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Co-ordination chemistry of *S*-methyl 2-methyldithiocarbazate and formation of $[M{\equiv}N]^{2+}$ (M = Tc or Re) species†

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Reaction of $[TcOCl_4]^-$ and $[ReOCl_3(PPh_3)_2]$ with *S*-methyl 2-methyldithiocarbazate $[H_2L = H_2NNMeC(S)SMe]$ under mild conditions gave the oxo-technetium(v) and -rhenium(v) S,N-chelated complexes $[MO(HL)_2]Cl$ (M = Tc or Re). These were transformed to the corresponding nitrido-complexes $[MNCl_2(PPh_3)_2]$ under reflux and in the presence of HCl and PPh_3. The technetium(IV) complex $[TcCl_4(PPh_3)_2]$ under reflux and in presence of an excess of H_2L and NEt_3 gave the nitrido-compound $[TcN(HL)_2]$. This was also obtained when $[TcNCl_2(PPh_3)_2]$ was used as precursor in the presence of NEt_3. The complex $[TcNCl_2\{NPr(CH_2CH_2PPh_2)_2\}]$ reacted with an excess of H_2L to give the monosubstituted compound $[TcN(HL)\{NPr(CH_2CH_2PPh_2)_2\}]X$ (X = Cl, BF_4 or BPh_4). A crystal structure determination of the complex $[ReO(HL)_2]Cl$ showed a distorted square-pyramidal geometry with the oxygen atom in apical position. The Cl^- ion is bound to NH groups by means of two hydrogen bonds. A set of reactions using ^{99m}Tc were carried out in order to understand the formation of the ^{99m}TcN core.

During the past two decades the co-ordination chemistry of technetium has rapidly expanded because of the use of its complexes in diagnostic nuclear medicine. The area most studied was that of compounds containing the $[Tc{=}O]^{2+}$ and $[TcO_2]^+$ groups since many of the complexes in clinical use have a polydentate ligand attached to a technetium(v) oxo- or dioxo-core. Recent developments have led to the synthesis of complexes containing organodiazenido,[1] organoimido[2] and nitrido[3] cores isoelectronic to technetium(v) but more stable than $[Tc{=}O]^{2+}$. It is well known that the technetium(v) compound $[TcOCl_3(PPh_3)_2]$ is not isolable due to facile oxygen transfer to the triphenylphosphine and formation of the technetium(IV) complex $[TcCl_4(PPh_3)_2]$, while the analogous $[ReOCl_3(PPh_3)_2]$ is often used as a starting material in rhenium syntheses. These new cores can constitute very useful intermediates in technetium chemistry and nuclear medicine in the development of new radiopharmaceuticals, owing to their high stability.[2b,4]

The first nitridotechnetium(v) complexes $[TcNCl_2(PR_3)_2]$ (PR_3 = tertiary phosphines) were obtained by Kaden *et al.*[3b] from the reaction of pertechnetate with hydrazine in the presence of a phosphine and HCl. Later, Baldas *et al.*[3a] reported the synthesis of tetrachloronitridotechnetate(VI) $[TcNCl_4]^-$ in very good yield from the reaction of pertechnetate with sodium azide and concentrated hydrochloric acid. Nitridotechnetium(v) complexes $[TcNCl_2(PR_3)_2]$ (PR_3 = tertiary phosphines and arsines) were obtained by reduction of $[TcNCl_4]^-$ with an excess of the corresponding phosphines or arsines.[3d] Bis(aryldiazenido)technetium complexes $[TcCl(PPh_3)_2(NNR)_2]$ were obtained from the reaction of $[TcCl_4(PPh_3)_2]$ with arylhydrazines,[1a] while the nitrido complex $[TcNCl_2(PPh_3)_2]$ was formed when the reaction was carried out with 1,1-diphenylhydrazine in refluxing solution for 6 h.[5] Analogous rhenium complexes were synthesized starting from $[ReOCl_3(PPh_3)_2]$.[6] More recently, bis(arydiazenido) compounds were also obtained from $[TcOCl_4]^-$ or directly from pertechnetate,[1b,c] they may be transformed into monodiazenido complexes with triphenylphosphine. Reaction of $[TcOCl_4]^-$ with 1-acetyl-2-phenylhydrazine and PPh_3 gave the phenylimido complex $[TcCl_3(NPh)(PPh_3)_2]$,[2,7] while with 1-hydrazinophthalazine (hydralazine hydrochloride) and PPh_3 the nitrido-complex $[TcNCl_2(PPh_3)_2]$ was obtained.[2a,5] The complex $[ReNCl_2(PPh_3)_2]$ was formed by the reaction of $[ReOCl_3(PPh_3)_2]$ with thiosemicarbazides, HCl and PPh_3.[8] We have previously described the co-ordination chemistry of technetium(v) nitrido- and oxo-complexes with compounds derived from the *S*-methyl ester of dithiocarbazic acid $[H_2NNRC(S)SMe$, R = H or Me$]$[9] and showed their ability to form nitrido species.[10] In particular, the *S*-methyl, 2-methyl ester of dithiocarbazic acid (H_2L) appeared to be the best donor of nitrido nitrogen.[10b] These reactions were used in the preparation of new ^{99m}TcN radiopharmaceuticals.[11] More recently, succinodihydrazide has been proposed as a new N^{3-} donor in kit formulation in place of H_2L due to its higher solubility in water.[12] All these results illustrate the complexity of hydrazine and its derivatives in technetium and rhenium co-ordination chemistry.

In this paper we report a more detailed study on the role of H_2L in the formation of the $[M{\equiv}N]^{2+}$ moiety (M = Tc or Re), the synthesis and reactivity of oxo- and nitrido-complexes and the crystal structure of $[ReO(HL)_2]Cl$.

Experimental

General

CAUTION: Technetium-99 emits a low energy β^- particle (0.292 keV, *ca.* 4.67×10^{-17} J) with a half-life of 2.12×10^5 y. Bremsstrahlung is not a significant problem due to the low energy of the emission, but normal radiation safety procedures must be used when this material is handled to prevent contamination.

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† Dedicated to the memory of Luciano Magon, Professor of Chemistry at the University of Ferrara, Italy.

All common laboratory chemical were reagent grade. Technetium, as the solid pertechnetate, was obtained from the Radiochemical Centre, Amersham, UK. The compounds $[AsPh_4][TcOCl_4]$,[13] $[TcNCl_2(PPh_3)_2]$,[3c,d] $[TcCl_4(PPh_3)_2]$,[14] $[ReOCl_3(PPh_3)_2]$[15] and H_2L[16] were prepared according to the literature methods.

Elemental analyses were performed using a Carlo Erba model 1106 instrument. Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Nicolet 510 P FTIR instrument in KBr using a Spectra-Tech collector diffuse reflectance accessory, ^1H NMR spectra of CD_2Cl_2 and $CDCl_3$ solutions of the complexes on a Varian Gemini 300 spectrometer with $SiMe_4$ as internal standard, and the ^1H NMR spectrum of H_2L was recorded in Me_2SO solution.

Syntheses

$[TcN(HL)_2]$ 1. The pink complex $[TcNCl_2(PPh_3)_2]$ (0.100 g, 0.14 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and a solution of H_2L (ratio 1 : 2) in ethanol was added with stirring. The mixture was heated under reflux until it became orange and some drops of NEt_3 were added whereupon it changed to bright yellow. Alternatively, $[TcCl_4(PPh_3)_2]$ (0.100 g, 0.13 mmol) was dissolved in CH_2Cl_2 (30 cm^3) at room temperature and an excess of H_2L in EtOH (2 cm^3) was added to the green solution. It was gently warmed for 20 min but no colour change was observed. Addition of NEt_3 gave rise to a variation from green to red and after few minutes to bright yellow. In both methods, the organic solvent was removed by slow evaporation and the resulting yellow precipitate was filtered off in air and washed with water, EtOH and dried with Et_2O (Found: C, 18.65; H, 3.65; N, 18.4; S, 33.15. $C_6H_{14}N_5S_4Tc$ requires C, 18.8; H, 3.7; N, 18.3; S, 33.4%). $\tilde{\nu}/cm^{-1}$ (KBr) 3285 (N–H), 1585 [δ(N–H)], 1219 (C=S), 1026–964 (NCSS) and 384 (Tc–S). δ(H) (CD_2Cl_2) 6.40 (2 H, br s, NH), 3.75 (6 H, s, NMe) and 2.80 (6 H, s, SMe).

$[TcN(HL)\{NPr(CH_2CH_2Ph_2)_2\}]X$ 2 (X = Cl, BPh_4 or BF_4). The complex $[TcNCl_2\{NPr(CH_2CH_2PPh_2)_2\}]$ was prepared as previously reported.[17] To a solution of this complex (0.060 g, 0.09 mmol) in CH_2Cl_2 (10 cm^3) at room temperature was added a three-fold molar excess of H_2L in stoichiometric ratio in EtOH (2 cm^3) and the solution was heated under reflux for 30 min. Addition of $Na[BPh_4]$ and slow evaporation of the solvent gave yellow crystals of complex **2** (X = BPh_4) (Found: C, 66.4; H, 5.95; N, 5.25; S, 5.75. $C_{58}H_{62}BN_4P_2S_2Tc$ requires C, 66.25; H, 5.95; N, 5.3; S, 6.1%). $\tilde{\nu}/cm^{-1}$ (KBr) 3356 (NH), 1581 [δ(N–H)], 1219 (C=S), 1045 (Tc≡N), 999, 972 (NCSS) and 382 (Tc–S). δ(H) (CD_2Cl_2) 7.6–6.8 (m, Ph), 5.1 (1 H, br d, NH), 3.45 (3 H, s, NMe), 2.65 (3 H, s, SMe), 2.9–2.2 (8 H, m, NCH_2CH_2P), 1.8 (4 H, m, NCH_2CH_2Me) and 0.65 (3 H, m, NCH_2CH_2Me).

$[TcO(HL)_2]Cl$ 3. The salt $[AsPh_4][TcOCl_4]$ (0.075 g, 0.117 mmol) was dissolved in EtOH–CH_2Cl_2 (2 : 1, 12 cm^3) at room temperature. An excess of solid H_2L was added in small portions with stirring until the solution turned dark green. It was left to evaporate overnight to give a dark green powder. This product was isolated, washed with isopropyl alcohol and dried with diethyl ether (Found: C, 17.15; H, 3.4; N, 13.0; S, 30.1. $C_6H_{14}ClN_4OS_4Tc$ requires C, 17.1; H, 3.35; N, 13.3; S, 30.4%). $\tilde{\nu}/cm^{-1}$ (KBr) 2980–2900 (N···HCl), 1558 [δ(N–H)], 1238 (C=S), 1088–987 (NCSS, Tc=O) and 390 (Tc–S). δ(H) ($CDCl_3$) 14.6 (2 H, br s, NH), 4.3 (s, 6 H, s, NMe) and 2.80 (6 H, s, SMe).

$[ReO(HL)_2]X$ 4 (X = Cl or BPh_4). To a suspension of $[ReOCl_3(PPh_3)_2]$ (0.14 g, 0.18 mmol) in CH_2Cl_2–C_6H_6 (1 : 1, 50 cm^3) was added H_2L (0.054 g, 0.4 mmol) dissolved in the minimum volume of CH_2Cl_2. The reaction mixture was refluxed with stirring for 30 min, producing an orange precipitate on partial evaporation of the solvent. The solution was cooled to room temperature and the precipitate was filtered off, washed with EtOH and dried with Et_2O. Crystals of $[ReO(HL)_2]Cl$ were grown from CH_2Cl_2–hexane (Found: C, 14.1; H, 2.7; N, 10.95; S, 25.6. $C_6H_{14}ClN_4OReS_4$ requires C, 14.2; H, 2.8; N, 11.0; S, 25.2%). $\tilde{\nu}/cm^{-1}$ 2994–2760 (N···HCl), 1597 [δ(N–H)], 1223 (C=S), 1003–952 (NCSS, Re=O) and 390 (Re–S). δ(H) (CD_2Cl_2) 13.1 (2 H, s, NH), 4.2 (6 H, s, NMe) and 2.9 (6 H, s, SMe). To provide better characterization, the analogous compound having $[BPh_4]^-$ as counter ion was synthesized. This gave better IR data: $\tilde{\nu}/cm^{-1}$ (KBr) 3318, 3295 (N–H), 1601 [δ(N–H)], 1223 (C=S), 972 (Re=O) and 390 (Re–S). δ(H) (CD_2Cl_2) 8.0 (2 H, s, NH), 7.5–6.8 (m, Ph), 3.3 (6 H, s, NMe) and 2.9 (6 H, s, SMe).

Crystallography

Crystal data. $C_6H_{14}ClN_4OReS_4$, M = 508.11, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 8.934(1), b = 9.751(1), c = 17.930(2) Å, U = 1561.9(2) $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections in the range $9 < \theta < 12°$, λ = 0.710 69 Å), Z = 4, D_c = 2.16 g cm^{-3}, μ = 85.64 cm^{-1}, $F(000)$ = 968, crystal dimensions 0.09 × 0.12 × 0.28 mm.

Data collection and processing. CAD4 diffractometer, ω–2θ scan, graphite-monochromated Mo-Kα radiation. 2157 Unique reflections measured ($2 \leqslant \theta \leqslant 28°$), giving 1825 with $I \geqslant 3\sigma(I)$, corrected for Lorentz-polarization and absorption (ψ-scan method, minimum transmission factor 0.84).

Structure analysis and refinement. Solution by Patterson and Fourier methods. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions except H(1) and H(3) which were refined isotropically. The weighting scheme $w = 4F_o^2/[\sigma^2(I) + (0.02F_o^2)^2]$ gave satisfactory agreement analyses. Final R = 0.023 and R' = 0.024. Goodness of fit = 1.11. Final difference-map peaks in the range ±0.49 e $Å^{-3}$. Programs used and sources of scattering factor data are given in ref. 18.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/81.

Results and Discussion

The technetium complexes $[TcNCl_2(PPh_3)_2]$ and $[TcNCl_2\{NPr(CH_2CH_2PPh_2)_2\}]$ react with *S*-methyl 2-methyldithiocarbazate $H_2NNMeC(S)SMe$ (H_2L) in CH_2Cl_2–EtOH under mild conditions to give a disubstituted $[TcN(HL)_2]$ **1** and a monosubstituted complex $[TcN(HL)\{NPr(CH_2CH_2PPh_2)_2\}]^+$ **2** respectively. The precursors $[TcOCl_4]^-$ and $[ReOCl_3(PPh_3)_2]$ react with H_2L to form the corresponding disubstituted cationic complexes $[MO(HL)_2]^+$ (M = Tc **3** or Re **4**). They are transformed to nitrido compounds $[MNCl_2(PPh_3)_2]$ when treated with an excess of hydrochloric acid and triphenylphosphine. The green technetium(IV) complex $[TcCl_4(PPh_3)_2]$ in the presence of NEt_3 gives the unexpected compound **1** in good yield. On the contrary, the analogous rhenium(IV) complex does not form the disubstituted nitrido species $[ReN(HL)_2]$ but, in any case, if the reaction mixture is treated with HCl and PPh_3 under reflux the complex $[ReNCl_2(PPh_3)_2]$ is invariably formed. All these complexes are air stable in the solid state; in solution they showed a slight decomposition after 2 weeks or longer. Although until now no single crystals suitable for X-ray crystallographic analysis have been obtained for complexes **1–3**, our formulation is supported by elemental analysis, IR and ^{1}H NMR spectra compared with those of the oxorhenium(v) complex **4** (X = Cl) for which suitable crystals were obtained by recrystallization from CH_2Cl_2–hexane. The infrared spectra of all these complexes present bands characteristic of the HL^- ligand. They exhibit a strong C=S band in the range 1238–1219 cm^{-1} as reported by Davison and co-workers[19] for technetium dithiocarbonate complexes. A set of bands in the range 1088–952 cm^{-1} attributed to the NC(S)S group[20,21] does not reveal with certainty the M≡X (M = Tc or Re; X = O or N) stretching vibrations. A band in the range 380–390 cm^{-1} may be assigned to the M–S bond (M = Tc or Re) in square-pyramidal complexes as previously reported.[9b] Finally, a band in the range 3295–3356 cm^{-1} is indicative of the presence of a deprotonated and co-ordinated NH_2 group.[21] The IR spectrum of H_2L shows bands at 3179–3291 cm^{-1} [ν(NH_2)], at 1607 cm^{-1} [NH_2 deformation mode, δ(N–H)], three strong bands at 955, 1055 and 1109 cm^{-1} [NC(S)S] and at 1223 cm^{-1} (C=S). The absence of a band at *ca.* 2500 cm^{-1} [ν(S–H)] indicates the thione nature of H_2L. In the IR spectra of the complexes the ν(N–H) bands are shifted to higher frequencies with respect to free H_2L which is diagnostic of deprotonation of the NH_2 group and of its co-ordination.[20,21] In addition, a split and a lowering of the bands attributed to the NC(S)S group upon co-ordination confirm the NS co-ordination.[20b,21] The complexes [TcN(HL)$_2$] **1** and [MO(HL)$_2$]Cl (M = Tc **3** or Re **4**) show comparable absorption frequencies confirming that they possess the same co-ordination sphere as also suggested by ^{1}H NMR spectra. The absorption corresponding to the M≡X multiple bond (M = Tc or Re; X = O or N) cannot be exactly assigned owing to the complexity of the IR spectra in the appropriate region.

Proton NMR spectra

The ^{1}H NMR spectra of complexes **1**, **3** and **4** are quite similar. They afford clear evidence that co-ordination occurs through the terminal deprotonated nitrogen atom and the thione sulfur. Moreover, the NH, NMe and SMe protons give rise to a set of three signals of relative area 1:3:3 at room temperature and it seems reasonable to assume that an equilibrium between *cis* and *trans* isomers is rapidly attained in solution. On the contrary, the spectrum of H_2L in Me_2SO at room temperature exhibits two resonances for each group of relative area 2:3:3 which correspond to the NH_2 (δ 5.65, 4.40), NMe (δ 3.70, 3.50) and SMe protons (δ 2.65, 2.45) respectively. When the temperature is increased to 70 °C each group collapses to a single resonance: broad peaks at δ 5.45 (NH_2), 3.55 (NMe) and 2.35 (SMe) respectively. Finally, at 120 °C the NH_2 peak (δ 5.50) broadens and the NMe and SMe signals narrow somewhat. This fact had been previously observed[22] and was attributed to the presence in solution of two isomers. X-Ray and theoretical studies on the methyl ester of dithiocarbazic acid and N-substituted derivatives are consistent with the presence in solution of conformers[23] and in particular it has been shown that the *N*-methyl derivative can exist in only two conformations.[23]

For all the complexes reported here the large downfield shift of these resonances with respect to H_2L (see Experimental section) is related both to a decrease in the electron density at the co-ordinated atoms and to electron delocalization over the whole molecule as indicated by deshielding of the SMe group which is not directly involved in the bonding. A larger downfield shift is observed for the oxo- compared to the nitrido-compounds and this deshielding could be attributable to a lower electron density on the metal ion in the oxo-species. The low-field shift of the NH and NMe resonances of the [ReO(HL)$_2$]Cl complex compared to [ReO(HL)$_2$][BPh$_4$] is indicative of an intramolecular N–H···Cl hydrogen bond. This pattern is consistent with the solid-state structure determined for [ReO(HL)$_2$]Cl and from these data it is possible to suggest that both oxo- and nitrido-disubstituted technetium complexes possess a square-pyramidal geometry. In contrast, the monosubstituted complex **2** was obtained in presence of an excess of H_2L; we have previously discussed the formation of mixed-ligand complexes.[17] In the ^{1}H NMR spectrum of this compound the NH and NMe resonances are shifted to higher field than those for free H_2L and other complexes.

Finally, it was observed that if the reaction of [TcNCl$_2$(PPh$_3$)$_2$] was carried out in the absence of NEt_3 a mixture of complexes was formed, as evidenced by the ^{1}H NMR spectrum which showed a multiplicity of signals in the range of the NMe and SMe protons. In conclusion, the ^{1}H NMR and IR spectra of these compounds give results in satisfactory agreement with those obtained for other transition metals.[20–22]

Formation of [MNCl$_2$(PPh$_3$)$_2$] (M = Tc or Re)

If to a solution of complex **3** or **4** an excess of PPh$_3$ and HCl is added and the mixture is heated under reflux for 30 min or longer the corresponding nitrido-complexes [MNCl$_2$(PPh$_3$)$_2$] are isolated in good yield. It seems that the formation of the M≡N multiple bond requires the ligand to be co-ordinated and the presence of an excess of H_2L is not indispensable. On the other hand, only when the technetium(IV) complex [TcCl$_4$(PPh$_3$)$_2$] is made to react in the presence of NEt_3 an excess of H_2L is required to produce the nitrido-complex [TcN(HL)$_2$]. We are not able to postulate a reaction mechanism because any attempt to identify the organic by-products has failed. Recently, Dilworth *et al.*[8] have reported the formation of rhenium(v) thiosemicarbazide complexes. These, under reflux, were transformed to imide hydrazide species which under further reflux gave the well known nitrido-complex [ReNCl$_2$(PPh$_3$)$_2$]. A different feature of these reactions is that the formation of nitrido-species requires the presence of HCl as well as an excess of thiosemicarbazide, moreover the reaction is slower than in our case. In our study the oxo-complexes **3** and **4** are transformed to nitrido-compounds [MNCl$_2$(PPh$_3$)$_2$] (M = Tc or Re) by adding HCl and PPh$_3$, while when the technetium(IV) complex [TcCl$_4$(PPh$_3$)$_2$] is used as precursor an excess of H_2L is required but not hydrochloric acid. We believe that the first step may be the formation of an oxo-species and in the second step this is transformed to the nitrido-complex [TcN(HL)$_2$] by the presence of an excess of H_2L. The oxidation of Tc^{IV} to Tc^{V} is not surprising;[1a,5] recently, we have observed it.[24] It seems certain that compounds containing a hydrazine N–N moiety give rise to the formation of nitrido-complexes of technetium and rhenium[8,10a] and as underlined by Dilworth, it appears very difficult to interpret these phenomena.

Crystal structure of [ReO(HL)$_2$]Cl 4

An ORTEP[25] view of the molecule is shown in Fig. 1. The asymmetric unit consists of a square-pyramidal [$Re^VO(HL)_2$]$^+$ cation and a Cl^- anion. The co-ordination around Re^V is distorted square pyramidal with the oxygen at the apical position and atoms N(1), N(3), S(1), S(3) of the ligands forming

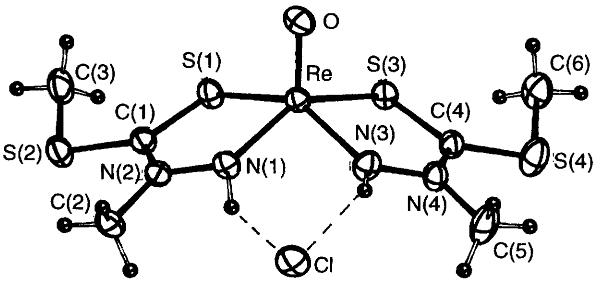


Fig. 1 An ORTEP view of complex **4** showing thermal ellipsoids at 30% probability

the basal plane. The Re atom is displaced from this mean plane toward the oxygen atom by 0.708(1) Å. The Cl^- ion is bound to the NH groups by means of two N–H ··· Cl hydrogen bonds with distances N(1) ··· Cl 3.113(6) and N(3) ··· Cl 3.172(6) Å (Table 1).

Comparing the structural data for this compound with those of other oxorhenium(v) N_2S_2, N_3S or NS_3 square-pyramidal complexes (Table 2) it is evident that the Re–N and Re–S bond distances are related to the charge and nature of the nitrogen and sulfur atoms. Taking into account the charged N^- of the amidic groups, the average Re–N^- distance of 2.00(2) Å is reasonably much longer than the analogous distances of 1.943(6) and 1.936(6) Å found in the present compound where the deprotonated nitrogens, belonging to hydrazinic groups, are less able than the amidic ones to delocalize the negative charge. Accordingly, the longest Re–N distances, average 2.19(4) Å, have been observed in compounds where N is a neutral aminic nitrogen atom. Similar variations are observed in Re–S bond distances. For instance, in thiolate complexes, where the sulfur atom is negatively charged, the average Re–S^- distance is 2.28(1) Å, while in the present compound where the S atoms are not charged the Re–S bond distances of 2.328(2) and 2.327(2) Å are significantly longer. The Re=O distance of 1.706(5) Å indicates multiple-bond character and is slightly longer than the average value of 1.678(9) Å.

Table 1 Selected bond distances (Å) and angles (°) of $[ReO(HL)_2]Cl$ with estimated standard deviations (e.s.d.s) in parentheses

Re–O	1.706(5)	S(3)–C(4)	1.747(7)
Re–S(1)	2.328(2)	N(1)–N(2)	1.397(8)
Re–S(3)	2.327(2)	N(3)–N(4)	1.387(8)
Re–N(1)	1.943(6)	N(2)–C(1)	1.307(8)
Re–N(3)	1.936(6)	N(4)–C(4)	1.304(9)
S(1)–C(1)	1.725(7)		
O–Re–S(1)	109.0(2)	S(1)–Re–N(1)	80.3(2)
O–Re–S(3)	107.9(2)	S(1)–Re–N(3)	140.8(2)
O–Re–N(1)	111.2(2)	S(3)–Re–N(1)	140.9(2)
O–Re–N(3)	110.2(2)	S(3)–Re–N(3)	80.1(2)
S(1)–Re–S(3)	89.7(1)	N(1)–Re–N(3)	84.2(2)
N(1) ··· Cl	3.113(6)	N(1)–H(1) ··· Cl	151(2)
N(3) ··· Cl	3.172(6)	N(3)–H(3) ··· Cl	152(2)

Conclusion

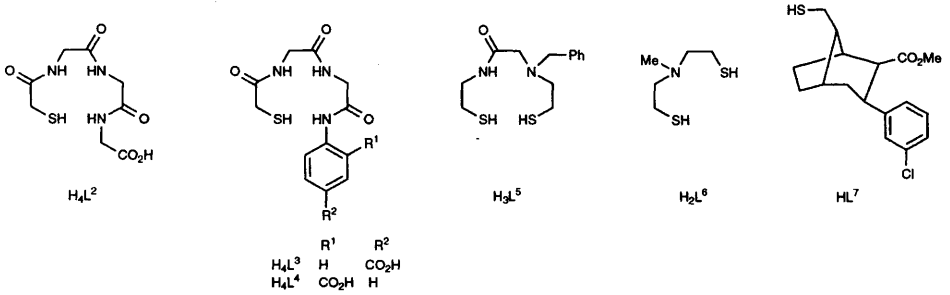
The present results seem to demonstrate that a necessary condition to transform an oxo-core $[M=O]^{3+}$ to a nitrido one $[M\equiv N]^{2+}$ (M = Tc or Re) is the co-ordination of the ligand and the presence of hydrochloric acid to promote cleavage of the hydrazinic group N–N but not the presence of an excess of ligand. Finally, taking into account the simplicity and similarity of the ^1H NMR and IR spectra of the complexes **1**, **3** and **4**, our formulation for **1** and **3** appears to be correct.

Technetium-99m chemistry

In our previous report we described a new procedure for the synthesis of nitridotechnetium-99m complexes and the real possibility of their use in the development of new radiopharmaceuticals.[10,11] This procedure is based on the reaction of $[^{99m}TcO_4]^-$ with the methyl ester of dithiocarbazic acid or its derivatives as a donor of nitride ions in presence of tertiary phosphines under acidic conditions. This reaction leads to the formation of a mixture of intermediate nitridotechnetium complexes the exact nature of which we were unable to determine. We observed the formation of only one compound when a chelating phosphine was used in the reaction mixture instead of tertiary phosphines.[17]

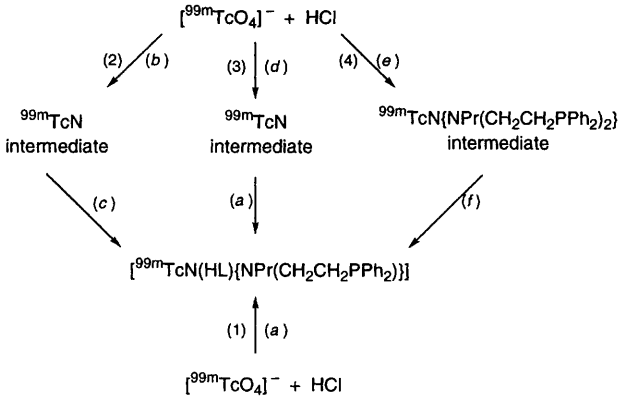
A set of reactions were performed in order to define the nature of this complex (Scheme 1). To simplify, we describe the procedure followed for reaction (1): a physiological saline solution of $Na[^{99m}TcO_4]$ (0.5 cm^3, 50 MBq), aqueous hydrochloric acid (1 mol dm^{-3}, 0.1 cm^3), EtOH (1 cm^3), and solid *S*-methyl 2-methyldithiocarbazate (0.001 g) were mixed in

Table 2 Comparison of selected bond distances (Å) in square-pyramidal oxorhenium(v) N_2S_2, N_3S or NS_3 complexes with e.s.d.s in parentheses



Complex *	Re=O	Re–N^- (amidic)	Re–N (aminic)	Re–S^-	Ref.
$[ReO(L^1)]^-$	1.662(5)	2.006(7) 1.995(7)		2.282(2) 2.284(3)	26
$[ReO(L^2)]^-$	1.68(1)	1.98(2) 2.04(2) 2.01(2)		2.285(7)	27
$[ReO(L^3)]^-$	1.670(5)	1.987(5) 1.984(5) 2.024(6)		2.283(2)	28
$[ReO(L^4)]^-$	1.684(4)	2.012(5) 1.976(4) 2.019(6)		2.295(2)	28
$[ReO(\textit{syn}\text{-}L^5)]$	1.683(4)	1.978(5)	2.182(5)	2.262(2) 2.270(2)	29
$[ReO(\textit{anti}\text{-}L^5)]$	1.680(2)	1.990(3)	2.151(3)	2.289(1) 2.246(1)	29
$[ReO(L^6)(L^7)]$	1.69(1)		2.23(1)	2.269(4) 2.269(4) 2.291(4)	30
Average	1.678(9)	2.00(2)	2.19(4)	2.28(1)	

* L^1 = 2,3-Bis(sulfanylacetamido)propanoate.



Scheme 1 (*a*) $NPr(CH_2CH_2PPh_2)_2$, H_2L; (*b*) H_2L, PPh_3; (*c*) $NPr(CH_2CH_2PPh_2)_2$; (*d*) NaN_3, PPh_3; (*e*) NaN_3, $NPr(CH_2CH_2PPh_2)_2$; (*f*) H_2L

a reaction vial and heated at 80 °C for 5 min. A solution of $NPr(CH_2CH_2PPh_2)_2$ (0.0015 g) (0.5 cm^3) in EtOH was added and the temperature was kept at 80 °C for 20 min. The radiochemical purity, in terms of free pertechnetate and yields, was determined by thin-layer chromatography (TLC) using silica gel plates developed with $EtOH–CHCl_3–C_6H_6$ (1.0 : 2 : 1.5 v/v). After development, the plates were dried and placed in contact with X-ray film (3M CRT7) overnight. The chromatographic analysis showed a dark spot ($R_f = 0.45$) indicating the location of the radioactivity due to the formation of a single compound. The presence of unreacted pertechnetate was not observed. Reactions (2)–(4) were carried out similarly. Taking into account that the formation of the $^{99m}Tc{\equiv}N$ group has been previously demonstrated,[10b,17] reactions (2)–(4) show that the same final product was always formed by these different routes. A chromatographic comparison between this compound and the corresponding technetium-99 complex **2** showed a difference in R_f value (0.30). We believe this may be attributed to the presence of a N–H • • • Cl network of inter- or intra-molecular bonds. In any case, this complex contains the ligand and the chelating phosphine $NPr(CH_2CH_2PPh_2)_2$. Finally, we observed that (*i*) the reaction takes place when the ligand concentration is 50 μg cm^{-3} or higher, (*ii*) it requires acidic conditions (pH < 5).

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