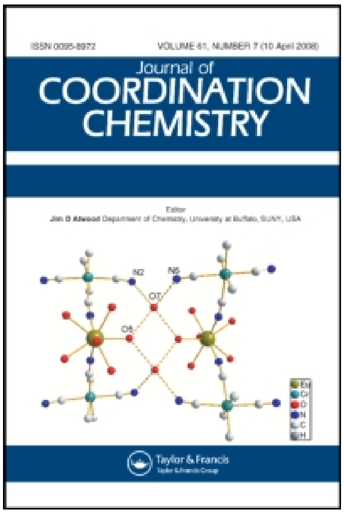

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Synthesis and Characterization of Six-Coordinate Cationic Technetium(V) And Rhenium(V) Complexes with *N*-(2-Oxidophenyl)Salicylideneiminate and Bidentate Aromatic Nitrogen-Donor Ligands

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SYNTHESIS AND CHARACTERIZATION OF SIX-COORDINATE CATIONIC TECHNETIUM(V) AND RHENIUM(V) COMPLEXES WITH *N*-(2-OXIDOPHENYL)SALICYLIDENEIMINATE AND BIDENTATE AROMATIC NITROGEN-DONOR LIGANDS

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Six-coordinate cationic complexes of rhenium(V) and technetium(V) with the tridentate *N*-(2-oxidophenyl)-salicylideneiminate ($OPhsal^{2-}$) and the bidentate aromatic nitrogen-donor ligands 2,2'-dipyridine, 1,10-phenanthroline, 2,2'-dipyridylamine and bis(2-pyridyl)ketone (NN) have been prepared. Complexes of general formula [MO(OPhsal)(NN)]X (M = Re, Tc; X = Cl, PF_6) were isolated by the reaction of $ReOCl(OPhsal)(PPh_3)$ and TcOCl(OPhsal) with the bidentate nitrogen-donor ligands. The reaction of TcOCl(OPhsal) with bis(2-pyridyl)ketone (dpk) in ethanol produced the complex [TcO(OPhsal)-(dpk.EtOH)]Cl, in which alcoholation of ethanol across the ketone double bond of dpk has occurred. Spectroscopic and analytical results obtained for all the isolated complexes suggest terdentate coordination of $OPhsal^{2-}$ in the equatorial plane *cis* to the oxo oxygen, with the bidentate pyridyl nitrogen-donor ligands bridging the fourth equatorial site and the position *trans* to the oxo group.

Keywords: Technetium(V), rhenium(V), six-coordination, cationic complexes

INTRODUCTION

During the last few years the coordination chemistry of the elements technetium and rhenium has received considerable attention.[1] The interest in these metals has been provided by the extensive use of Tc-99m in diagnostic imaging nuclear medicine[2] and the application of Re-186 as a potential radiotherapeutic agent for cancer,[3] as well as the realization that advances in these applications will depend on basic research into the inorganic chemistry of these metals. As the chemistry of technetium becomes more explored, it is becoming increasingly evident that it parallels that of rhenium to a large extent. Although major chemical differences between these two metals do exist, the relatively well studied chemistry of rhenium continually serves as a useful guide for basic studies of technetium.

The +5 oxidation state is the predominant state of the majority of technetium radiopharmaceuticals and it is undoubtedly the best defined in terms of the metal's inorganic chemistry. The most common core in this oxidation state is MO^{3+} (M = Tc, Re), which strongly influences the coordination of the ancillary ligands and configurations of the complexes formed. This influence of the MO^{3+} core is best illustrated by

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complexes containing Schiff base ligands. X-ray structure determinations have shown that the geometry of such complexes depends on the nature of the ligands. The neutral species [TcOCl(OPhsal)] (OPhsal = *N*-(2-oxidophenyl)salicylideneiminate) is a five-coordinate complex with a square-pyramidal configuration,[4] while the [TcO(OPhsal)(8-quinolinate)][5] and [TcOCl(Phsal)$_2$][6] (Phsal = phenylsalicylideneiminate) are six-coordinate complexes with distorted octahedral geometry. The vast majority of monooxotechnetium(V) complexes have a square-pyramidal or a distorted octahedral geometry, as is the case with the majority of monooxorhenium(V) complexes.

Examples of cationic six-coordinate complexes containing the MO^{3+} (M = Tc, Re) core are extremely scarce in the literature. Only one example of technetium, the complex [$Tc^{V}O(L)$][ClO_4] (L = pentadentate chelate with $N_3O_2^{2-}$ donor atoms), could be traced in the literature.[7] Rare examples of six-coordinate cationic monooxorhenium(V) complexes are [$ReOCl_2$(tacn)]X (X = Cl, BPh_4; tacn = triazacyclononane),[8] [$ReOCl_2(tu)_2(H_2O)$]Cl (tu = thiourea)[9] and [ReO(cyclam)(H_2O)]Cl_3 (cyclam = 1,4,8,11-tetraazacyclotetradecane).[10]

This paper deals with the synthesis of cationic six-coordinate monooxotechnetium(V) and monooxorhenium(V) complexes. Monocationic six-coordinate complexes of technetium in the oxidation states +1 and +3 have shown promise as myocardial imaging agents,[11] and thereby illustrate the propensity of the heart to accumulate positively charged metal ions.

The monocationic six-coordinate monooxometalate complexes reported in this account were prepared by substitution of TcOCl(OPhsal) and ReOCl(PPh_3)(OPhsal) with neutral, bidentate, aromatic nitrogen-donor ligands.

EXPERIMENTAL

Health Precautions

All references to technetium in this paper are to the isotope ^{99}Tc, which is a β-emitter (0.292 MeV) with a half-life of 2.12×10^5 years. Normal glassware gives adequate protection against this weak β-emission if this material is handled in milligram amounts. Secondary bremsstrahlung (X-rays) only presents a health hazard with larger amounts of technetium. Normal radiation safety procedures must be applied at all times, especially with the handling of solid samples, to prevent contamination and inhalation. All operations were carried out with gloves and in a fume hood.

Materials

The compounds (*n*-Bu_4N)[$TcOCl_4$][12] and *trans*-$ReOCl_3(PPh_3)_2$[13] were prepared according to literature procedures. The ligand H_2OPhsal was prepared by the condensation of salicylaldehyde with 2-aminophenol in ethanol. The aromatic nitrogen-donor ligands were obtained commercially (Fluka AG), and were used as received. All solvents were of analytical grade and were purified and dried by standard methods.[14] All common laboratory chemicals were of analytical grade and were used without further purification.

Apparatus

Infrared spectra were recorded on a Shimadzu FTIR-4100 and a Nicolet 20 DXC

FTIR spectrophotometer in the 4000–250 cm^{-1} range in KBr pellets. Optical spectra were obtained with a Shimadzu UV-3100 and a Perkin Elmer 330 spectrophotometer. ^{1}H NMR spectra were obtained at 300K with a Varian Gemini 200 MHz spectrometer. Thermogravimetric analyses were carried out using a Perkin Elmer thermogravimetric balance and a System 4 Microprocessor Controller. A Phillips PW 9509 digital conductometer was used to perform conductivity measurements, and elemental analyses were obtained with a Heraeus Rapid Analyzer. Chloride was determined by potentiometric titration with standard silver nitrate of solutions of the compounds decomposed by the Shoeniger method. Melting points were determined in capillaries using a Gallenkamp apparatus.

Synthesis of the Complexes

[ReOCl(PPh$_3$)(OPhsal)]

To 200 mg (240 μmol) of *trans*-ReOCl$_3$(PPh$_3$)$_2$ in 10 cm^3 of ethanol was added 150 mg (703 μmol) of H$_2$OPhsal in 5 cm^3 of ethanol. The reaction mixture was heated under reflux for an hour, during which time its colour changed from orange-yellow to dark maroon. After heating was stopped, the hot solution was filtered, and the volume decreased under reduced pressure. The maroon precipitate that formed was collected by filtration, washed with benzene and diethyl ether, and dried under vacuum. It was recrystallized from dichloromethane to give a yield of 78%; mp 167°C. Anal.; Calcd. for $C_{31}H_{24}NPO_3ClRe$: C, 52.36; H, 3.40; N, 1.97; Cl, 4.99%. Found: C, 52.80; H, 3.63; N, 2.02; Cl, 5.19%. Conductivity (10^{-3} M, CH$_3$CN): 3.1 ohm^{-1} cm^2 mol^{-1}. The same product was previously prepared[15] by the reaction of *cis*- or *trans*-[ReOCl(MeOH)(OPhsal)] with PPh$_3$ in methanol.

[TcOCl(OPhsal)]

This complex was prepared according to a literature procedure;[4] mp 274°C. Anal. Calcd. for $C_{13}H_9NO_3ClTc$: C, 43.17; H, 2.51; N, 3.87; Cl, 9.80%. Found: C, 43.31; H, 2.56; N, 3.56; Cl, 9.96%. ^{1}H n.m.r. [(CD$_3$)$_2$SO]: δ9.59 ppm (s, H, -C*H*=N-).

[ReO(OPhsal)(bipy)]PF$_6$

A solution of 100 mg (141 μmol) of ReOCl(PPh$_3$)(OPhsal) in 10 cm^3 of ethanol was added with stirring to 44 mg (282 μmol) of 2,2′-dipyridine (bipy) in 5 cm^3 of ethanol. This mixture was heated under reflux for 30 min, and after cooling to room temperature it was filtered and 2 cm^3 of a saturated ethanolic solution of NH$_4$PF$_6$ was added. After standing for a few minutes at room temperature, a fine, microcrystalline, dark golden-brown precipitate formed, which was removed by filtration, washed with diethyl ether and dried under vacuum. The yield was 76%, based on Re; mp > 250°C. The complex is soluble in acetonitrile and dichloromethane, weakly soluble in chloroform and insoluble in benzene, diethyl ether and hexane. Anal.; Calcd. for $C_{23}H_{17}N_3O_3F_6PRe$: C, 38.66; H, 2.40; N, 5.88%. Found: C, 38.74; H, 2.20; N, 5.67%. Conductivity (10^{-3} M, CH$_3$CN): 122 ohm^{-1} cm^2 mol^{-1}. ^{1}H n.m.r. [(CD$_3$)$_2$SO]: δ9.55 ppm (s, H, -C*H*=N-).

[ReO(OPhsal)(phen)]Cl

A solution of 56 mg (282 μmol) of 1,10-phenanthroline hydrate in 5 cm^3 of ethanol was added to 100 mg of ReOCl(PPh$_3$)(OPhsal) in 10 cm^3 of ethanol. After heating under reflux for 30 min, the solution was cooled to room temperature and filtered.

The solvent was partially removed under vacuum to about 3 cm^3, and *n*-heptane was added to precipitate a dark red-brown solid, which was removed by filtration, washed with diethyl ether and dried under vacuum. Recrystallization from dichloromethane gave fine, dark red-brown microcrystals. The yield was 72%; mp 217°C. The complex is soluble in ethanol, acetonitrile and dichloromethane, weakly soluble in chloroform and ethyl acetate, and insoluble in benzene, diethyl ether and hydrocarbons. Anal.; Calcd. for $C_{25}H_{17}N_3O_3ClRe$: C, 47.73; H, 2.72; N, 6.68; Cl, 5.64%. Found: C, 47.63; H, 2.50; N, 6.69; Cl, 5.99%. Conductivity (10^{-3} M, CH_3CN): 145 ohm^{-1} cm^2 mol^{-1}. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ9.54 ppm (s, H, -C*H*=N-).

[ReO(OPhsal)(bpa)]PF$_6$

To a solution of 100 mg of $ReOCl(PPh_3)$(OPhsal) in 10 cm^3 of dichloromethane was added 73 mg (426 μmol) of 2,2′-dipyridylamine (bpa) in 10 cm^3 of dichloromethane. After heating the mixture under reflux for 2 h, the solvent was removed under reduced pressure. The residue was dissolved in 10 cm^3 of ethanol, and 2 cm^3 of a saturated ethanolic solution of NH_4PF_6 were added. After standing overnight, the fine, microcrystalline, dark maroon product was filtered, washed with diethyl ether and dried under vacuum. No recrystallization was necessary to obtain a pure product. The yield was 81%; mp 178–180°C. The compound is soluble in ethanol, acetonitrile, dichloromethane and ethyl acetate, and insoluble in chloroform, benzene, diethyl ether and water. Anal.; Calcd. for $C_{23}H_{18}N_4O_3F_6PRe$: C, 37.86; H, 2.49; N, 7.68%. Found: C, 37.63; H, 2.80; N, 8.76%. Conductivity (10^{-3} M, CH_3CN): 132 ohm^{-1} cm^2 mol^{-1}. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ9.58 ppm (s, H, -C*H*=N-).

[TcO(OPhsal)(bipy)]PF$_6$

A mass of 86 mg (550 μmol) of 2,2′-dipyridyl was added to 100 mg (276 μmol) of TcOCl(OPhsal) in 15 cm^3 of acetonitrile. After heating under reflux for 30 min, the solution was cooled to room temperature and filtered. After reducing the volume to about 5 cm^3 under reduced pressure, a saturated ethanolic solution of NH_4PF_6 (2 cm^3) was added. After standing overnight, the dark green crystalline precipitate was removed, washed with ether, and dried under vacuum. No recrystallization was necessary to obtain an analytically pure sample. The yield was 81%; mp > 300°C. Anal; Calcd. for $C_{23}H_{17}N_3O_3F_6PTc$: C, 44.03; H, 2.73; N, 6.70%. Found: C, 44.21; H, 2.91; N, 6.29%. Conductivity (10^{-3} M, CH_3CN): 161 ohn^{-1} cm^2 mol^{-1}. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ10.15 ppm (s, H, -C*H*=N-).

[TcO(OPhsal)(phen)]Cl.H$_2$*O*

To a solution of 100 mg of TcOCl(OPhsal) in 10 cm^3 of ethanol was added 109 mg (552 μmol) of 1,10-phenanthroline hydrate in 5 cm^3 of ethanol. After heating under reflux for 30 min, the solution was cooled and filtered. After partial removal of the solvent under vacuum to about 3 cm^3, *n*-heptane was added to precipitate a green solid, which was collected by filtration, washed with diethyl ether and dried under vacuum. The product was recrystallized to give a yield of 69%; mp 168°C (decomp). The complex is soluble in ethanol, acetonitrile, dichloromethane and chloroform, and insoluble in benzene, diethyl ether and hexane. Anal.; Calcd. for $C_{25}H_{19}N_3O_4ClTc$: C, 53.63; H, 3.42; N, 7.51; Cl, 6.33%. Found: C, 53.83; H, 3.42; N, 7.51; Cl, 6.57%. Conductivity (10^{-3} M, CH_3CN): 125 ohm^{-1} cm^2 mol^{-1}. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ10.28 ppm (s, H, -C*H*=N-).

[TcO(OPhsal)(dpk.EtOH)]Cl

A mixture of 100 mg of TcOCl(OPhsal) in 10 cm^3 of ethanol and 100 mg (543 μmol) bis(2-pyridyl)ketone (dpk) in 5 cm^3 of ethanol was heated under reflux for 30 min. After cooling the solution to room temperature, the solvent was partially removed under vacuum, and *n*-heptane was added to precipitate a grey-green solid. After washing with diethyl ether, the product was recrystallized from ethanol/ether. The complex is soluble in ethanol, acetonitrile, dichloromethane, chloroform and carbon tetrachloride, and insoluble in hydrocarbons, water and ethyl acetate. The yield was 77%; mp>250°C. Anal.; Calcd. for $C_{26}H_{23}N_3O_4ClTc$: C, 52.76; H, 3.92; N, 7.10; Cl, 5.99%. Found: C, 52.42; H, 4.09; N, 6.87; Cl, 6.24%. Conductivity (10^{-3} M, CH_3CN): 137 ohm^{-1} cm^2 mol^{-1}. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ9.58 ppm (s, H, -C*H*=N-); 3.64 (q, 2H, -CH_2-); 1.29 (t, 3H, -CH_3).

RESULTS AND DISCUSSION

Oxorhenium(V) Complexes

Six-coordinate cationic monooxorhenium(V) complexes of general formula [ReO(Ophsal)(NN)]X (Ophsal^{2-} = *N*-(2-oxidophenyl)salicylideneiminate; NN = 2,2′-dipyridine, 1,10-phenanthroline, 2,2′-dipyridylamine; X = Cl, PF_6) were prepared by the reaction of ReOCl(OPhsal)(PPh_3) and neutral bidentate aromatic nitrogen-donor ligands under aerobic conditions in ethanol at refluxing temperature. The formation of these products is independent of the ligand-metal molar ratio, but the best yields and purest compounds were obtained with a 2:1 ligand-metal molar ratio. These complexes are all dark red-brown in colour, and they are soluble in a variety of polar solvents, in which they dissolve to give orange-red solutions. Conductivity measurements of the complexes in acetonitrile showed that they are 1:1 electrolytes, with Λ_M values of 10^{-3} M solutions in the range 122–145 ohm^{-1} cm^2 mol^{-1} (Λ_M in acetonitrile for 1:1 electrolytes = 120–160 ohm^{-1} cm^2 mol^{-1}).[16]

The reactions of ReOCl(OPhsal)(PPh_3) with bis(2-pyridyl)ketone and 2,2′:6′,2″-terpyridine in ethanol, benzene and dichloromethane led to the isolation of impure products, for which no sensible analyses could be obtained.

We have prepared the starting complex ReOCl(OPhsal)(PPh_3) by the reaction of *trans*-$ReOCl_3(PPh_3)_2$ with H_2OPhsal in a 3:1 ligand-metal ratio by heating under reflux in ethanol. The maroon-coloured complex is a non-electrolyte, with ν(Re=O) and ν(C=N) at 972 and 1603 cm^{-1}, respectively, in the solid state infrared spectrum. The presence of the PPh_3 molecule is indicated by the P-sensitive absorption at 1098 cm^{-1}, and there are no peaks which could be ascribed to ν(O—H). A single strong absorption at 1302 cm^{-1} is ascribed to ν(C—O), which indicates that both negatively charged oxygen atoms of the OPhsal^{2-} group coordinate to rhenium(V) in the plane *cis* to the oxo group.

The complex ReOCl(OPhsal)(PPh_3) has previously been prepared[15] by the reactions of [$ReOCl_3$(HOPhsal)]$^-$ or *cis*- or *trans*-[ReOCl(MeOH)(OPsal)] with PPh_3 in methanol at room temperature. The colour of the product was described as dark red violet, and the reported infrared data [ν(Re=O) = 975; ν(C=N) = 1605; ν(C—O) = 1298 cm^{-1}] correspond closely to our results. The value of the Re=O stretching vibration was considered[15] to be in agreement with the chlorine atom in the position *trans* to the oxo oxygen group, and a crystal structure determination[15] of ReOCl(OPhsal)(PMe_2Ph) has shown that coordination of the terdentate ligand

OPhsal^{2-} occurs in the equatorial plane *cis* to the oxo group, with the chlorine in the *trans* position.

Elemental analyses and spectroscopic evidence are consistent with the formulations of the cationic complexes [ReO(OPhsal)(NN)]X. The principal infrared spectral data are reported in Table I. The Re=O stretching vibration for the complexes [ReO(OPhsal)(bipy)]PF$_6$ and [ReO(OPhsal)(phen)]Cl appear at 984 and 980 cm^{-1}, respectively, with the corresponding vibration for [ReO(OPhsal)(bpa)]PF$_6$ appearing at a much lower frequency at 969 cm^{-1}. These values are in the range that was previously found for monooxorhenium(V) complexes. Complexes with a chloride in the *trans* position to the rhenyl oxo group in neutral distorted octahedral complexes[17–19] have the ν(Re=O) stretch in the 970–990 cm^{-1} region, while in complexes with a neutral solvent molecule in that position[15,20] it occurs in the narrow range 980–985 cm^{-1}. Complexes containing a charged phenolate oxygen in the *trans* position[5,21] have ν(Re=O) in the range 950–970 cm^{-1}. The Re=O stretching frequency in the neutral six-coordinate complexes ReOCl$_2$L (L = tridentate Schiff base ligands with an ONN donor atom set), with a nitrogen in the *trans* position to the rhenyl oxo oxygen,[22] occurs in the range 963–969 cm^{-1}.

There are no peaks in the near infrared region of the rhenium complexes prepared in this study which could be ascribed to ν(Re–Cl) and the band at 1098 cm^{-1} in the starting complex ReOCl(OPhsal)(PPh$_3$), ascribed to the presence of a coordinated PPh$_3$ molecule, disappears in the complexes [ReO(OPhsal)(NN)]X.

The PF$_6^-$ salts of the complexes contain no chloride, and the strong broad bands at about 843 cm^{-1} are reminiscent of the presence of ν(P–F). These results indicate that both the Cl$^-$ and PPh$_3$ have been substituted in ReOCl(OPhsal)(PPh$_3$) by the bidentate nitrogen donor ligands. A single strong peak in the range 1291–1296 cm^{-1} indicates that both negatively charged oxygen donor atoms of the OPhsal^{2-} ligand coordinate in the plane *cis* to the rhenyl oxo oxygen in the complexes. The ν(N–H) band in the complex [ReO(OPhsal)(bpa)]PF$_6$ occurs at 3121 cm^{-1} and is characteristic of coordination through the pyridyl nitrogen atoms.

^{1}H NMR spectra of the complexes in (CD$_3$)$_2$SO show the presence of the aldiminic protons at around δ9.60 ppm and the aromatic protons fall in the region δ6.7–8.5 ppm. The absence of O–H phenolic proton signals further supports the bis-phenolate coordination of the ligand OPhsal^{2-}.

TABLE I

Principal infrared spectral parameters (in cm^{-1}) of the complexes.*

Compound	ν(M=O)	ν(C=N)$^{\#}$	ν(C—O)
ReOCl(PPh$_3$)(OPhsal)	972	1603	1302
TcOCl(OPhsal)	986	1603	1291
[ReO(OPsal)(bipy)]PF$_6$	984	1607	1296
[ReO(OPhsal)(phen)]Cl	980	1603	1291
[ReO(OPhsal)(bpa)]PF$_6$	969	1604	1296
[TcO(OPhsal)(bipy)]PF$_6$	965	1607	1298
[TcO(OPhsal)(phen)]Cl	957	1601	1294
[TcO(OPhsal)(dpk.EtOH)]Cl	957	1605	1294

*In KBr discs. $^{\#}$ Of the coordinated ligand OPhsal^{2-}.

TABLE II
Electronic spectrum bands for the complexes in acetonitrile.

Complex	λ_{max}, nm (ε/M^{-1}cm^{-1})
[ReO(OPhsal)(bipy)]PF_6	489(3100), 403(5700), 336 sh, 296(29600). 239 sh
[ReO(OPhsal)(phen)]Cl	486(2950), 398 sh, 333 sh(6700), 291 sh, 269(25600)
[ReO(OPhsal)(bpa)]PF_6	506(1520), 406(1710), 325(13700), 286(8700), 248 sh
[TcO(OPhsal)(bipy)]PF_6	552(2100), 362 sh, 335(13500), 285(19600), 234(30300)
[TcO(OPhsal)(phen)]Cl	558(1350), 365 sh, 330(6800), 266(22700), 247(32200)
[TcO(OPhsal)(dpk.EtOH)]Cl	502(1550), 362(12400), 334(12750), 268(34500), 228 sh

The electronic spectra (Table II) of the rhenium complexes in acetonitrile are of a complex nature, and display intense absorption maxima around 250 and 290 nm, which are ascribed to the $\pi \rightarrow \pi^*$ transitions of the nitrogen donor ligands. The peak around 330 nm is assigned to the oxo oxygen-to-rhenium(V) charge transfer, as was previously assigned in rhenium(V) complexes with Schiff base ligands.[20-22] Additional bands of lower intensity around 400 and 500 nm are probably due to ligand-to-metal charge transfer absorptions.

The spectroscopic and analytical results obtained suggest that the complexes [ReO(OPhsal)(NN)]X are cationic six-coordinate compounds, with $OPhsal^{2-}$ acting as a terdentate and the nitrogen-donor ligands acting as bidentates. The ligand $OPhsal^{2-}$ with its ONO donor atom set coordinates in the equatorial plane *cis* to the rhenyl oxo group, and the bidentate nitrogen donor ligands span the fourth equatorial and *trans* coordination site.

Examples of cationic rhenium(V) monooxo complexes are rare. The six-coordinate species [$ReOCl_2$(tacn)]Cl was prepared by the reaction of (n-Bu_4N)[$ReOCl_4$] or $ReOCl_3(PPh_3)_2$ with the terdentate nitrogen donor ligand tacn,[23] and it was shown to have a nitrogen atom in the position *trans* to the rhenyl oxo group,[8] with ν(Re=O) at 979 cm^{-1}. The complex [ReOL]BPh_4, where L = the quinquedentate ligand 3,3′-diamino-*N*-methyldipropylamine with a $ONNNO^{2-}$ donor atom set, has ν(Re=O) at 957 cm^{-1} and it was suggested that the coordination site *trans* to the rhenyl oxo group is occupied by a negatively charged phenolate oxygen atom.

Oxotechnetium(V) Complexes

Complexes of general formula [TcO(OPhsal)(NN)]X (NN = 2,2′-dipyridine, 1,10-phenanthroline, X = PF_6, Cl) were isolated in good yield by heating a twofold excess of the bidentate nitrogen-donor ligands with TcOCl(OPhsal) in ethanol or acetonitrile under aerobic conditions. The use of equimolar quantities of reactants in these reactions gave the same products, but lower yields. The complexes are dark green in colour, and are 1:1 electrolytes in acetonitrile. They dissolve in most polar organic solvents to give green solutions, which are stable for hours.

The reaction of a twofold excess of bis(2-pyridyl)ketone with TcOCl(OPhsal) in ethanol led to the isolation of a grey-green product, which we formulate as [TcO(OPhsal)(dpk.EtOH)]Cl. Spectroscopic and analytical data (see above) suggest alcoholation of ethanol across the ketone double bond of dpk. This complex is a 1:1 electrolyte in acetonitrile, and it dissolves in most polar organic solvents to give green solutions.

The reaction of TcOCl(OPhsal) with 2,2′-dipyridylamine and 2,2′:6′,2″-terpyridine in ethanol led to the oxidation of technetium(V) and the isolation of impure products in low yields. A very strong broad peak around 900 cm^{-1} in the infrared spectra of these oxidation products is indicative of multiple $Tc^{VII}=O$ stretches.

The starting complex TcOCl(OPhsal) was prepared previously,[4] and a crystal structure determination[4] revealed that the $OPhsal^{2-}$ ligand occupies three of the four coordination sites of the basal plane of an approximate square pyramid around technetium. The fourth equatorial site is occupied by the chlorine atom, and the position *trans* to the oxo oxygen, in the apical position, is vacant. This vacant *trans* site in square-pyramidal Schiff base complexes of monooxotechnetium(V) has been shown[24] to be readily occupied in solution by monodentate ligands such as pyridine and diethylamine. We therefore suggest that the formation of the technetium(V) complexes prepared in this study proceeds by attack of a pyridine nitrogen of the bidentate ligands at the vacant site *trans* to the oxo oxygen, followed by chelation and substitution of the chloride in TcOCl(OPhsal).

In the infrared spectra of the complexes prepared in this study, the Tc=O stretching vibration occurs in the narrow range 957–965 cm^{-1} (Table I), which is in the region (920–1020 cm^{-1}) normally found for monooxotechnetium(V) complexes. It is on average 20 cm^{-1} lower in frequency than for similar oxorhenium(V) complexes. Cationic square-pyramidal complexes of oxotechnetium(V)[25] have ν(Tc=O) in the range 978–984 cm^{-1}, and in neutral six-coordinate complexes with a nitrogen atom in the *trans* position[22] in the range 950–956 cm^{-1}.

The cationic complexes prepared in this study contains no peaks in the infrared spectra ascribable to ν(Tc–Cl), and a single strong peak in the range 1294–1298 cm^{-1} is assigned to ν(C–O), indicating that both negatively charge phenolate oxygen atoms of the ligand $OPhsal^{2-}$ coordinate in the equatorial plane *cis* to the oxo group. The salt $[TcO(OPhsal)(bipy)]PF_6$ displays a strong broad absorption around 840 cm^{-1}, indicative of the presence of multiple P–F stretching vibrations.

The ν(C=O) band at 1675 cm^{-1} in the free ligand dpk disappears upon coordination in ethanol, and there are no peaks in the infrared spectrum of the complex [TcO(OPhsal)(dpk.EtOH)]Cl which could be assigned to a C=O stretching vibration. A broad peak at 3484 cm^{-1} indicates the presence of an OH group in the complex, and an additional peak at 1089 cm^{-1} is ascribed to the presence of the ether group $>C-O-CH_2-$. In the ^1H NMR spectrum of the complex, there is a three-proton triplet at δ1.29 ppm ($-CH_3$) and a two-proton quartet at δ3.69 ppm ($-CH_2-CH_3$), which differ from that of free ethanol. It is thus clear that ethanol adds across the ketone of the *N*,*N*-coordinated dpk, and that the ligand is present in the form $(C_5H_4N)_2C(OH)(OCH_2CH_3)$ in the complex.

Similar additions of protic molecules across the ketone in dpk metal complexes have previously been observed. Bis(2-pyridyl)ketone can exhibit two modes of coordination: *N*,*O*-coordination generating a five-membered chelate ring and *N*,*N*-coordination (six-membered chelate). Several transition metal complexes with dpk have been prepared and were proposed to be *N*,*N*-chelated,[26] and it has been shown that water adds across the ketone of *N*,*N*-coordinated dpk to afford stable *gem*-diols.[27] Further studies[28,29] have demonstrated that nucleophiles add after the formation of the *N*,*N*-coordinated complex. It was proposed[28] that the possible driving force for the metal-promoted ketone hydration of dpk, in which the sp^2-hybridized ketonic carbon atom of dpk is replaced by a tetrahedral centre, may be thermodynamically favoured in the presence of a metal ion in that it enables the ligand to coordinate by the maximum number of strong metal-nitrogen bonds without introducing at the same time non-bonded repulsive interactions with *trans* ligands or angle strain. Ketones do not normally hydrate to any significant extent unless they are flanked on either side by very strong electron-withdrawing groups.

In the ^{1}H NMR spectra of the complexes [TcO(OPhsal)(NN)]X, the presence of the aldiminic protons is indicated by a signal around δ10.2 ppm, and the aromatic (δ6.7–8.8 ppm) region integrates for 16 protons for all the complexes.

The electronic spectra of the complexes are very similar to those of other oxotechnetium(V) complexes containing Schiff base and nitrogen-donor ligands,[7,20,22,25] and they reveal intense absorption maxima in the ultraviolet region around 270 nm, which are ascribed to $\pi \rightarrow \pi^*$ transitions of the dipyridyl ligands. The peaks around 330 nm are assigned to the oxo oxygen-to-technetium(V) charge transfer, and the two additional absorptions of lower intensity in the visible region are the result of ligand-to-metal charge transfer transitions.

The spectroscopic and analytical results obtained in this study for the cationic six-coordinate complexes $[MO(OPhsal)(NN)]^+$ (M = Re, Tc) suggest terdentate coordination of the ligand $OPhsal^{2-}$ in the equatorial plane *cis* to the oxo oxygen, with the bidentate pyridyl nitrogen-donor ligands spanning the fourth equatorial site and the position *trans* to the oxo group.

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