Complexes of Technetium, Rhenium, and Rhodium with Sexidentate Schiff-Base Ligands

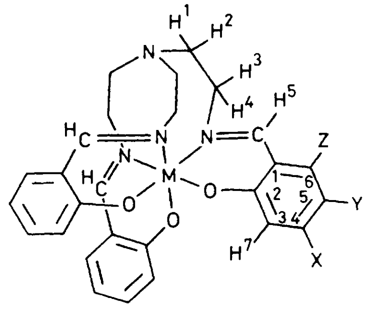
Geoffrey Hunter* and Neil Kilcullen
Department of Chemistry, The University, Dundee DD1 4HN

The monocationic technetium(IV) and rhenium(IV) complexes with the sexidentate Schiff-base ligands tris[2-(2′-hydroxybenzylideneethyl)]amine and its substituted derivatives have been prepared and their electrochemical properties studied. The variable-temperature 90.6 MHz $^{13}C-\{^1H\}$ n.m.r. spectrum of the rhodium(III) complex of tris[2-(2-hydroxy-5′-isopropylbenzylideneethyl)-amine] has been observed, indicating fluxionality at temperatures above 218 K.

In diagnostic nuclear medicine a radionuclide is used to visualise organs and tissues of the body. Technetium-99m, as a result of its ready availability and highly suitable nuclear properties, has emerged as the radionuclide of choice in nuclear medicine and technetium in its various chemical forms is routinely used to image the brain, liver, kidneys, lungs, thyroid, and skeleton.[1] In the search for practical ^{99m}Tc heart imaging agents the generally adopted approach has followed that of Deutsch *et al.*[2] who found that technetium complexes carrying a single positive charge apparently accumulate in myocardial tissue. Thus technetium(I) complexes such as $[Tc(CNR)_6]^+$ and $[Tc(dmpe)_3]^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$) and technetium(III) complexes such as $[Tc(pdma)_2Cl_2]^+$ [pdma = *o*-phenylenebis(dimethylarsine)] and $[Tc(dmpe)_2Cl_2]^+$ have been extensively investigated as potential heat imaging agents.

As part of our investigations of complexes of technetium with potential application to myocardial imaging, we now report the preparation and characterisation of stable monocationic complexes of this metal and of its heavier congener, rhenium, in their IV oxidation state with sexidentate Schiff-base ligands formed by the condensation of tris(2-aminoethyl)amine (tren) with salicylaldehyde (H_3L^1) and its 4′-methoxy (H_3L^2) and 4′,6′-dimethoxy (H_3L^3) derivatives (Figure 1). While many technetium and rhenium complexes of mono-,[3] bi-,[4] tri-,[5] quadri,[6] and quinque-dentate[7] Schiff-base ligands have been reported, to our knowledge there have been no reports of complexes of these metals in any oxidation state with sexidentate Schiff-base ligands. This paper also addresses the question of the fluxionality of these chiral complexes of C_3 symmetry and describes the variable-temperature $^{13}C-\{^1H\}$ n.m.r. spectrum of the neutral, diamagnetic rhodium(III) complex, $[RhL^4]$. Biodistribution studies of the radioactive $[TcL^1]^+$ complexes will be reported elsewhere.

It has become apparent that, at physiological pH, sexidentate Schiff bases can have considerably greater binding strength towards metal ions than do some better known sexidentate ligands such as *N,N,N′,N′*-ethylenediaminetetra-acetic acid (H_4edta).[8] Moreover, as substituents on the Schiff-base ligand can be varied prior to complexation, there is the added advantage of being able to modify the charge and/or the lipophilicity of a complex while still retaining the same metal ion in a given formal oxidation state and in the same co-ordination environment. Potentially, therefore, sexidentate Schiff bases can provide the basis for a versatile series of ligands, able to form stable metal complexes with a common skeletal geometry but with overall charge and lipophilicity tailored to a specific requirement. There is, however, a practical limitation to the general synthesis of these metal complexes: most neutral Schiff-base ligands do not dissolve in water and those that do undergo rapid hydrolysis, as do some metal ions, particularly those of high charge density. Nevertheless, by judicious choice of a non-aqueous solvent system it may still be possible to prepare water-soluble Schiff-base complexes which are unobtainable from aqueous solution.



$[ML]^{n+}$ (M = Tc, Re, or Rh)

	X	Y	Z
L^1	H^8	H^9	H^{10}
L^2	OMe	H^9	H^{10}
L^3	OMe	H^9	OMe
L^4	H^8	Pr^i	H^{10}
L^5	H^8	Cl	H^{10}

Figure 1. Idealised structure for the $[ML]^{n+}$ [n = 0 or 1] complexes showing the numbering scheme used in assigning ^1H n.m.r. resonances of the ligands (Experimental section)

Results and Discussion

Technetium has no stable isotopes and the work described below was performed using long-lived ^{99}Tc ($t_{\frac{1}{2}}$, 2.13 × 10^5y).

The reactions of $[MCl_6]^{2-}$ (M = Tc or Re) with trianionic sexidentate Schiff-base ligands should produce monocationic complexes, although particularly for technetium it would not be unexpected for halide substitution to be accompanied by changes in oxidation state. In aqueous solution at high pH or at elevated temperature both $[TcCl_6]^{2-}$ and $[ReCl_6]^{2-}$ rapidly disproportionate while the Schiff bases are insoluble. However, after investigating a number of non-aqueous solvents such as methanol, ethanol, and acetonitrile, we found glacial acetic acid to be particularly suitable. Deprotonation of the Schiff base was assisted by the addition of sodium acetate as proton scavenger to the reaction mixture. The salts $[NH_4]_2[TcCl_6]$ and

Table 1. I.r., h.p.l.c., and elemental analysis data

Compound	Infrared absorptions (cm^{-1})			H.p.l.c.[a]	Elemental analyses[b] (%)		
	ν(C=N)	ν(C–O)	ν(P–F)	t_R(min)	C	H	N
H_3L^1	1 634	1 281					
$[TcL^1]PF_6$	1 603	1 295	845	8.10			
$[ReL^1]PF_6$	1 604	1 298	845	8.10	41.6 (41.2)	3.7 (3.5)	6.9 (7.1)
H_3L^2	1 625	1 292					
$[TcL^2]PF_6$	1 610	1 301	845	8.85			
$[ReL^2]PF_6$	1 611	1 303	845	8.85	39.5 (41.1)	3.1 (3.8)	6.2 (6.4)
H_3L^3	1 621	1 231					
$[TcL^3]PF_6$	1 600	1 295	845	9.00			
$[ReL^3]PF_6$	1 611	1 308	845	9.00	40.2 (41.0)	3.8 (4.1)	6.1 (5.8)

[a] Conditions and gradient profile as described in the Experimental section. [b] Calculated values in parentheses. Identification of the technetium complexes was by their electrophoretic behaviour and h.p.l.c. retention times identical to those of their rhenium homologues.

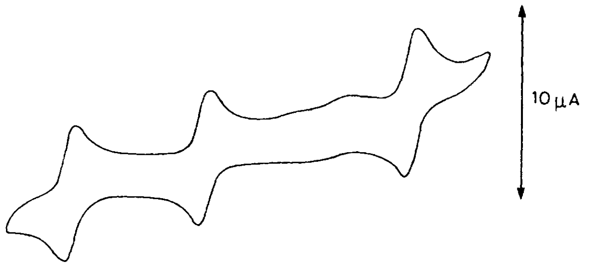


Figure 2. Cyclic voltammogram of $[ReL^1]PF_6$ in CH_2Cl_2 solution. Scan rate 200 mV s^{-1}

$K_2[ReCl_6]$ are insoluble in glacial acetic acid but nevertheless halide substitution proceeded smoothly on reflux to give intensely coloured solutions of the desired complexes. As rhenium halides have been previously shown to react with acetic acid,[9] rather surprisingly no traces of technetium or rhenium acetates were detected among the reaction products. Removal of the solvent under reduced pressure, extraction of the cationic metal complex with water, and the addition of an aqueous solution of ammonium hexafluorophosphate to the extract caused precipitation of $[ML]PF_6$ ($L = L^1$—L^3), the purity of which was confirmed by high-performance liquid chromatography (h.p.l.c.). Although all of the complexes (Table 1) were obtained as microcrystalline powders soluble in polar organic solvents, in no case did recrystallisation give crystals of a quality suitable for *X*-ray crystallographic analysis. Molar conductance measurements in acetonitrile gave values in the range anticipated for 1:1 electrolytes and electrophoresis experiments showed that the metal complex ion migrated towards the cathode.

Cyclic Voltammetry.—The $[ReL^1]PF_6$ (complex) in dichloromethane exhibits three redox couples (Figure 2), each deemed to be quasi-reversible as the $E_{pa} - E_{pc}$ values are close to the Nernstian value of 59 mV and each of the ratios of anodic to cathodic peak currents is close to unity. The first wave observed, with $E_{\frac{1}{2}} = -0.57$ V (*vs.* Ag–AgNO$_3$), was assigned to the reduction of the $[ReL^1]^+$ cation to the neutral $[ReL^1]$ species (*i.e.* $Re^{IV} \rightleftharpoons Re^{III}$). The neutral species then exhibited a further reduction to the $[ReL^1]^-$ anion ($Re^{III} \rightleftharpoons Re^{II}$) with $E_{\frac{1}{2}} = -1.67$ V. The $[ReL^1]^+$ cation can also be oxidised to the $[ReL^1]^{2+}$ species ($Re^{IV} \rightleftharpoons Re^V$), $E_{p_a} = +0.18$ V, which can then be reduced back to the original $[Re(L^1)]^+$ species ($E_{\frac{1}{2}} = +0.15$ V).

The addition of a methoxy group to the aromatic rings renders the complex less susceptible to reduction, since the initial reduction reaction ($E_{pa} - E_{pc} = 120$ mV, $I_{pa}/I_{pc} = 1$) was not observed until $E_{\frac{1}{2}} = -0.69$ V. A further reduction of $[ReL^2]$ to $[ReL^2]^-$ ($Re^{III} \rightleftharpoons Re^{II}$) ($E_{pa} - E_{pc} = 140$ mV, $I_{pa}/I_{pc} = 1$) was observed at $E_{\frac{1}{2}} = -1.89$ V. On oxidation, $[ReL^2]^+$ appears to lose two electrons ($E_{pa} = -0.03$ V, $I_{pa}/I_{pc} = 2$) to yield the rhenium(^{VI}) species $[ReL^2]^{3+}$, but the return wave is a single-electron reduction of $[ReL^2]^{2+}$ to $[ReL^2]^+$ ($E_{pc} = +0.33$ V, $I_{pa}/I_{pc} = 1$) and the reduction Re^{VI} to Re^V was not observed. The oxidation of the Re^{IV} to the Re^{VI} for the substituted complex therefore occurred at only a slightly higher potential than the oxidation of $[ReL^1]^+$ to $[ReL^1]^{2+}$ (*viz.* $E_{pa} = +0.32$ V, *cf.* $+0.18$ V *vs.* Ag–AgNO$_3$). The methoxy-substituted complex is thus easier to oxidise but more difficult to reduce than $[ReL^1]^+$.

The $[TcL^3]^+$ species was reduced to the neutral species with relative ease ($Tc^{VI} \rightleftharpoons Tc^{III}$, with $E_{\frac{1}{2}} = -0.53$ V *vs.* Ag-AgNO$_3$), and we consider that the reduction would have been reversible but for the electrode being poisoned by the reduced species. The ease of reduction, compared with the rhenium complexes studied, can be attributed to the generally easier reduction of Tc compared with Re.[1] No oxidation of the initial technetium(^{IV}) species to higher oxidation states was observed.

Comparisons with literature data (Table 2) show $[ML^1]^+$ to be more susceptible to reduction than either $[M(dmpe)_2Cl_2]^+$ or $[M(pdma)_2Cl_2]^+$. However, the addition of methoxy-groups stabilises the +IV oxidation state to the extent that $[TcL^3]$ is comparable with $[Tc(dmpe)_2Cl_2]^+$ and less susceptible to reduction than $[Tc(pdma)_2Cl_2]^+$. In contrast, $[Tc(PEt_3)_2(acen)]^+$ [acen = *NN'*-ethylenebis(acetylacetoneiminate)] shows a remarkable range of stability for the technetium(III) oxidation state.

Fluxionality of Metal Complexes of Sexidentate Schiff-base Ligands.—*X*-Ray crystallographic structures have been reported for the neutral metal (III) complexes $[ML^5]$ (M = Fe,[10] Cr,[11] or Mn[11]). As might be anticipated the overall geometry of these complexes is apparently controlled by the steric constraints imposed by the crowded sexidentate encapsulating ligand. In all three cases an octahedral arrangement of the ligand (N_3O_3) atoms about the metal was observed and there was no indication of heptadentate behaviour by the ligand. The overall molecular symmetry was C_3, with the three-fold axis passing through the metal and the apical nitrogen of the $N(CH_2CH_2)_3$ part of the ligand. These molecules are of course chiral, the usual helicity of metal-tren complexes in this case being accentuated by the three-bladed propeller-like conformation adopted by the salicylaldehyde fragment. The two

Table 2. Comparison of the reduction of technetium and rhenium cations by cyclic voltammetry

Cation	Redox couple	$E_0{}^a$/V	Ref.
$[Tc(dmpe)_2Cl_2]^+$	M^{III}–M^{II}	-0.55^b	*c*
$[Tc(PEt_3)_2(acen)]^+$	M^{III}–M^{II}	-1.43^d	*e*
$[Tc(pdma)_2Cl_2]^+$	M^{III}–M^{II}	-0.38^b	*f*
$[TcL^3]^+$	M^{IV}–M^{III}	$-0.53^{g,h}$	This work
$[Re(dmpe)_2Cl_2]^+$	M^{III}–M^{II}	-0.72^b	*i*
$[Re(pdma)_2Cl_2]^+$	M^{III}–M^{II}	-0.64^j	*k*
$[ReL^1]^+$	M^{IV}–M^{III}	-0.57^e	This work
$[ReL^2]^+$	M^{IV}–M^{III}	-0.69^e	This work

[a] For the purposes of comparison, the potentials quoted are E_0 *vs.* Ag–AgNO$_3$. The conversions applied are: saturated calomel electrode *vs* Ag–AgNO$_3$, −0.29 V; Ag–AgCl–NaCl (3 mol dm^{-3}) *vs.* Ag–AgNO$_3$, −0.32 V. [b] Background electrolyte $[NEt_4][ClO_4]$ in dmf (0.5 mol dm^{-3}). [c] A. Ichimura, W. R. Heineman, J.-L. Vanderheyden, and E. Deutsch, *Inorg. Chem.*, 1984, **23**, 1272. [d] Background electrolyte $[NEt_4][ClO_4]$ in propylene carbonate (0.5 mol dm^{-3}). [e] A. Ichimura, W. R. Heineman, and E. Deutsch, *Inorg. Chem.*, 1985, **24**, 2134. [f] R. W. Hurst, W. R. Heineman, and E. Deutsch, *Inorg. Chem.*, 1981, **20**, 3298. [g] Background electrolyte $[NBu_4][PF_6]$ in CH_2Cl_2 (0.2 mol dm^{-3}). [h] Irreversible reaction, E_{pc} quoted. [i] J.-L. Vanderheyden, M. J. Heeg, and E. Deutsch, *Inorg. Chem.*, 1985, **24**, 1666. [j] Background electrolyte $[NEt_4][ClO_4]$ in MeCN (0.1 mol dm^{-3}). [k] J. R. Kirchhoff, W. R. Heineman, and E. Deutsch, *Inorg. Chem.*, 1987, **26**, 3108.

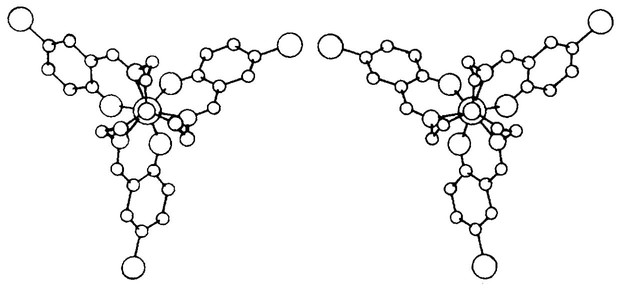


Figure 3. The two enantiomers of $[FeL^5]$ viewed along the three-fold axis passing through the Fe and apical N atoms[10]

enantiomers of C_3 symmetry for the L^5 complexes are shown in Figure 3.

The simplest mechanism for enantiomer interconversion in these complexes is the Bailar twist whereby one trigonal face is rotated with respect to the opposite face about the C_3 axis. An examination of space-filling molecular models indicates that additional rigidity will be imposed by steric crowding in the $N(CH_2CH_2)_3$ part of the molecule in the trigonal prismatic transition state. Moreover, it has been recently reported that the water-soluble complex [tris(2-hydroxy-5-sulphonatobenzylideneethyl)amine]indate(3−) is rigid on the n.m.r. time-scale at ambient temperature. It was also observed that the 1,1,1-tris(2-hydroxy-5-sulphonatobenzylidenemethyl)ethane complexes of In^{III} and Tl^{III} are fluxional whereas those of the smaller Group 3 cations Al^{III} and Ga^{III} are rigid at ambient temperature, the inference being that the smaller the metal cation the more rigid is the complex.[8] The In–Cl distances in $[InCl_6]^{3-}$ are in the range 2.508—2.569 Å,[12] whereas the M–Cl distance in both $[TcCl_6]^{2-}$[13] and $[ReCl_6]^{2-}$[14] is only 2.35 Å, suggesting that Tc^{IV} and Re^{IV} have significantly smaller metal cations than does In^{III}. There was thus the possibility that the stereoisomerisation barrier would be raised to a sufficient degree to support optical activity in these complexes.

As a probe to the height of this barrier, the salicylaldehyde moiety was substituted with an isopropyl group in the 5 position. In a chiral metal complex the two methyl carbon atoms of an isopropyl group are diastereotopic and, provided that enantiomeric interconversion is slow on the n.m.r. time-scale, should have separate ^{13}C n.m.r. signals. The complexes of Tc^{IV} and Re^{IV} are paramagnetic and hence are not suitable for this type of study by n.m.r. spectroscopy. Replacement of the metal by rhodium(III), which appears to have a similar-sized metal cation to Tc^{IV} and Re^{IV} (Rh–Cl distances in $[RhCl_6]^{3-}$ range from 2.302 to 2.366 Å),[15] gave the low-spin diamagnetic complex $[RhL^4]$ which was soluble in dichloromethane and gave well resolved ^{13}C n.m.r. spectra. At temperatures below 218 K two signals were observed in the 90.6-MHz ^{13}C-{^{1}H} n.m.r. subspectrum of the isopropyl methyl carbon atoms. At higher temperatures these signals coalesced to give a single line. These variable-temperature spectra are shown in Figure 4. Separate resonances were observed for small amounts of free ligand added to the solution of the complex so intermolecular exchange can be ruled out as a source of the coalescence phenomenon, which must be indicative of the onset of stereoisomerisation rapid on the n.m.r. time-scale. The small chemical shift separation (only 17 Hz in the slow-exchange limit spectrum) combined with the relatively broad lines make full line-shape fitting inappropriate. Nevertheless, the temperature of coalescence indicates a maximum value for the barrier to enantiomer interconversion, $\Delta G^{\ddagger}_{218} \approx 46$ kJ mol^{-1}, which is much too low to support optical activity in the rhodium(III) complex. It seems unlikely that this barrier will be any higher for the complexes of Tc^{IV} and Re^{IV} and hence there is no prospect for resolution of the enantiomers. It is also apparent that considerations of metal cation size alone are not adequate to explain the ambient-temperature fluxionality or otherwise of metal complexes of sexidentate Schiff-base ligands.

Experimental

All experiments involving technetium were performed using ^{99}Tc ($t_{\frac{1}{2}} = 2.13 \times 10^5$ y) in the radiochemical laboratories of Amersham International plc.

Syntheses.—Ammonium hexachlorotechnetate(IV) was prepared from ammonium pertechnetate[16] (a gift by Amersham International plc), and potassium hexachlororhenate(IV) from potassium perrhenate[17] (Johnson-Matthey) were prepared by published procedures.

Tris[2-(2′-hydroxybenzylideneethyl)]amine (H_3L^1) and its substituted derivatives, tris[2-(2′-hydroxy-4′-methoxybenzylideneethyl)]amine (H_3L^2) and tris[2-(2-hydroxy-4′,6′-dimethoxybenzylideneethyl)]amine (H_3L^3), were prepared by published procedures,[18] whereby tris(2-aminoethyl)amine was treated with the stoicheometric amount of salicylaldehyde, or the appropriately substituted derivative, in hot ethanol. The compounds H_3L^2 and H_3L^3 were initially obtained as brown oils but gradually became crystalline on standing over a period of some weeks. Tris[2-2′-hydroxy-5′-isopropylbenzylideneethyl]amine (H_3L^4) was kindly supplied by Dr. Walter Weissensteiner. Proton n.m.r. spectral data in CD_2Cl_2 at ambient temperature: H_3L^1, δ 2.79 ($H^{1,2}$), 3.50 ($H^{3,4}$), 6.11 (H^7), 6.59 (H^8), 6.93 (H^9), 7.25 (H^{10}), 7.81 (H^5), and 13.75 (OH), $J(H^7H^8)$ 7.61, $J(H^7H^9)$ 1.67, $J(H^8H^9)$ 7.39, $J(H^8H^{10})$ 1.06, and $J(H^9H^{10})$ 8.33 Hz; H_3L^2, δ 2.79 ($H^{1,2}$), 3.49 ($H^{3,4}$), 3.79 (OCH_3), 6.18 (H^9), 6.35 (H^7), 6.42 (H^{10}), and 7.80 (H^5), $J(H^7H^9)$ 2.40 and $J(H^9H^{10})$ 8.60 Hz; H_3L^3, δ 2.87 ($H^{1,2}$), 3.56 ($H^{3,4}$), 3.73, 3.74 (OCH_3), 5.61 (H^9), 5.83 (H^7), 8.38 (H^5), and 14.20 (OH), $J(H^7H^9)$ 2.15 Hz; H_3L^4, δ 1.25 (CH_3), 2.85 (CH), 2.94 ($H^{1,2}$), 3.66 ($H^{3,4}$), 6.88 (H^7), 7.02 (H^{10}), 8.28 (H^5), and 14.20 (OH), $J[H\text{-}H(Pr^i)]$ 6.9, $J(H^7H^8)$ 8.44, and $J(H^8H^{10})$ 2.27 Hz.

$[TcL^1]PF_6$. To a stirred suspension of ammonium hexachlorotechnetate (0.17 g, 0.5 mmol) in glacial acetic acid (50

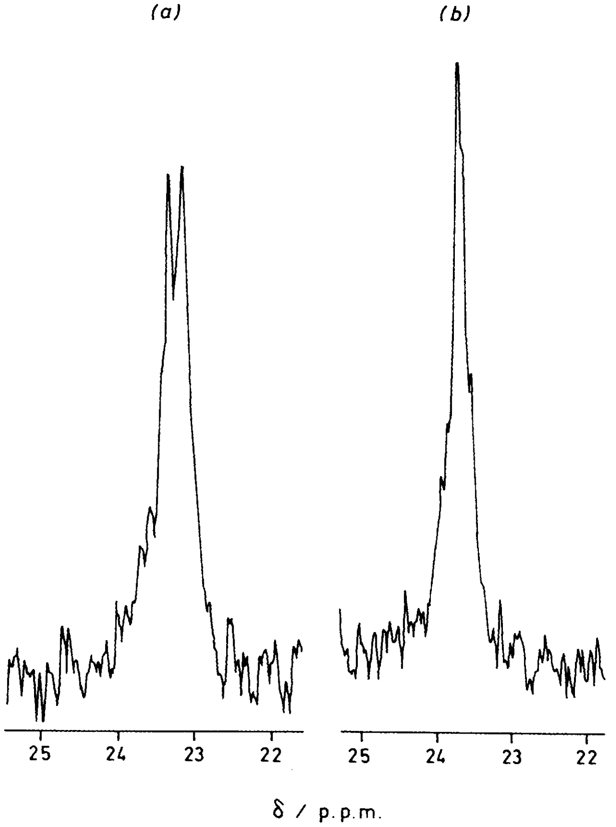


Figure 4. 90.6-MHz $^{13}C-\{^1H\}$ N.m.r. subspectrum of the isopropyl methyl carbons of $[RhL^4]$ in CD_2Cl_2 solution at (*a*) 178 K and (*b*) 228 K

cm³) were added H_3L^1 (0.23 g, 0.5 mmol) and sodium acetate (0.5 g). After refluxing for 2 h the violet reaction mixture was filtered while hot and the solvent removed by evaporation at reduced pressure. The residue was dissolved in dichloromethane and after filtration the complex was precipitated as the chloride salt by the addition of a mixture of diethyl ether and light petroleum (b.p. 40—60 °C). The complex was collected by filtration and allowed to dry at ambient temperature. It was then dissolved in water, the solution filtered, and the hexafluorophosphate salt precipitated by the addition of an aqueous solution of ammonium hexafluorophosphate. Recrystallisation from methanol yielded a violet microcrystalline solid. The complexes $[TcL^2]PF_6$ and $[TcL^3]PF_6$ were prepared in a similar manner.

$[ReL^1]PF_6$. To a stirred suspension of potassium hexachlororhenate (0.48 g, 1 mmol) in glacial acetic acid (100 cm³) were added H_3L^1 (0.46 g, 1 mmol) and sodium acetate (1 g). After the reaction mixture had been stirred at reflux for 8 h the solution was filtered and the filtrate evaporated under reduced pressure. The residue was then dissolved in water, the solution filtered, and the hexafluorophosphate salt precipitated by the addition of an aqueous solution of potassium hexafluorophosphate. It was recrystallised from a mixture of dichloromethane and light petroleum (b.p. 40—60 °C) as a dark red microcrystalline solid. The complexes $[ReL^2]PF_6$ and $[ReL^3]PF_6$ were prepared similarly and obtained as dark brown microcrystalline solids. Microanalytical data are reported in Table 1.

$[RhL^4]$. To a solution of hydrated rhodium trichloride (0.2 g) (Johnson-Matthey) and sodium acetate (0.3 g) in ethanol (10 cm³) were added H_3L^4 (0.584 g, 1.0 mmol) dissolved in ethanol (5 cm³). The immediate brown precipitate dissolved on warming the reaction mixture. The solvent was removed under reduced pressure and the residue extracted with dichloromethane, the extract filtered, and the solvent removed to leave a glassy brown solid (Found: C, 57.1; H, 6.4; N, 7.7. Calc. for $[RhL^4]\cdot CH_2Cl_2$: C, 57.8; H, 6.1; N, 7.3%).

High-performance Liquid Chromatography.—H.p.l.c. analysis was performed using a Hamilton PRP-1 column (no. 794 25) of dimensions 150 mm × 4.1 mm. The apparatus consisted of a Dynamic Mixer (model 802C), a pump (model 303), and a chart recorder (model N2), all by Gilson. The experimental conditions were controlled by an Apple Micro (2e) computer. The flow rate was 2 cm³ min⁻¹ and the solvents used were mixtures of 10 mmol dm⁻³ phosphate buffer (A) and tetrahydrofuran (B). The gradient profile used was: time/min (%B); O(0), 15(100), 18(100), 25(0), and 30(0). Detection of the eluants was by spectrophotometry (Gilson Holochrome Detector) and/or radiometry (ESI Nuclear Rate meter).

Electrophoresis.—These experiments were performed with a Shandon Tank equipped with a Pharmacia power supply (e.p.s. 500/400), using a 50 mmol dm⁻³ phosphate buffer (pH 7.4), and Whatman 541 paper strips. The applied electric field was 300 V, maintained for a period of 50 min.

Cyclic Voltammetry.—The electrochemical data were obtained using either an EG and G PARC Potentistat/Galvistat (model 175) and a Universal programmer with a JJ 'XY' plotter (rhenium complexes), or a Metrohm VA scanner (model E612) and a Metrohm VA detector (model E611), again using a JJ (XY) plotter (technetium complexes). In both cases, measurements were made using dichloromethane solutions with $[NBu_4][PF_6]$ as supporting electrolyte (*ca.* 0.2 mol dm⁻³). In the first instance the cell consisted of two platinum-wire microelectrodes with an Ag–$AgNO_3$ (0.1 mol dm⁻³ in MeCN) reference electrode and in the second the cell consisted of a platinum rotating-disc working electrode with a glassy carbon-rod counter electrode and a Ag–AgCl–NaCl (3 mol dm⁻³) reference electrode.

Spectroscopy.—Infrared spectra were obtained using a Perkin-Elmer spectrophotometer (model 683) coupled to a Perkin-Elmer data station (model 3600), n.m.r. spectra using a Bruker WH 360 spectrometer at 360.13 MHz for ^1H and 90.56 MHz for ^{13}C. Proton sub-spectral analysis was performed using the LAOCN3 program.[19]

Acknowledgements

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References

1 E. Deutsch, K. Libson, S. Jurisson, and L. F. Lindoy, *Prog. Inorg. Chem.*, 1983, **30**, 75.
2 E. Deutsch, K. A. Glavan, V. J. Sodd, H. Nishiyama, D. L. Fergusson, and S. J. Lukes, *J. Nucl. Med.*, 1981, **22**, 897.
3 A. Duatti, R. Rossi, L. Magon, and U. Mazzi, *Transition Met. Chem.* (*Weinheim, Ger.*), 1983, **8**, 170.
4 A. Marchi, A. Duatti, R. Rossi, L. Magon, U. Mazzi, and A. Pasquetto, *Inorg. Chim. Acta*, 1984, **81**, 15; G. Bandoli, U. Mazzi, D. A. Clemente, and E. Roncari, *J. Chem. Soc., Dalton Trans.*, 1982, 2455; A. Duatti, A. Marchi, S. A. Luna, G. Bandoli, U. Mazzi, and F. Tisato, *ibid.*, 1987, 867; F. Refosco, U. Mazzi, E. Deutsch, J. R. Kirchhoff, W. R. Heineman, and R. Seeber, *Inorg. Chem.*, 1988, **27**,

4121; A. Marchi, A. Duatti, R. Rossi, L. Magon, R. Pasqualini, V. Bertolasi, V. Ferretti, and G. Gilli, *J. Chem. Soc., Dalton Trans.*, 1988, 1743.

5 U. Mazzi, F. Refosco, G. Bandoli, and M. Nicolini, *Transition Met. Chem. (Weinheim, Ger.)*, 1985, **10**, 121; F. Tisato, F. Refosco, U. Mazzi, G. Bandoli, and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 1987, 1693; 1986, 1623; J. G. H. DuPreez, T. I. A. Gerber, and O. Knoesen, *Inorg. Chim. Acta*, 1987, **130**, 9; A. Duatti, A. Marchi, L. Magon, E. Deutsch, V. Bertolasi, and G. Gilli, *Inorg. Chem.*, 1987, **26**, 2182.

6 G. Bandoli, M. Nicolini, U. Mazzi, and F. Refosco, *J. Chem. Soc., Dalton Trans.*, 1984, 2505; S. Jurisson, L. F. Lindoy, K. P. Dancey, M. McPartlin, P. A. Tasker, D. K. Uppal, and E. Deutsch, *Inorg. Chem.*, 1984, **23**, 227; S. Jurisson, K. Dancey, M. McPartlin, P. A. Tasker, and E. Deutsch, *ibid.*, p. 4743.

7 F. Tisato, F. Refosco, and U. Mazzi, Proc. Sixth Int. Symp. Radiopharm. Chem. (Boston), 1986, p. 144; F. Refosco, F. Tisato, U. Mazzi, G. Bandoli, and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 1988, 611, 847.

8 D. F. Evans and D. A. Jakubovic, *J. Chem. Soc., Dalton Trans.*, 1988, 2927; *Polyhedron*, 1988, **7**, 1881.

9 F. Taha and G. Wilkinson, *J. Chem. Soc.*, 1963, 5406; F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, 1967, **6**, 223.

10 D. F. Cook, D. Cummins, and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 1976, 1369.

11 N. W. Alcock, D. F. Cook, E. D. McKenzie, and J. M. Worthington, *Inorg. Chim. Acta*, 1980, **38**, 107.

12 A. Schlimper and M. C. Ziegler, *Z. Naturforsch.*, 1972, **276**, 377.

13 R. C. Elder, G. W. Estes, and E. Deutsch, *Acta Crystallogr., Sect.* B, 1979, **35**, 136.

14 E. Adman and T. N. Margulis, *Inorg. Chem.*, 1967, **6**, 210.

15 P. J. Cresswell, J. E. Fergusson, A. R. Penfold, and D. E. Scaife, *J. Chem. Soc., Dalton Trans.*, 1972, 254.

16 J. D. Eakins, D. G. Humphreys, and C. E. Mellish, *J. Chem. Soc.*, 1963, 6012.

17 G. W. Watt and R. J. Thompson, *Inorg. Synth.*, 1963, **7**, 189.

18 T. A. Broomhead and D. J. Robinson, *Aust. J. Chem.*, 1968, **21**, 1365.

19 A. A. Bothner-by and S. Castellano, Quantum Chemistry Program Exchange Program 111, 1970.

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