ν(Tc=O) 963; ν(C=N) 1561, 1611; ν(Tc–Cl) 296, 318 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: $\delta(H_{6,6'})$ 8.48(dt,2H,5Hz), $\delta(H_{5,5'})$ 7.65(dt,2H), $\delta(H_{1,1'})$ 8.30(dd,2H,3.5Hz), $\delta(H_{2,2'})$ 8.06(dd,2H), $\delta(H_{3,3'4,4'})$ 8.14–8.20(m,4H) ppm. Conductivity (10^{-3}M, DMF): 38 $ohm^{-1}cm^2mol^{-1}$. Electronic spectrum (DMF, nm ($\varepsilon M^{-1}cm^{-1}$)): 336(11500), 274(17300).

[$ReOCl_2(OEt)(DPQ)$]

A mass of 232 mg (816 μmol) of DPQ in 75 cm^3 of acetone was added with stirring to 104 mg (177 μmol) of (n-Bu_4N)[$ReOCl_4$] in 10 cm^3 of acetone. The colour of the solution turned red immediately on addition. After heating under reflux for 15 min, the red solution was decreased in volume (to about 15 cm^3) and 20 cm^3 of ethanol were added. The addition of ethanol changed the colour of the solution to green. Slow evaporation of the solvent led to the formation of small, dark green crystals, which were washed with ethanol and acetone after removal from solution. Yield = 66% (based on Re); m.p. = 238°C. Anal; calcd. for $C_{20}H_{17}N_4O_2Cl_2Re$: C, 39.87; H. 2.84; N, 9.30; Cl, 11.77%. Found: C, 40.10; H, 3.05; N, 9.47; Cl, 11.71%. IR(KBr): ν(Re=O) 955; δ(OEt) 911; ν(C=N) 1561, 1603; ν(Re–Cl) 326 cm^{-1}. ^{1}H NMR [$(CD_3)_2SO$]: $\delta(H_{6,6'})$ 8.52(dt,2H,5.5Hz), $\delta(H_{5,5'})$ 7.69(ddd,2H), $\delta(H_{1,1'})$ 8.32(dd,2H,3.1Hz), $\delta(H_{2,2'})$ 7.95(dd,2H), $\delta(H_{3,3',4,4'})$ 8.19–8.27(m,4H), $\delta(OCH_2)$ concealed by d$_6$-DMSO signal, $\delta(CH_3)$ 1.08(t,3H) ppm. Conductivity (10^{-3}, DMF): 34 ohm^{-1}cm^{2}mol^{-1}. Electronic spectrum (DMF, nm (εM^{-1}cm^{-1})): 422(400), 333(7400), 273(16000). This complex was also prepared in low yields by the heating under reflux of *trans*-$ReOCl_3(PPh_3)_2$ with DPQ in acetone/ethanol.

RESULTS AND DISCUSSION

Complexes with DPP

[$TcOCl_3$(DPP)]·$2H_2O$, [$TcOCl_3$(DPP·HCl)] and [$TcOCl_3$](μ-DPP)[$TcOCl_2$(OEt)]

The green-coloured complex [$TcOCl_3$(DPP·HCl)] was prepared in good yield by the reaction of (n-Bu_4N)[$TcOCl_4$] with DPP in an equimolar ratio in ethanolic aqueous HCl. In at the absence of hydrochloric acid, the complex $TcOCl_3$(DPP) was formed under the same experimental conditions. The dinuclear complex [$TcOCl_3$](μ-DPP)[$TcOCl_2$(OEt)] was synthesized by heating a twofold molar excess of (n-Bu_4N)[$TcOCl_4$] with DPP in ethanol under reflux conditions. The compounds are insoluble in common organic solvents, and they are poorly soluble in nitromethane, DMSO and DMF. Once in solution, the monomeric complexes decompose fairly rapidly (within a matter of minutes). This instability made recrystallization impossible, and it was therefore not worthwhile to study solution phenomena. As a result, ^{1}H NMR and electronic spectroscopic data are not reported and discussed. However, the complexes precipitated analytically pure from solution. They are stable for weeks in the solid state. The dinuclear compound is diamagnetic and dissolves to give orange-coloured solutions, which is stable enough to allow solution studies. Decomposition was only significant after about an hour.

There are major differences in the infrared spectra of the two monomeric complexes (see Figure 2). $TcOCl_3$(DPP) displays a strong band at 982 cm^{-1}, which is ascribed to the Tc^V=O stretching frequency. This frequency appears at 951 cm^{-1} in the complex $TcOCl_3$(DPP·HCl). These values are in agreement with those found for neutral six-coordinate oxotechnetium(V) complexes,[23–24] which normally occur in the region 920–985 cm^{-1}. In the complexes $TcOCl_3$(dipy) and $TcOCl_3$(phen),[25] with a nitrogen in the coordination site *trans* to the oxo oxygen, ν(Tc=O) appears at 980 and 977 cm^{-1}, respectively. Technetium(V) complexes with a chloride in this

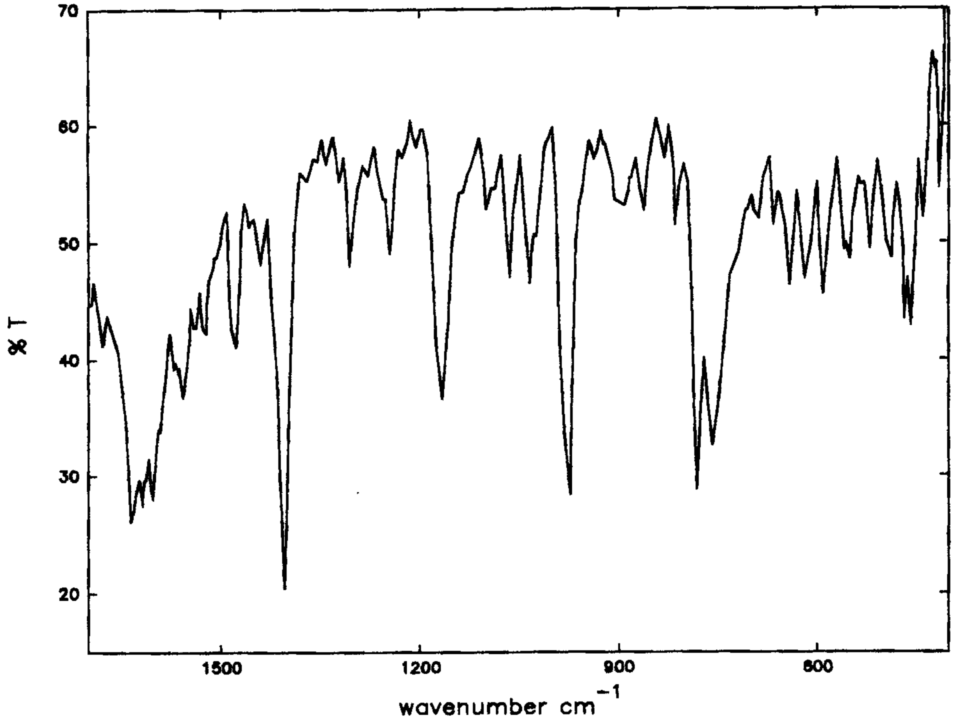

Figure 2 Infrared spectrum of [$TcOCl_3$(DPP)] in the range 400–1700 cm^{-1}.

trans position have the Tc=O stretching frequencies in the range[26–28] 930–960 cm^{-1}. Both complexes display three bands in the range 1600–1640 cm^{-1} due to ν(C=N) of the two pyridine and one pyrazine ring. These three bands imply that the two pyridine rings in the complexes are not equivalent. Similar results, together with a crystal structure determination,[5] have been used to corroborate the mode of coordination of DPQ to the metal in the complex [Ru(DPQ)$(dipy)_2$]$(PF_6)_2$ to be a five-membered ring involving chelation through a pyrazine and pyridine nitrogen atom. The complex $TcOCl_3$(DPP) exhibits only two bands for the three chlorides in the near-infrared at 316 and 321 cm^{-1}, and these frequencies are assigned to the Tc-Cl stretching vibrations, with the chlorides in positions *cis* to the oxo oxygen. These bands appear at 318 and 296 cm^{-1} in the compound $TcOCl_3$(DPP•HCl), with the latter value being ascribed to a chloride in the site *trans* to the Tc=O bond.

Two strong absorption bands at 986 and 936 cm^{-1} are displayed in the infrared spectrum of [$TcOCl_3$](μ-DPP)[$TcOCl_2$(OEt)]. The value 986 cm^{-1} has previously been related to a Tc=O bond having a nitrogen donor atom in the position *trans* to the oxo oxygen, while the 936 cm^{-1} value corresponds to that found for complexes with an ethoxide coordinated in the site *trans* to a technetyl oxo group. In $TcOCl_2$(OEt)(dipy), with the ethoxide *trans* to the Tc=O bond, ν(Tc=O) appears at 922 cm^{-1}. Only two bands are displayed for deformation vibrations of the two pyridine and pyrazine rings at 1603 and 1617 cm^{-1}. The frequencies appear at 1564 and 1586 cm^{-1} in the free ligand DPP. After coordination to the metal ions, there is a considerable increase in these frequencies, implying that coordination occurs through both the pyrazine as well as through both pyridinic nitrogen atoms. The only way that this can be achieved by the coordination of DPP to two metal ions is if the mode of coordination is a five-membered chelate ring involving bidentate coordination through a pyrazine and a pyridine nitrogen atom, with the pyridine rings placed in a *trans* conformation (as is shown in Figure 1). A peak of medium intensity at 321 cm^{-1} with a shoulder at 318 cm^{-1} is indicative of ν(Tc–Cl), with the chlorides in *cis* positions to the oxo oxygen.

The electronic spectrum of the free ligand DPP in acetonitrile is dominated by an intense absorption at 285 nm with a shoulder at 315 nm, and these are solvent independent. They have previously been ascribed to intraligand $\pi \rightarrow \pi^*$ transitions of the pyrazine and pyridine rings. In the metal complex these peaks shift to 278 and 325 nm respectively, and the new absorption at 436 nm is assigned to a ligand-to-metal charge transfer.

The ^1H NMR spectrum of the complex (Figure 3) illustrate the equivalence of the two pyridine rings, and also the equivalence of protons 2 and 2' after coordination. The spectrum integrates for a total of 15 protons, as is required for the formulation of the complex. The pattern of the spectrum is similar in most respects to that of the free ligand, except that the proton resonances are shifted further downfield. Protons 2 and 2' appear the furthest downfield as a singlet that integrates for two protons, at δ8.93 ppm. The equivalence of the two pyridine rings in the complex is

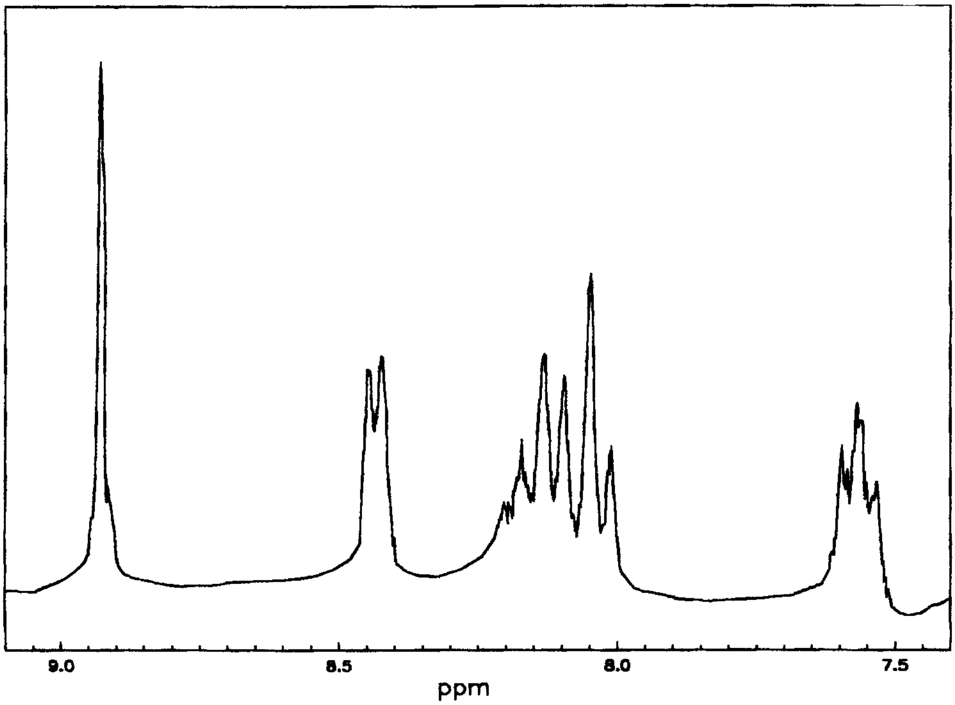

Figure 3 ^1H NMR spectrum of $[TcOCl_3](\mu\text{-DPP})[TcOCl_2(OEt)]$ in the range δ7.40–9.10 ppm.

illustrated by the equivalence of the corresponding protons on the two rings. The signal arising from the protons α to the nitrogen atom of the pyridine rings (protons 6 and 6') appears as a doublet at δ8.44 ppm, while the triplet the furthest upfield in the aromatic region at δ7.57 ppm is assigned to the equivalent protons 5 and 5'. The presence of the ethoxide is shown by a three-proton triplet at δ0.95 ppm and a two-proton quartet at δ3.18 ppm.

$[ReOCl_2(OEt)(DPP)]$ and $(\mu\text{-DPP})[ReOCl_2(OEt)]_2$

The mononuclear and dinuclear complexes were prepared by the reaction of an equimolar and twofold molar excess of $(n\text{-}Bu_4N)[ReOCl_4]$ with DPP under reflux conditions in ethanol, respectively. Both compounds are insoluble in common organic solvents, and moderately soluble in DMF, acetonitrile and DMSO. They were stable enough to allow solution studies, and decomposition in solution in the absence of oxygen did not present a problem. The complexes are non-electrolytes in DMF and acetonitrile, and they are stable in the solid state for months.

In the infrared spectrum the Re=O stretching frequencies appear in the expected range (940–960 cm^{-1}) for neutral six-coordinate rhenium(V) complexes with an ethoxide *trans* to the oxo group.[29] Three peaks in the range 1570–1605 cm^{-1} illustrate the inequivalence of the two terminal pyridine rings in the complex $[ReOCl_2(OEt)(DPP)]$, while only two bands appear in this region for the dinuclear complex. Only one peak is observed in the near-infrared for the ν(Re–Cl) in each complex, suggesting that the chlorides are coordinated *cis* to the oxo oxygen.

The inequivalence of the two pyridine rings in $[ReOCl_2(OEt)(DPP)]$ is illustrated by the ^1H NMR spectrum of the complex. If it is assumed that coordination of DPP occurs through nitrogens N_A and N_B, the one-proton doublet that appears the furthest downfield at δ9.10 ppm is assigned to proton 2, with the signal due to proton 2' appearing as a one-proton doublet at δ8.63 ppm. The data given in the Experimental Section for the complex illustrates the non-equivalence of the corresponding protons on the two pyridine rings.

The proton NMR spectrum of $(\mu\text{-DPP})[ReOCl_2(OEt)]_2$ provides ultimate proof that each rhenium ion is coordinated to DPP through a pyrazine and a pyridine nitrogen, forming a five-membered chelate ring. Proton 2 and 2' appear as a singlet the furthest downfield, with the equivalent protons 6 and 6' forming a doublet at δ8.53 ppm. All the other corresponding protons on the pyridine rings are shown to be equivalent.

Electronic spectra provide little information concerning properties of the complexes, and they are dominated by the intense absorptions due to the $\pi \rightarrow \pi^*$ transitions of the ligand DPP. The bands at 285 and 315 nm in the free ligand both undergo a red shift in the complexes.

Complexes with DPQ

The complexes $[MOCl_2(OEt)(DPQ)]$(M=Re, Tc) were prepared by the reaction of a molar excess of $(n\text{-}Bu_4N)[MOCl_4]$ with DPQ in the presence of ethanol. The compound $TcOCl_3(DPQ)$ was formed by performing the synthesis in an ethanolic aqueous hydrochloric acid solution. The formation of these products is independent of the molar ratio of reactants, and mononuclear compounds were isolated in every case. Bimetallic complexes with the ligand DPQ could not be isolated. The best solubility of these complexes is in the solvents DMSO, DMF and acetonitrile, in which they are non-conductors. The insolubility of the compounds in common organic solvents made it impossible for the growing of crystals for the purpose of a crystal structure determination.

Elemental analyses and spectroscopic evidence are consistent with the given formulations of the complexes. The M=O stretching vibrations for the complexes (see Figure 4) appear in the range expected for monooxometallate(V) complexes. All three complexes display only two bands in the range 1560–1611 cm^{-1}, which are assigned to ν(C=N) of the pyrazine and pyridine rings. These frequencies appear at 1560 and 1590 cm^{-1} in the free ligand DPQ. After the coordination to the metal, there is an increase in frequency of the 1590 cm^{-1} band, while the shift in the 1560 cm^{-1} band is insignificant. The significant shift of only the one band is indicative of coordination occuring through the nitrogen atoms of the pyridine rings, with the two pyrazine nitrogens not being coordinated at all. This implies that the two pyridine rings are in a *cis* conformation when coordinated in the complexes, and thus forming an unusual seven-membered chelate ring (in Figure 1 the ligand DPQ is shown in the *trans* conformation). A single peak of medium intensity in the near-infrared around 320 cm^{-1} for the complexes [$MOCl_2(OEt)(DPQ)$] suggests that the chlorides are in *cis* positions with respect to the oxo oxygen, with the ethoxide therefore occupying the *trans* site, as was found previously for similar compounds. $TcOCl_3(DPQ)$ has an additional band at 296 cm^{-1}, which is assigned to ν(Tc–Cl) of a *trans* chloride.

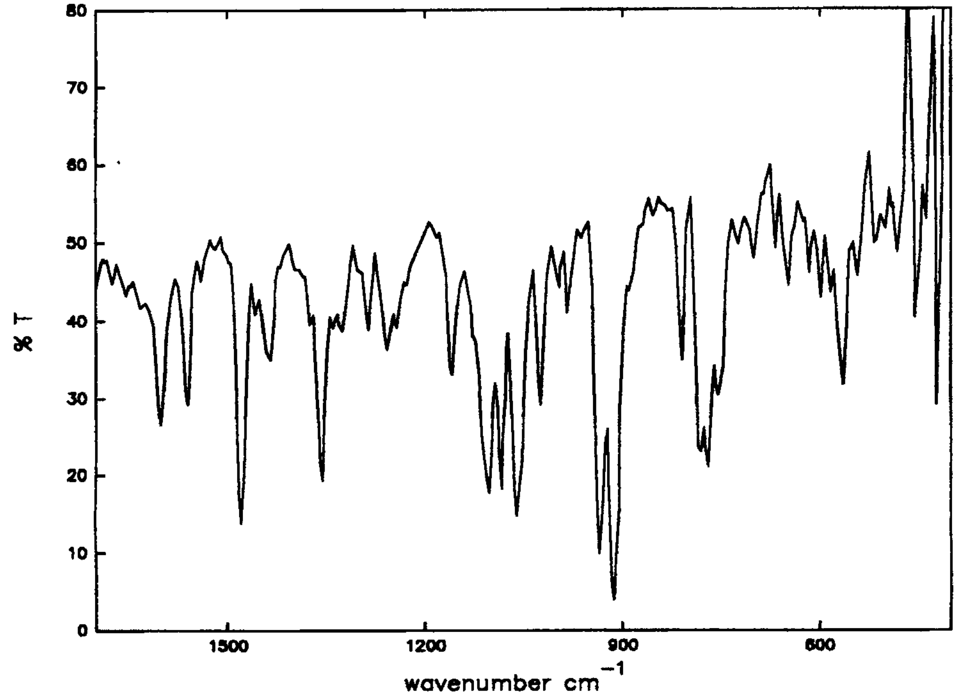

Figure 4 Infrared spectrum of [$TcOCl_2(OEt)(DPQ)$] in the range 400–1700 cm^{-1}.

The ^{1}H NMR spectra of the complexes (See Figure 5 for $TcOCl_2(OEt)(DPQ)$) provide convincing evidence for the existence of a seven-membered chelate ring in the DPQ complexes. They show that the pyridine rings in each of the three complexes are equivalent. The only way in which this can be achieved in mononuclear DPQ complexes is if the pyridine nitrogens are in *cis* positions relative to each other, and thus forming a seven-membered chelate ring *i.e.*, coordination occurs through nitrogens N_A and N_B. Protons 6 and 6' appear the furthest downfield as a two-proton doublet of a triplet around δ8.48 ppm (at δ8.26 ppm in free DPQ) (J_{H6-H5} = 5Hz for Tc complexes, 5.5 Hz for Re), and it couples with protons 5 and 5', which appear the furthest upfield in the aromatic region, as a doublet of a triplet for the technetium and as a doublet of a doublet of doublets for the rhenium complex, at around δ7.60 ppm (at δ7.36 ppm in free DPQ). The two doublets of doublets at about δ8.3 and δ8.0 ppm in the spectra are assigned to protons 1,1' and 2,2' respectively, which appear at δ8.23 and δ7.94 ppm in the spectrum of free DPQ (see Figure 1 for notation of protons). The very small downfield shift in the signals of these protons show their non-involvement in coordination to the metals. The presence of coordinated ethoxide in the complexes is again shown by a three-proton triplet around δ1.07 ppm and a quartet at about δ3.5 ppm.

Study of the technetium(V) and rhenium(V) complexes formed by the ligands DPP and DPQ was slightly hampered by solubility and stability problems, which prevented the growing of crystals suitable for crystal structure analyses. With the molecule DPP as ligand, the monometallic complexes $[MOCl_2(X)(DPP)]$ (M=Tc,

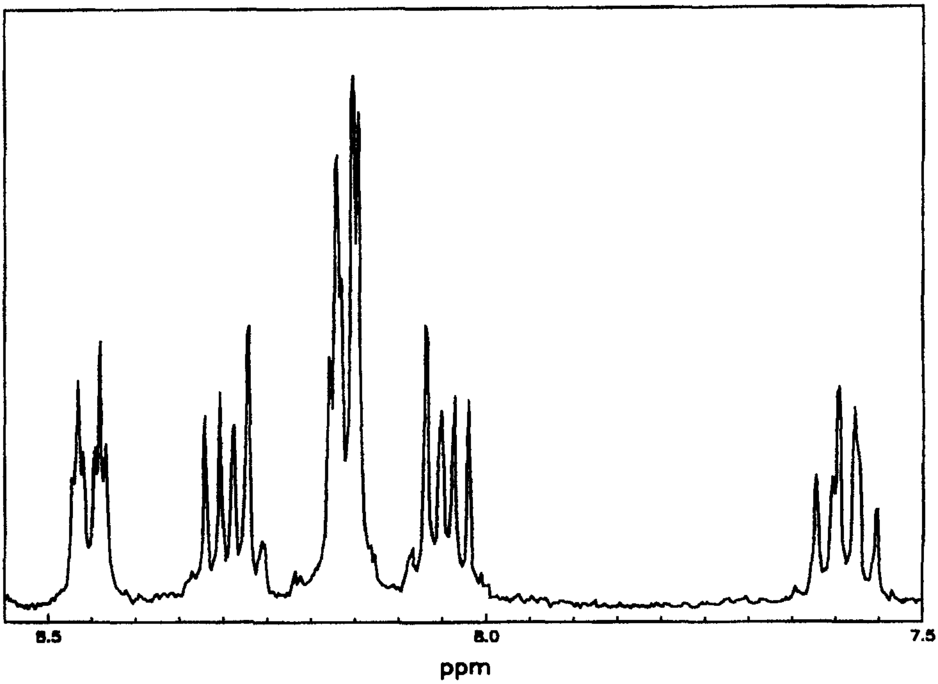

Figure 5 ^{1}H NMR spectrum of $[TcOCl_2(OEt)(DPQ)]$ in the range δ7.50–8.55 ppm.

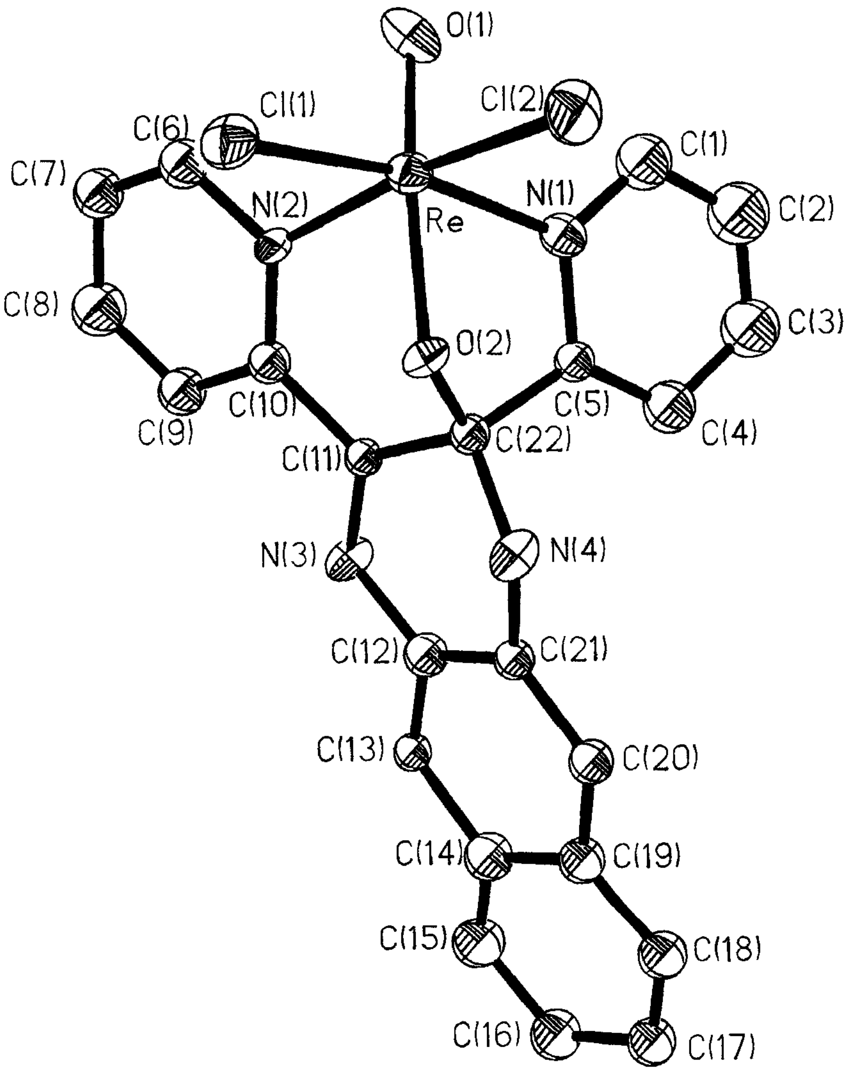

Figure 6 ORTEP drawing[30] of the complex [ReOCl_2(BBQ•OH)].

Re; X = Cl, OEt) and the bimetallic compounds [MOCl_2(X)] (μ-DPP)[MOCl_2(OEt)] (X = Cl for M = Tc; X = OEt for M = Re) were isolated. Spectroscopic and spectrometric evidence suggests the coordination of DPP to the metals to occur in a bidentate fashion through one pyrazine and one pyridine nitrogen atom, to form a five-membered metallocycle.

Only monometallic complexes of formulation [MOCl_2(X)(DPQ)](X = Cl, OEt) could be isolated with DPQ as ligand, irrespective of the molar ratio of reactants. The acquired experimental data could only be interpreted in terms of bidentate coordination of DPQ to the metals through the two pyridine nitrogen atoms, with the two quinoxaline nitrogens not participating in bonding to the metals, to form a single seven-membered chelate ring.

This major difference in the coordination behaviour of the ligands DPP and DPQ in technetium(V) and rhenium(V) complexes is ascribed to the fact that the fused benzo group in DPQ acts as an efficient blocking group in these complexes, with the hydrogen atoms on carbons 1 and 1' interacting sterically with any ligands in positions *trans* to the coordinating nitrogen atoms N_A and N_B in complexes where a five-membered chelate ring would be present.

It was recently shown[30] that the related ligand 2,3-bis(2-pyridyl)benzoquinoxaline (BBQ) forms a seven-membered chelate ring when coordinated to rhenium(V), and that coordinated BBQ undergoes metal-promoted nucleophilic addition of water to produce the condensation product "BBQH•OH". Deprotonation of this hydroxyl derivative enables the BBQ•OH moiety to act as a terdentate N,O^-, N-donor ligand. The crystal structure[30] of $ReOCl_2$(BBQ•OH) is illustrated in Figure 6. While bimetallic complexes of the ligand DPP are quite common in the literature,[1,17,31,32] it is rather surprising, based on the abovementioned arguments, that few studies on DPQ bimetallic complexes have appeared.[33-35].

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