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FULL PAPER

Technetium(V) and rhenium(V) complexes of biguanide derivatives. Crystal structures

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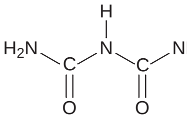
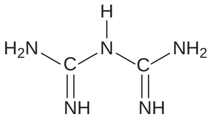
Biguanidine ligands HL^n (HL^1 = 1,1-dimethylbiguanide, HL^2 = 1-phenethylbiguanide, HL^3 = 1-phenylbiguanide) formed disubstituted cationic oxo- and nitrido-complexes $[MO(HL^n)_2]^{3+}$ (M = Tc or Re) and $[TcN(HL^n)_2(H_2O)]^{2+}$. They are characterised by the presence of a network of N–H · · · X (X = Cl or H_2O) intra- and inter-molecular hydrogen bonds. The imido precursor of Re^V $[Re(NMe)(PPh_3)_2Cl_3]$ formed monosubstituted complexes $[Re(NMe)(HL^{1,2})(PPh_3)Cl]^{2+}$. In alkaline solutions deprotonation of ligands occurs and monocationic, disubstituted oxo- and imido-species $[MO(L^n)_2]^+$ (M = Tc or Re), $[Re(NCH_3)(L^{1,3})_2]^+$ and neutral nitrido complexes $[TcN(L^n)_2]$ are obtained. Elemental analyses, FT-IR and NMR spectroscopy and conductivity measurements are consistent with the proposed formulations. Crystal structures of $[TcO(L^1)_2]^+$ and $[TcN(HL^1)_2(H_2O)]^{2+}$ were determined. The former shows a square pyramidal geometry in which the C–N bond distances are equivalent and indicative of π delocalisation on the chelate ring. The latter displays a pseudo-octahedral geometry with a water molecule *trans* to the Tc≡N multiple bond. The C–N bond distances inside the ligands (1.30 and 1.38 Å) are consistent with single and double bond character, and less π delocalisation through the whole ligands.

Introduction

Biguanide and its N-substituted derivatives are bidentate ligands which contain nitrogen donor atoms. From a chemical and structural point of view biguanide may be considered as derived from the substitution of both the oxygen atoms of biuret by imino =NH groups.



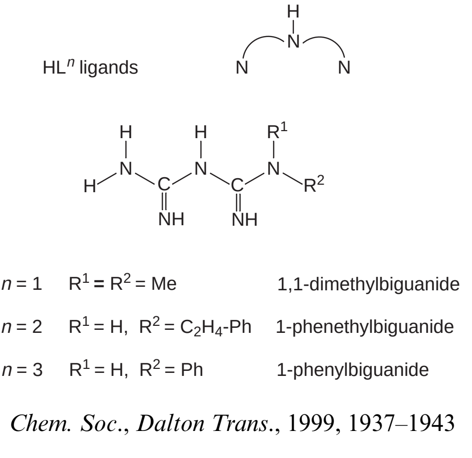
Biuret



Biguanide

These compounds are considered strong σ- and π-donating ligands which form stable complexes with transition metal ions in high or usual oxidation states utilising the availability of vacant d orbitals of the metal which may overlap with the filled π orbitals of the ligand.[1] They are highly coloured and complexes of bivalent metals such as copper, nickel, and cobalt with biguanides have long been known.[2] In 1961 Ray[3] reported a systematic investigation of the syntheses and properties of these and other metal complexes including the first oxorhenium(V) complex $[ReO(Big)_2(OH)][OH]_2$ (Big = biguanide). More recently, some oxorhenium(V) complexes of biguanide and 1,1-dimethylbiguanide have been formulated as $[ReO(HL)_2X]X_2$, $[ReO(L)_2X]$ (X = Cl$^-$ or OH$^-$) and $[Re(HL)_2(OH)_2]Cl_3$ (HL = biguanide) on the basis of elemental analysis and IR spectra.[4] Up to now and to our knowledge, no technetium complex has been described. From a chemical point of view the formation of a complex has been considered similar to a protonation process.[5] Moreover, EPR and UV spectral studies have been carried out to understand the chemical and pharmaceutical properties of this class of molecules.[1b,6] Biguanides have attracted considerable attention for their hypoglycaemic activity[7] and, in particular, metformin (1,1-dimethylbiguanide) is an antidiabetic medication which has been used for over 30 years. This class of compounds has been also studied as antimalarial drugs[8] and more recently for therapeutic treatment of pain, anxiety, and memory disorders.[9]

The present paper deals with the synthesis and characterisation of rhenium(V) and technetium(V) complexes of biguanide derivatives HL^n and the first structurally characterised oxo- and nitrido-complexes of technetium.



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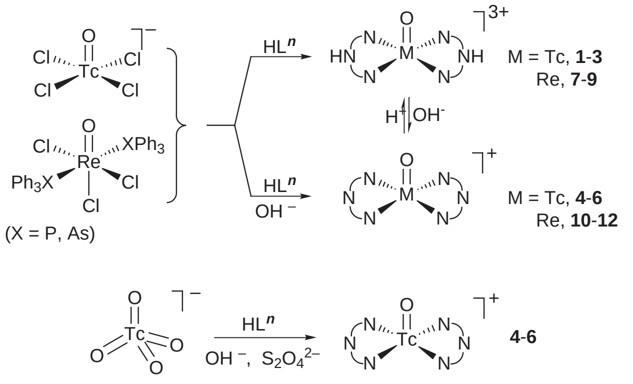
Results and discussion

Syntheses

Oxotechnetium(V) and oxorhenium(V) complexes. The violet complexes $[\mathrm{TcO(HL}^n)_2]^{3+}$ **1**–**3** were prepared by reaction of $[\mathrm{TcOCl_4}]^-$ precursor with HL^n ligands under mild conditions. The corresponding oxorhenium(V) complexes $[\mathrm{ReO(HL}^n)_2]^{3+}$ **7**–**9** were obtained by exchange reactions of $[\mathrm{ReO(XPh_3)_2Cl_3}]$ (X = P or As) (Scheme 1). The oxorhenium(V) precursors showed a lower reactivity than $[\mathrm{TcOCl_4}]^-$ salt which readily reacted with HL^n ligands. No difference of reactivity was observed between the two oxorhenium(V) compounds. Complexes $[\mathrm{MO(HL}^n)_2]^{3+}$ are violet, air stable and soluble in water, MeOH, $\mathrm{Me_2SO}$. Conductivity measurements in $\mathrm{Me_2SO}$ solution seem in agreement with 3 : 1 electrolytes. The oxometal complexes $[\mathrm{TcO(L}^n)_2]^+$ **4**–**6** and $[\mathrm{ReO(L}^n)_2]^+$ **10**–**12** were synthesized in good yields following two different procedures. When the reactions were carried out in the presence of base (KOH in MeOH) deprotonation of ligands occurred and the corresponding monocationic species formed. These compounds were also isolated starting from solutions of **1**–**3** or **7**–**9** by adding some drops of alkaline solution. The formation of $[\mathrm{ReO_4}]^-$ was observed in the syntheses of **10**–**12** since these reactions were performed in air, at neutral or weakly alkaline pH values and under these conditions $[\mathrm{ReO_4}]^-$ replaced Cl^- as counter ion. On the contrary, $[\mathrm{TcO_4}]^-$ anion was never detected in the syntheses of **4**–**6** because technetium complexes are more difficult to oxidise than are their rhenium analogs.[10]

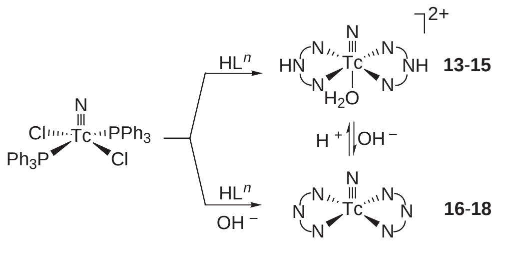


Scheme 1

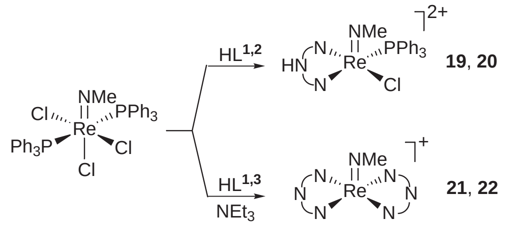
In order to evaluate the possibility to form oxotechnetium compounds starting from pertechnetate ion, reactions in aqueous basic solution with $\mathrm{Na_2S_2O_4}$ as reducing agent were performed. Substitution of the OH^- counter ion with $[\mathrm{BPh_4}]^-$ gave good crystals of **4** for X-ray diffraction analysis. All of these oxo complexes $[\mathrm{MO(L}^n)_2]^+$ are yellow and air stable in both the solid state and solution. They are soluble in MeOH, $\mathrm{Me_2SO}$ and behave as monoelectrolytes in solution.

Nitridotechnetium(V) complexes. Cationic complexes $[\mathrm{TcN(HL}^n)_2(\mathrm{H_2O})]^{2+}$ **13**–**15** were prepared starting from the precursor $[\mathrm{TcN(PPh_3)_2Cl_2}]$ (Scheme 2). When the reactions were carried out with $\mathrm{HL}^{1,2}$ ligands the presence of $\mathrm{NEt_3}$ was required since the former were available as their HCl salts. The corresponding neutral species **16**–**18** were obtained in basic solution (KOH in MeOH) or alternatively after dissolution of **13**–**15** in MeOH and addition of alkaline solution. Cationic $[\mathrm{TcN(HL}^n)_2(\mathrm{H_2O})]^{2+}$ and neutral $[\mathrm{TcN(L}^n)_2]$ compounds are yellow, air stable and soluble in $\mathrm{CH_2Cl_2}$, MeOH, $\mathrm{Me_2SO}$. Conductivity measurements in $\mathrm{Me_2SO}$ are in accord with the proposed formulations. Crystals suitable for X-ray diffraction studies of $[\mathrm{TcN(HL}^1)_2(\mathrm{H_2O})]^{2+}$ **13** were grown from dichloromethane–ethanol.

Imidorhenium(V) complexes. Monosubstituted imido complexes $[\mathrm{Re(NMe)(HL}^{1,2})(\mathrm{PPh_3})\mathrm{Cl}]^{2+}$ **19**, **20** were synthesized starting from the easily available species $[\mathrm{Re(NMe)(PPh_3)_2Cl_3}]$ (Scheme 3). Even if the ligands were used in a 1 : 2 stoichiometric ratio, attempts to obtain the corresponding disubstituted compounds failed. Monocationic disubstituted compounds **21** and **22** were recovered in the presence of base ($\mathrm{NEt_3}$). The complexes $[\mathrm{Re(NMe)(HL}^{1,2})(\mathrm{PPh_3})\mathrm{Cl}]^{2+}$ and $[\mathrm{Re(NMe)(L}^{1,3})_2]^+$ behave as 2 : 1 and 1 : 1 electrolytes, respectively in $\mathrm{Me_2SO}$ solution. Intentionally, we decided to synthesize only some imido complexes with the aim to make a comparison of reactivity between oxo- and imido-rhenium(V) precursors.



Scheme 2



Scheme 3

Spectroscopy

In this discussion we report FT-IR wavenumbers of the ligands for an easier comparison with those of complexes. Infrared spectra of the HL^n (n = 1–3) ligands exhibit an intense absorption band in the range 3100–3500 cm^{-1} assignable to the stretching vibration of the NH groups. It is probable that inter- or intra-molecular hydrogen bonds overlap with NH vibrations and are responsible for this broad band. The presence of intramolecular hydrogen bonds was confirmed by structural studies of biguanides.[5b,11] A set of strong bands observed in the range 1500–1700 cm^{-1} may be attributed to C=N stretch and NH deformation.

All IR spectra of the complexes $[\mathrm{MO(HL}^n)_2]^{3+}$ (M = Tc **1**–**3** or Re **7**–**9**), $[\mathrm{TcN(HL}^n)_2(\mathrm{H_2O})]^{2+}$ **13**–**15**, and $[\mathrm{Re(NMe)(HL}^{1,2})(\mathrm{PPh_3})\mathrm{Cl}]^{2+}$ **19**, **20** display a broad intense band in the range 3100–3500 cm^{-1} due to the stretching vibrations of the N–H groups and overlapped with stretchings of $\mathrm{H_2O}$ or ROH (R = Me or Et) involved in hydrogen bonds. The strong bands observed in the range 1640–1700 cm^{-1} are assigned to the ν(C=NH) of co-ordinated groups, and those at 1500–1610 cm^{-1} attributed to ν(C–N–C) (ring) and δ(NH).[1a,12] A new band appearing at 1320–1220 cm^{-1} was assigned to ring vibration and supports the formation of a chelate ring.[12b] The infrared spectra of technetium and rhenium oxo complexes exhibit a strong M=O (M = Tc or Re) absorption peak at 980–997 and at 990–1007 cm^{-1}, respectively. These MO stretching values are comparable with those observed for other square-pyramidal oxo complexes of Tc and Re containing σ- and π-donating ligands.[13] The spectra of nitrido complexes show a medium-intensity band which falls in the appropriate range for the Tc≡N moiety (1059–1088 cm^{-1}). Finally, a band at *ca.* 1095 cm^{-1} indicates the presence of $\mathrm{PPh_3}$ in **19** and **20**. The IR spectra of the deprotonated complexes do differ marginally from those discussed above. For some of them, the region 3100–3500 cm^{-1} appears better resolved, probably due to the absence of hydrogen bonds (see Experimental section). Indeed there is an appreciable low frequency shifting of ν(C=N) (1600–1620 cm^{-1}) with respect to the values of the corresponding protonated species, as well as to HL$''$ unco-ordinated ligands. This fact may be attributed to π-electron delocalisation on the chelate ring. Moreover, in these complexes M=O and Tc≡N stretching vibrations are observed at lower wavenumbers. Finally, disappearance of the characteristic band of the PPh$_3$ moiety in [Re(NMe)(L^{1,3})$_2$]Cl **21**, **22** is consistent with the formulation of the disubstituted complexes.

Proton NMR spectra of the metal complexes, recorded in Me$_2$SO-d_6 solution, show a downfield shift of the NH resonances with respect to those of the unco-ordinated ligands, while aliphatic and aromatic protons do not undergo significant chemical shifts. For the technetium and rhenium oxo complexes, containing the ligands in their protonated as well as deprotonated form, the =NH resonances are the more significant data in the ^{1}H NMR spectra. In particular the spectra for the oxorhenium complexes exhibit signals at higher values than those of corresponding technetium compounds.

Comparing [MO(HL$''$)$_2$]$^{3+}$ (M = Tc **1**–**3** or Re **7**–**9**) with [MO(L$''$)$_2$]$^+$ (M = Tc **4**–**6** or Re **10**–**12**) complexes an analogous NH pattern may be observed in all spectra, although the signals for the latter compounds are shifted upfield with respect to the former. A similar behaviour is also observed for the corresponding nitrido derivatives. This trend may be discussed in terms of an increased shielding arising from a strong π conjugation along the chelate ring, in accord with the C–N bond distances of complexes [TcO(L^1)$_2$]$^+$ **4** and [TcN(HL^1)$_2$(H$_2$O)]$^{2+}$ **13** (see description of the structures) which indicate a more extensive π delocalization over the whole ligand molecule in **4** than in **13**. It is interesting that complex **4** possesses a *trans* configuration while the corresponding compound **13** is *cis*. Although isomers could be expected, NMR experiments in solution and at room temperature did not reveal their presence for all oxo- and nitrido-complexes. This fact cannot be attributed to steric impediments as well as electronic factors and it is hard to explain it. The presence of only one isomer could be due to a high energy barrier which does not allow inversion.

The ^{31}P and ^{1}H NMR spectra of imido complexes **19**, **20** are consistent with the formation of monosubstituted compounds such as [Re(NMe)(HL^{1,2})(PPh$_3$)Cl]$^{2+}$. In particular, the phosphorus NMR spectra exhibit singlets at $\delta -8.95$ and -6.38 for the co-ordinated PPh$_3$ moiety of **19** and **20**, respectively. The ^{1}H NMR spectra show two singlets in the range δ 10.95–8.6 attributable to (=NH) protons. For the complexes [Re(NMe)(L^1)$_2$]$^+$ **21** and [Re(NMe)(L^2)$_2$]$^+$ **22**, the ^{1}H spectra recorded at room temperature, as well as at 60 °C, are clearly consistent with the presence of two molecules of the ligand. In particular there is a set of four singlets (δ 11.3–9.1) having equal intensity and attributed to the four =NH protons of the co-ordinated ligands. Another set of two singlets, twice as intense, at δ 7.0–6.4 is assigned to NH$_2$ groups. This NMR feature could suggest the presence of a 1 : 1 mixture of *cis* and *trans* isomers about the metal as well as a linear–bent isomerisation at the nitrene ligand. However, NMR spectra of the oxo- or nitrido-complexes, discussed above, did not display a *cis*–*trans* isomerization in solution at room temperature, and we believe that for **21** and **22** a non-axial disposition of the ReN–R bond is a plausible explanation.[14]

A series of UV absorption spectra and their pH dependence were studied in air to evaluate the basicity constants of co-ordinated biguanide ligand and which complexes are present in solution at different pH values. In these experiments a 0.5 M solution of H$_3$PO$_4$ (25 cm^3) was mixed in various ratios with a 1.0 M solution of NaOH and nine solutions at pH values ranging from 1.9 to 6.9 were prepared. All solutions were adjusted to ionic strength I = 0.1 M with Na$_2$SO$_4$. To a 10^{-4} M aqueous solution (10 cm^3) of the complex **7** an aliquot (1.0 cm^3) of each solution was added and UV spectra recorded. The UV spectra collected in the pH range 1.9–3.5 show the presence of both [ReO(HL^1)$_2$]$^{3+}$ and [ReO(HL^1)(L^1)]$^{2+}$ species, while at pH 3.55–4.35 [ReO(HL^1)(L^1)]$^{2+}$ and [ReO(L^1)$_2$]$^+$ are present. The latter was stable until pH 6.9 while at higher pH values oxidation of rhenium(v) to [ReO$_4$]$^-$ took place and it was complete at pH 12 after 2.5 h. From these experiments a pK_1 of 3.55 and a pK_2 of 4.35 have been estimated. In conclusion, we may assert that deprotonation of two molecules of ligand occurs in two well distinct steps although the two pK values are very similar. In addition, at physiological pH value the species in solution are those that contain both ligands in deprotonated form. These results may be also extended to other complexes taking into account that technetium(v) is more difficult to oxidise than rhenium(v)[10] and the Tc≡N fragment is more stable than Tc=O in alkaline solution.

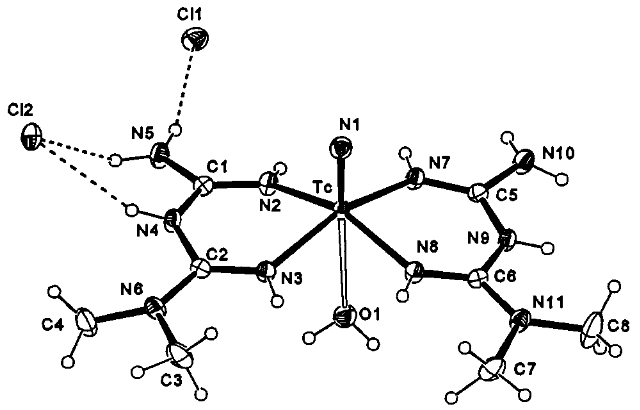


Fig. 1 An ORTEP[15] view of the cation of compound **4** showing thermal ellipsoids at 30% probability.

Crystal structures

The [TcO(C$_4$H$_{10}$N$_5$)$_2$]$^+$ cation of complex **4** displays a non-crystallographic C_2 symmetry and a square-pyramidal geometry around Tc with two deprotonated 1,1-dimethylbiguanide molecules on the basal plane and an oxygen at the apex (Fig. 1). The Tc atom is displaced from the plane defined by N(1), N(2), N(6) and N(7) atoms toward O(1) by 0.6777(3) Å. The Tc=O(1) bond distance of 1.645(3) Å (Table 1) indicating strong multiple bond character is in agreement with the distances found in other square-pyramidal technetium(v) oxo complexes.[13a,16] The Tc–N bond distances, in the range 1.97–2.01 Å, are shorter than those observed in compound **13** due to the concomitant presence of a Tc=O(oxo) group, which is a softer base than Tc≡N-(nitrido) group, and partial negative charges on the enaminic NH moieties. The C–N bonds within the two deprotonated dimethylbiguanide ligands display, in fact, almost equivalent distances, from 1.32 to 1.35 Å, indicative of a delocalisation of the double bonds and negative charges throughout the whole ligands. In the crystal packing the cation complexes are linked by hydrogen bonds between aminic hydrogens and deprotonated nitrogens while the N(1)–H and N(7)–H enaminic groups are engaged in the capture of a methanol molecule.

The [TcN(C$_4$H$_{12}$N$_5$)$_2$(H$_2$O)]$^{2+}$ cation belonging to complex **13** displays a non-crystallographic C_s symmetry and an approximately octahedral geometry with two molecules of 1,1-dimethylbiguanide on the basal plane and a water molecule at the apical position *trans* to the nitrido group (Fig. 2). The four basal N atoms lie approximately on a plane and the Tc atom is displaced from this plane by 0.4384(2) Å toward N(1). The Tc≡N triple bond distance of 1.616(2) Å is comparable with other reported distances for technetium(v) nitrido complexes.[17] The long Tc–OH$_2$ distance of 2.691(2) Å is ascribed to the strong *trans* influence of the nitrido ligand and is in agreement with the distances, in the range 2.48–2.95 Å, found in analogous compounds.[18] These Tc–O bonds are abnormally long and can

Table 1 Selected bond distances (Å) and angles (°) for complexes $[TcO(L^1)_2]^+$ **4** and $[TcN(HL^1)_2(H_2O)]^{2+}$ **13** with estimated standard deviations in parentheses

$[TcO(L^1)_2]^+$ **4**			
Tc–O(1)	1.645(3)		
Tc–N(1)	1.973(2)	Tc–N(6)	1.984(2)
Tc–N(2)	2.012(3)	Tc–N(7)	2.006(2)
N(1)–C(1)	1.333(4)	N(6)–C(5)	1.353(4)
N(2)–C(2)	1.336(4)	N(7)–C(6)	1.352(4)
N(3)–C(1)	1.324(4)	N(8)–C(5)	1.340(4)
N(3)–C(2)	1.347(3)	N(8)–C(6)	1.345(3)
N(4)–C(1)	1.343(4)	N(9)–C(5)	1.318(4)
N(5)–C(2)	1.331(4)	N(10)–C(6)	1.342(4)
O(1)–Tc–N(1)	112.0(1)	O(1)–Tc–N(7)	112.7(1)
O(1)–Tc–N(2)	108.4(1)	O(1)–Tc–N(6)	106.4(1)
N(1)–Tc–N(2)	82.9(1)	N(6)–Tc–N(7)	83.5(1)
N(1)–Tc–N(7)	83.4(1)	N(2)–Tc–N(6)	84.0(1)
N(1)–Tc–N(6)	135.2(1)	N(2)–Tc–N(7)	145.2(1)
$[TcN(HL^1)_2(H_2O)]^{2+}$ **13**			
Tc–N(1)	1.616(2)	Tc–O(1)	2.691(2)
Tc–N(2)	2.069(2)	Tc–N(7)	2.071(2)
Tc–N(3)	2.080(2)	Tc–N(8)	2.076(2)
N(2)–C(1)	1.292(2)	N(7)–C(5)	1.292(2)
N(3)–C(2)	1.299(2)	N(8)–C(6)	1.303(2)
N(4)–C(1)	1.381(2)	N(9)–C(5)	1.380(2)
N(4)–C(2)	1.375(2)	N(9)–C(6)	1.380(2)
N(5)–C(1)	1.331(2)	N(10)–C(5)	1.338(3)
N(6)–C(2)	1.344(2)	N(11)–C(6)	1.341(2)
N(1)–Tc–N(2)	104.9(1)	N(1)–Tc–N(7)	101.9(1)
N(1)–Tc–N(3)	100.9(1)	N(1)–Tc–N(8)	101.2(1)
N(2)–Tc–N(7)	89.5(1)	N(3)–Tc–N(8)	90.6(1)
N(2)–Tc–N(3)	84.2(1)	N(7)–Tc–N(8)	85.4(1)
N(2)–Tc–N(8)	153.9(1)	N(3)–Tc–N(7)	157.2(1)
N(1)–Tc–O(1)	177.3(1)		

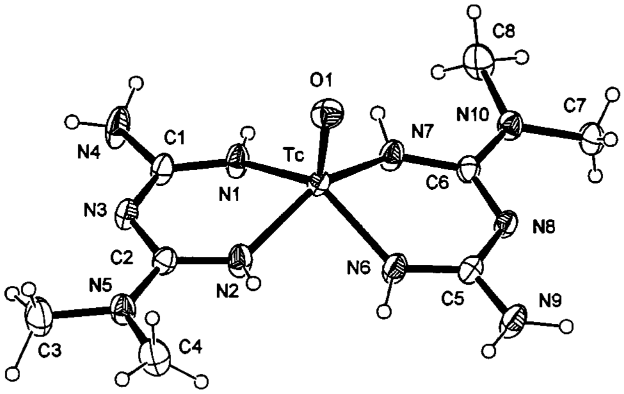


Fig. 2 An ORTEP[15] view of compound **13** showing thermal ellipsoids at 30% probability.

be considered as secondary bonds, intermediate between true bonds and van der Waals contacts. The presence of a water molecule in *trans* position is associated with a decreasing pyramidalisation of the technetium co-ordination polyhedron measured by the N≡Tc–N(*cis*) mean angle, *a*, which is 102° in the present compound, and in typical square-pyramidal technetium nitrido complexes falls in the range 105–108°. The shortening of the Tc–N (sp^2, enaminic) bond distances, observed in the range 2.07–2.08 Å, with respect to the Tc–N (sp^3, aminic) ones of 2.15–2.22 Å,[19] can be attributed to the different hybridisations of the N atoms. The C–N single and double bond distances inside the ligands, of 1.30 and 1.38 Å on average respectively, display a small degree of delocalisation, the standard values of C=N and C(sp^2)–N(sp^2) bond lengths being 1.27 and 1.41 Å, respectively. The crystal packing is determined by a complex network of hydrogen bonds involving all the aminic hydrogens, the chloride anions, the water molecule and the enaminic N(2)–H group.

Conclusion

The paucity of relevant IR and NMR spectral data available in the literature[1a,12a,20] makes difficult any comparison with our results. The complexes here reported have been synthesized by facile exchange reactions between ligands and appropriate technetium and rhenium precursors. They have been fully characterised by FT-IR and NMR spectroscopy and the crystal structures of **4** and **13** determined. Conductivity measurements in Me_2SO solution, of all cationic complexes, seem in agreement with literature data[21] for 1 : 1, 2 : 1 and 3 : 1 electrolytes. The charge on the complexes is neutralised by a network of N–H · · · Cl hydrogen bonds as demonstrated by crystal structure determinations.[22] We have demonstrated that it is possible to promote deprotonation of the co-ordinated ligand and consequently to change the charge of the final complex. This aspect is of great importance in the development of ^{99m}TC and $^{186/188}$Re radiopharmaceuticals and studies in order to understand which species are present in the biological environment could be performed. Syntheses of the corresponding ^{99m}TcO complexes and preliminary biodistribution studies *in vivo* are reported elsewhere.[23]

Experimental

Materials and methods

CAUTION: Technetium-99 is a low-energy β^- emitter ($E = 292$ keV, $t_{1/2} = 2.12 \times 10^5$ years). When this material is handled, normal radiation safety procedures must be used to prevent contamination. All manipulations of solids or solutions were performed in a laboratory approved for low-level radioactivity.

Unless otherwise noted, all chemicals were reagent grade used without further purification. The salt $[NH_4][^{99}TcO_4]$ was obtained from the Radiochemical Centre, Amersham, UK; $[AsPh_4][TcOCl_4]$,[24] $[TcN(PPh_3)_2Cl_2]$,[25] $[ReO(XPh_3)_2Cl_3]$[26] (X = P or As) and $[Re(NMe)(PPh_3)_2Cl_3]$[27] were prepared according to literature methods. The ligands 1,1-dimethylbiguanide (HL^1), 1-phenylbiguanide (HL^3) (Sigma) and 1-phenethylbiguanide (HL^2) (Janssen Chimica) are commercially available products. Biguanide was synthesized according to the procedure of Karipides and Fernelius.[28]

Elemental analyses were performed using a Carlo Erba Instruments model EA1110 apparatus. FT-IR Spectra were recorded in the range 4000–200 cm^{-1} on a Nicolet 510P FT-IR instrument in KBr, using a Spectra-Tech collector diffuse reflectance accessory, UV-Vis spectra on a Perkin-Elmer Lambda 5 spectrophotometer. pH Measurements were made with a Hanna HI-8417 Digital pH-meter using commercial buffer solutions (pH 4 and 7) as reference points. Proton NMR spectra of Me_2SO-d_6 solutions of complexes were examined on a Varian Gemini 300 spectrometer with $SiMe_4$ as internal standard, ^{31}P-{^1H} NMR spectra on the same instrument in Me_2SO-d_6 solutions with a 85% H_3PO_4 solution as external standard. Conductivities were measured with an Amel Model 134 conductivity meter. The conductivity data were obtained at sample concentrations of *ca.* 1×10^{-4} M in Me_2SO solutions at room temperature (21 °C).

Synthesis of complexes

Oxotechnetium(v) complexes $[TcO(HL^n)_2]Cl_3$ 1–3 (*n* = 1–3). To the salt $[AsPh_4][TcOCl_4]$ (80 mg, 0.12 mmol) dissolved in 30 cm^3 of CH_2Cl_2 the ligand (0.48 mmol) was added as a solution in MeOH (1 cm ^{3}). The reaction mixture was gently warmed for 20 min and a change from pale green to violet was observed. Upon slow evaporation of solvent reddish violet crystals of the complexes were obtained. The solid was filtered off, washed with EtOH and dried with Et_2O. Yields were determined on starting technetium complex.

$[TcO(HL^1)_2]Cl_3$ **1**. Yield 90% (Found: C, 20.3; H, 4.6; N, 29.0. $C_8H_{22}Cl_3N_{10}OTc$ requires C, 20.0; H, 4.6; N, 29.2%). IR (KBr):

997 [ν(Tc=O)], 1595, 1630, 1668 [ν(C–N–C), δ(NH), ν(C=N)], and 3140, 3275 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 11.0 (2 H, s, C=NH), 9.85 (2 H, s, C=NH), 9.0 (2 H, s, CNHC), 7.7 (4 H, br s, NH$_2$) and 3.0 [12 H, s, N(CH$_3$)$_2$]. Λ_M (Me$_2$SO, 1.5×10^{-4} M) 65 S cm^2 mol^{-1}.

[TcO(HL^2)$_2$]Cl$_3$ **2**. Yield >90% (Found: C, 38.1; H, 4.7; N, 22.1. $C_{20}H_{30}Cl_3N_{10}OTc$ requires C, 38.0; H, 4.8; N, 22.2%). IR (KBr): 982 [ν(Tc=O)], 1607–1690 [ν(C–N–C), δ(NH), ν(C=N)] and 3100–3300 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 10.9 (2 H, br s, C=NH), 7.4–7.2 (20 H, m, C=NH, CNHC, C$_6$H$_5$, NH$_2$, PhC$_2$H$_4$NH), 3.7 (4 H, m, CH$_2$) and 2.8 (4 H, m, CH$_2$). Λ_M (Me$_2$SO, 1.2×10^{-4} M) 80 S cm^2 mol^{-1}.

[TcO(HL^3)$_2$]Cl$_3$ **3**. Yield 70% (Found: C, 37.4; H, 5.8; N, 19.7. $C_{16}H_{22}Cl_3N_{10}OTc\cdot 3C_2H_5OH$ requires C, 37.0; H, 5.6; N, 19.6%). IR (KBr): 997 [ν(Tc=O)], 1489–1642 [ν(C–N–C), δ(NH), ν(C=N)] and 3171–3312 cm^{-1} [ν(NH, NH$_2$, OH)]. NMR (Me$_2$SO-d_6): δ_H 11.0 (2 H, s, C=NH), 10.0–9.8 (4 H, 2 s, C=NH, CNHC), 8.0–7.0 (16 H, m, C$_6$H$_5$, PhNH, NH$_2$), 3.45 (6 H, q, J = 7.0, CH$_2$) and 1.06 (9 H, t, J = 7.0 Hz, CH$_3$). Λ_M (Me$_2$SO, 1.3×10^{-4} M) 74 S cm^2 mol^{-1}.

[TcO(L^n)$_2$]Cl 4–6 (*n* = 1–3). The corresponding monocationic yellow complexes were obtained following the same procedure but in the presence of base. Some drops (3–5) of a saturated solution of KOH in MeOH were added to the violet solution. The reaction mixture became yellow, it was heated at 40 °C for 10 min and concentrated *in vacuo*. The residue was treated with water, filtered off, washed with EtOH and dried with Et$_2$O. Alternatively, these compounds can be also obtained starting from TcO(HL^n)$_2$Cl$_3$ complexes dissolved in the minimum volume of MeOH and 1 or 2 drops of KOH solution added at room temperature. Slow evaporation of the yellow solutions gave crystals of the final products. Similar products were isolated starting from [^{99}TcO$_4$]$^-$. A typical preparation is as follows: to a solution of [NH$_4$][TcO$_4$] in hot water (30 mg, 0.166 mmol, 2 cm^3) the hydrochloride salt of HL^1 (55 mg, 0.33 mmol) dissolved in 0.05 M NaOH (1 cm^3) was added. Sodium dithionite (60 mg, 0.345 mmol) in 1 M NaOH (2 cm^3) was added and the reaction mixture heated at 80 °C for 30 min. During this time a yellow powder of [TcO(L^1)$_2$]OH was formed. It was filtered off, washed with water, EtOH and dried with Et$_2$O. Crystals suitable for X-ray analysis were obtained when Na[BPh$_4$] was added to a solution of the complex in MeOH.

[TcO(L^1)$_2$]Cl **4**. Yield 85% (Found: C, 23.3; H, 4.9; N, 34.2. $C_8H_{20}ClON_{10}Tc$ requires C, 23.6; H, 5.0; N, 34.4%). IR (KBr): 976 [ν(Tc=O)], 1435, 1501, 1557, 1608 [ν(C–N–C), δ(NH), ν(C=N)] and 3202, 3318, 3474 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 10.2 (2 H, s, C=NH), 8.6 (2 H, s, C=NH), 6.8 (4 H, br s, NH$_2$) and 3.2 [12 H, s, N(CH$_3$)$_2$]. Λ_M (Me$_2$SO, 1.2×10^{-4} M) 22 S cm^2 mol^{-1}.

[TcO(L^2)$_2$]Cl **5**. Yield 60% (Found: C, 43.4; H, 5.1; N, 24.9. $C_{20}H_{28}ClON_{10}Tc$ requires C, 43.0; H, 5.0; N, 25.1%). IR (KBr): 986 [ν(Tc=O)], 1449–1574 [ν(C–N–C), δ(NH), ν(C=N)] and 3231, 3314, 3418 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 9.0 (2 H, br s, C=NH), 8.8 (2 H, br s, PhC$_2$H$_4$NH), 7.4–7.0 (16 H, m, NH$_2$, C$_6$H$_5$, C=NH), 3.65 (4 H, t , CH$_2$) and 2.8 (4 H, t, CH$_2$). Λ_M (Me$_2$SO, 1.4×10^{-4} M) 26 S cm^2 mol^{-1}.

[TcO(L^3)$_2$]OH **6**. Yield 70% (Found: C, 40.0; H, 4.4; N, 28.7. $C_{16}H_{21}N_{10}O_2Tc$ requires C, 39.7; H, 4.4; N, 28.9%). FT-IR (KBr): 970 [ν(Tc=O)], 1420–1609 [ν(C–N–C), δ(NH), ν(C=N)] and 2900–3400 cm^{-1} [ν(NH, NH$_2$, OH)]. NMR (Me$_2$SO-d_6): δ_H 10.2–9.6 (4 H, br s, C=NH, PhNH) and 7.8–7.0 (16 H, m, C$_6$H$_5$, NH$_2$, C=NH). Λ_M (Me$_2$SO, 1.5×10^{-4} M) 19 S cm^2 mol^{-1}.

Oxorhenium(V) complexes [ReO(HL^n)$_2$]Cl$_3$ 7–9 (*n* = 1–3). A solution of ligand (0.36 mmol) in MeOH (1 cm^3) was added to precursor [ReO(XPh$_3$)$_2$Cl$_3$] (X = P or As; 0.18 mmol) dissolved in 40 cm^3 of CH$_2$Cl$_2$. The reaction mixture was stirred and heated under reflux for 40 min. The violet solution was concentrated *in vacuo* and the residue treated with CH$_2$Cl$_2$. Violet solids formed upon addition of diethyl ether were filtered off, washed with EtOH and dried with Et$_2$O. Yields were determined on starting metal compounds. Recrystallisation from CH$_2$Cl$_2$–EtOH produced violet crystals.

[ReO(HL^1)$_2$]Cl$_3$ **7**. Yield 80% (Found: C, 16.7; H, 4.0; N, 24.3. $C_8H_{22}Cl_3N_{10}ORe$ requires C, 17.0; H, 3.9; N, 24.7%). IR (KBr): 1007 [ν(Re=O)], 1597, 1630, 1678 [ν(C–N–C), δ(NH), ν(C=N)] and 3100–3300 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 13.0 (2 H, br s, C=NH), 12.05 (2 H, br s, C=NH), 11.1 (2 H, br s, CNHC), 7.7 (4 H, br s, NH$_2$) and 3.0 [12 H, s, N(CH$_3$)$_2$]. Λ_M (Me$_2$SO, 1.4×10^{-4} M) 84 S cm^2 mol^{-1}.

[ReO(HL^2)$_2$]Cl$_3$ **8**. Yield >90% (Found: C, 33.0; H, 4.1; N, 19.3. $C_{20}H_{30}Cl_3N_{10}ORe$ requires C, 33.4; H, 4.2; N, 19.5%). IR (KBr): 960–990 [ν(Re=O)], 1539, 1634, 1688 [ν(C–N–C), δ(NH), ν(C=N)] and 3060–3300 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 12.0 (2 H, br s, C=NH), 8.4, 8.2 (4 H, br s, C=NH, CNHC), 7.5–7.1 (16 H, m, C$_6$H$_5$, PhC$_2$H$_4$NH, NH$_2$), 4.0, 2.9 (8 H, m, CH$_2$CH$_2$). Λ_M (Me$_2$SO, 1.3×10^{-4} M) 85 S cm^2 mol^{-1}.

[ReO(HL^3)$_2$]Cl$_3$ **9**. Yield 70% (Found: C, 29.1; H, 4.1; N, 21.1. $C_{16}H_{22}Cl_3N_{10}ORe$ requires C, 29.0; H, 3.4; N, 21.1%). IR (KBr): 993 [ν(Re=O)], 1570–1685 [ν(C–N–C), δ(NH), ν(C=N)] and 3100–3350 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 10.6–10.25 (6 H, s, C=NH, CNHC), 9.65 (2 H, br s, PhNH), 7.6, 7.3 and 7.1 (14 H, d, m, C$_6$H$_5$, NH$_2$). Λ_M (DMSO, 1.1×10^{-4} M) 82 S cm^2 mol^{-1}.

[ReO(L^n)$_2$]Cl 10–12 (*n* = 1–3). These complexes were obtained as reported for the corresponding oxotechnetium complexes.

[ReO(L^1)$_2$]Cl **10**. Yield 80% (Found: C, 21.8; H, 5.0; N, 25.4. $C_8H_{20}ClN_{10}ORe\cdot CH_3OH$ requires C, 21.5; H, 5.1; N, 25.1%). IR (KBr): 993 [ν(Re=O)], 1437–1615 [ν(CNC), δ(NH), ν(C=N)] and 3204, 3319, 3462 cm^{-1} [ν(NH, NH$_2$, OH)]. NMR (Me$_2$SO-d_6): δ_H 11.1 (2 H, s, C=NH), 9.8 (2 H, s, C=NH), 7.1 (4 H, br s, NH$_2$), 4.25 (1 H, q, J = 5.2, OH), 3.2 (3 H, d, J = 5.2 Hz, CH$_3$) and 3.0 [12 H, s , N(CH$_3$)$_2$]. Λ_M (Me$_2$SO, 1.2×10^{-4} M) 24 S cm^2 mol^{-1}.

[ReO(L^2)$_2$]Cl **11**. Yield <50% (Found: C, 37.4; H, 4.4; N, 21.5. $C_{20}H_{28}ClN_{10}ORe$ requires C, 37.2; H, 4.4; N, 21.7%). IR (KBr): 997 [ν(Re=O)], 1450–1595 [ν(C–N–C), δ(NH), ν(C=N)] and 3227, 3310, 3416 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 10.2 (2 H, br s, C=NH), 10.0 (2 H, br s, PhC$_2$H$_4$NH), 7.4–7.1 (16 H, m, C$_6$H$_5$, C=NH, NH$_2$), 3.45 (4 H, m, CH$_2$) and 2.8 (4 H, m, CH$_2$). Λ_M (Me$_2$SO, 1.3×10^{-4} M) 29 S cm^2 mol^{-1}.

[ReO(L^3)$_2$][ReO$_4$] **12**. Yield 40% (Found: C, 23.9; H, 2.7; N, 17.1. $C_{16}H_{20}N_{10}O_5Re_2$ requires C, 24.0; H, 2.5; N, 17.4%). IR (KBr): 910 [ν(ReO$_4$)], 966 [ν(Re=O)], 1423–1640 [ν(C–N–C), δ(NH), ν(C=N)] and 3285, 3420 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 10.5–10.4 (4 H, s, C=NH), 9.8 (2 H, br s, PhNH) and 7.8–7.0 (14 H, m, C$_6$H$_5$, NH$_2$). Λ_M (Me$_2$SO, 1.4×10^{-4} M) 30 S cm^2 mol^{-1}.

Nitrido-complexes of technetium(V) [TcN(HL^n)$_2$(H$_2$O)]Cl$_2$ 13–15 (*n* = 1–3). The pink compound [TcN(PPh$_3$)$_2$Cl$_2$] (100 mg, 0.14 mmol) in CH$_2$Cl$_2$ (40 cm^3) was heated and stirred until all the solid dissolved. A solution of ligand (0.28 mmol, MeOH 1 cm^3) was added and the reaction mixture heated under reflux. Addition of some drops of NEt$_3$ (it was not necessary for HL^3) produced a change from pink to bright yellow. After 30 min the heating was turned off, the solution concentrated under reduced pressure and the residue taken up in CH$_2$Cl$_2$. The NEt$_3$·HCl salt was filtered off and washed with CH$_2$Cl$_2$ (2 × 5 cm^3). To the combined organic solutions EtOH (5 cm^3) was added. Slow evaporation of solvent provided yellow crystals of the desired product. It was washed with ethanol and diethyl ether and recrystallised twice from dichloromethane–ethanol. Yields are based on starting technetium complex.

[TcN(HL^1)$_2$(H$_2$O)]Cl$_2$ **13**. Yield 85% (Found: C, 20.7; H, 5.2; N, 33.8. $C_8H_{24}Cl_2N_{11}OTc$ requires C, 20.85; H, 5.25; N, 33.5%).

IR (KBr): 1088 [ν(Tc≡N)], 1497, 1632, 1668 [ν(C–N–C), δ(NH), ν(C=N)] and 3173–3337 cm^{-1} [ν(NH, NH$_2$, OH)]. NMR (Me$_2$SO-d_6): δ_H 9.65 (2 H, s, CNHC), 7.75 (4 H, br s, NH$_2$), 7.3, 7.2 (4 H, s, C=NH), 3.35 (2 H, s, H$_2$O) and 3.2 [12 H, s, N(CH$_3$)$_2$]. Λ_M (Me$_2$SO, 1.4 × 10^{-4} M) 54 S cm^2 mol^{-1}.

[TcN(HL^2)$_2$(H$_2$O)]Cl$_2$ **14**. Yield 90% (Found: C, 39.5; H, 5.2; N, 25.3. C$_{20}$H$_{32}$Cl$_2$N$_{11}$OTc requires C, 39.3; H, 5.30; N, 25.2%). IR (KBr): 1072 [ν(Tc≡N)], 1531, 1580, 1682 [ν(C–N–C), δ(NH), ν(C=N)] and 3200–3400 cm^{-1} [ν(NH, NH$_2$, OH)]. NMR (Me$_2$SO-d_6): δ_H 10.4 (2 H, br s, CNHC), 7.6–7.0 (20 H, m, NH$_2$, C$_6$H$_5$, C=NH, PhC$_2$H$_4$NH), 3.6 (4 H, t, CH$_2$), 3.35 (2 H, s, H$_2$O) and 2.85 (4 H, t, CH$_2$). Λ_M (Me$_2$SO, 1.4 × 10^{-4} M) 64 S cm^2 mol^{-1}.

[TcN(HL^3)$_2$(H$_2$O)]Cl$_2$ **15**. Yield 65% (Found: C, 34.6; H, 4.25; N, 27.6. C$_{16}$H$_{24}$Cl$_2$N$_{11}$OTc requires C, 34.5; H, 4.35; N, 27.7%). IR (KBr): 1063 [ν(Tc≡N)], 1516–1655 [ν(C–N–C), δ(NH), ν(C=N)] and 3020–3470 cm^{-1} [ν(NH, NH$_2$, OH)]. NMR (Me$_2$SO-d_6): δ_H 9.45 (2 H, s, CNHC), 7.4–7.0 (20 H, 2m, NH$_2$, C$_6$H$_5$, C=NH, PhNH) and 3.35 (2 H, s, H$_2$O). Λ_M (Me$_2$SO, 1.2 × 10^{-4} M): 46 S cm^2 mol^{-1}.

[TcN(L^n)$_2$] 16–19 (*n* = 1–3). These compounds were isolated following the procedure described for the analogous oxo-complexes.

[TcN(L^1)$_2$] **16**. Yield 90% (Found: C, 24.5; H, 6.6; N, 35.0. C$_8$H$_{20}$N$_{11}$Tc·CH$_3$OH·2H$_2$O requires C, 24.7; H, 6.5; N, 35.2%). IR (KBr): 1059 [ν(Tc≡N)], 1450–1616 [ν(C–N–C), δ(NH), ν(C=N)] and 3181, 3299, 3461 cm^{-1} [ν(NH, NH$_2$, OH)]. NMR (Me$_2$SO-d_6): δ_H 5.95 (2 H, s, C=NH), 5.6 (2 H, s, C=NH), 5.45 (4 H, s, NH$_2$), 4.25 (1 H, q, J = 5.2 Hz, OH), 3.35 (7 H, br s, CH$_3$, H$_2$O) and 3.0 [12 H, s, N(CH$_3$)$_2$].

[TcN(L^2)$_2$] **17**. Yield 90% (Found: C, 46.1; H, 5.5; N, 29.2. C$_{20}$H$_{28}$N$_{11}$Tc requires C, 46.0; H, 5.4; N, 29.5%). IR (KBr): 1067 [ν(Tc≡N)], 1450–1640 [ν(C–N–C), δ(NH), ν(C=N)] and 3197, 3310, 3407 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 7.3–7.1 (10 H, m, C$_6$H$_5$), 6.2–5.4 (10 H, m, PhC$_2$H$_4$NH, C=NH, NH$_2$), 2.8 (4 H, t, CH$_2$) and 2.5 (4 H, t, CH$_2$).

[TcN(L^3)$_2$] **18**. Yield 65% (Found: C, 40.9; H, 5.3; N, 29.4. C$_{16}$H$_{20}$N$_{11}$Tc·2CH$_3$OH: C, 40.8; H, 5.3; N, 29.1%). IR (KBr): 1072 [ν(Tc≡N)], 1480–1640 [ν(C–N–C), δ(NH), ν(C=N)] and 3150–3312 cm^{-1} [ν(NH, NH$_2$, OH)]. NMR (Me$_2$SO-d_6): δ_H 7.6–6.6 (20 H, 4m, NH$_2$, C$_6$H$_5$, C=NH, PhNH), 4.25 (2 H, q, J = 5.2, OH) and 3.2 (6 H, d, J = 5.2 Hz, CH$_3$).

Imido-complexes of Re^V [Re(NMe)(HL^{1,2})(PPh$_3$)Cl]Cl$_2$ 19, 20. To a solution of the precursor [Re(NCH$_3$)(PPh$_3$)$_2$Cl$_3$] (0.1g, 0.118 mmol) in CH$_2$Cl$_2$ (50 cm^3) ligand dissolved in the minimum volume of MeOH and in a 1 : 2 stoichiometric ratio was added. The reaction mixture was stirred and heated under reflux for 30 min. During this time a pink solid was formed. It was filtered off, washed with CH$_2$Cl$_2$, EtOH and dried with Et$_2$O. These complexes were recrystallised by slow evaporation of MeOH solutions. Yields are based on the starting rhenium complex.

[Re(NMe)(HL^1)(PPh$_3$)Cl]Cl$_2$ **19**. Yield 70% (Found: C, 38.3; H, 4.2; N, 11.9. C$_{23}$H$_{29}$Cl$_3$N$_6$PRe requires C, 38.7; H, 4.1; N, 11.8%). IR (KBr): 1094 [ν(PPh$_3$)], 1435–1680 [ν(C–N–C), δ(NH), ν(C=N)] and 3000, 3233, 3365 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 10.65 (1 H, s, C=NH), 9.5 (1 H, s, C=NH), 8.0–7.0 (18 H, m, PPh$_3$, CNHC, NH$_2$), 2.75 [6 H, s, N(CH$_3$)$_2$] and 2.5 [3 H, s, Re(NCH$_3$)]. δ_P −8.95. Λ_M (Me$_2$SO, 1.15 × 10^{-4} M) 77 S cm^2 mol^{-1}.

[Re(NMe)(HL^2)(PPh$_3$)Cl]Cl$_2$ **20**. Yield >90% (Found: C, 44.4; H, 4.2; N, 10.7. C$_{29}$H$_{33}$Cl$_3$N$_6$PRe requires C, 44.1; H, 4.2; N, 10.6%). IR (KBr): 1096 [ν(PPh$_3$)], 1435, 1524, 1663 [ν(C–N–C), δ(NH), ν(C=N)] and 3206, 3335, 3416 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 10.95 (1 H, br s, C=NH), 9.8–8.6 (3 H, s, CNHC, C=NH, PhC$_2$H$_4$NH), 8.0–7.0 (22 H, m, C$_6$H$_5$, PPh$_3$, NH$_2$), 2.5 [3 H, s, Re(NCH$_3$)], 2.25, 1.8 (4 H, m, CH$_2$CH$_2$). δ_P −6.38. Λ_M (Me$_2$SO, 1.0 × 10^{-4} M) 66 S cm^2 mol^{-1}.

[Re(NMe)(L^{1,3})$_2$]Cl 21, 22. These complexes were obtained following the procedure previously described but in the presence of NEt$_3$. When the pink solid was formed 10 drops of base were added. The mixture was heated until the solid disappeared and the solution became clear and yellow (*ca.* 1 h). The solution was concentrated to dryness and the residue taken up in CH$_2$Cl$_2$ and EtOH. Slow evaporation of solvent gave a yellow ochre powder. The complexes were recrystallised from MeOH solutions. Yields were determined based on the starting metal precursor.

[Re(NMe)(L^1)$_2$]Cl **21**. Yield 80% (Found: C, 21.3; H, 4.6; N, 29.9. C$_9$H$_{23}$ClN$_{11}$Re requires C, 21.3; H, 4.6; N, 30.4%). IR (KBr): 1505, 1559, 1611 [ν(C–N–C), δ(NH), ν(C=N)], 3212, 3318, 3447 cm^{-1} [ν(NH, NH$_2$)]. NMR (Me$_2$SO-d_6): δ_H 11.3, 10.25, 9.9, 9.1 (4 H, s, C=NH), 7.0 (2 H, br s, NH$_2$), 6.4 (2 H, br s, NH$_2$), 3.2, 3.15 [12 H, s, N(CH$_3$)$_2$] and 2.5 [3 H, s, Re(NCH$_3$)]. Λ_M (Me$_2$SO, 1.4 × 10^{-4} M) 33 S cm^2 mol^{-1}.

[Re(NMe)(L^3)$_2$]Cl **22**. Yield 80% (Found: C, 32.5; H, 4.3; N, 24.6. C$_{17}$H$_{23}$ClN$_{11}$Re·H$_2$O requires C, 32.9; H, 4.1; N, 24.8%). IR (KBr): 1480, 1537, 1645 [ν(C–N–C), δ(NH), ν(C=N)] and 3100–3400 cm^{-1} [ν(NH, NH$_2$, OH)]. NMR (Me$_2$SO-d_6): δ_H 10.6–9.4 (6 H, br s, PhNH, C=NH), 7.8–7.0 (14 H, m, C$_6$H$_5$, NH$_2$), 3.35 (2 H, s, H$_2$O) and 2.5 [3 H, s, Re(NCH$_3$)]. Λ_M (Me$_2$SO, 1.2 × 10^{-4} M) 45 S cm^2 mol^{-1}.

Crystallography

Crystal data. [TcO(C$_4$H$_{10}$N$_5$)$_2$]$^+$[B(C$_6$H$_5$)$_4$]$^-$·CH$_3$OH **4**, M = 722.49, monoclinic, space group $P2_1/c$ (no. 14), a = 11.589(2), b = 15.918(2), c = 18.962(4) Å, β = 96.97(1)°, U = 3472(1) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.71069 Å), Z = 4, D_c = 1.38 g cm^{-3}, μ = 4.60 cm^{-1}, F(000) = 1504, crystal dimensions 0.38 × 0.41 × 0.45 mm.

[TcN(C$_4$H$_{11}$N$_5$)$_2$(H$_2$O)]$^{2+}$2Cl$^-$ **13**, M = 460.16, monoclinic, space group $C2/c$ (no. 15), a = 19.620(3), b = 7.576(1), c = 25.074(3) Å, β = 102.40(1)°, U = 3640.1(9) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.71069 Å), Z = 8, D_c = 1.68 g cm^{-3}, μ = 11.05 cm^{-1}, F(000) = 1872, crystal dimensions 0.18 × 0.40 × 0.48 mm.

Data collection and processing. CAD-4 diffractometer, ω–2θ scan mode, graphite-monochromated Mo-K radiation, T = 295 K. Compound **4**: 7561 unique reflections measured ($2 \leqslant \theta \leqslant 28$) giving 6172 with $I \geqslant 3\sigma(I)$, corrected for Lorentz-polarisation and absorption (Ψ scan method, minimum transmission factor 0.86) effects. Compound **13**: 4367 unique reflections measured ($2 \leqslant \theta \leqslant 28$) giving 3918 with $I \geqslant 3\sigma(I)$, corrected as for **4** (minimum transmission factor 0.87).

Structure analysis and refinement. Solution by Patterson and Fourier methods. For compound **4**, full-matrix least-squares refinement with all non-hydrogen atom anisotropic and hydrogen isotropic, except those of methyl groups which were placed at fixed calculated positions. The Tc and O(1) atoms were disordered and refined over two positions, with occupancies 0.8 and 0.2 respectively, over and under the plane formed by N(1), N(2), N(6) and N(7) atoms. Final R = 0.042 and R' = 0.062. Goodness of fit = 2.23. Final difference map peaks in the range ± 0.43 e Å^{-3}. For compound **13**, full-matrix least-squares refinement on F with all non-hydrogen atoms anisotropic and hydrogens isotropic. Final R = 0.021 and R' = 0.027. Goodness of fit = 2.34. Final difference map peaks in the range ±0.14 e Å^{-3}. Programs used and source of scattering factors are given in ref. 29 and the structures were drawn using ORTEP.[15]

CCDC reference number 186/1435.

See http://www.rsc.org/suppdata/dt/1999/1937/ for crystallographic files in .cif format.

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