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Synthesis and structural characterization of technetium and rhenium complexes containing derivatized amino acids

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A novel N_2S tridentate ligand system (H_2L^n) for the formation of Re^V=O, $^{99}Tc^V$=O and $^{99}Tc^V$≡N complexes has been synthesized. N-Protected amino acids conjugated with *S*-methyl 2-methyldithiocarbazate gave chelate complexes [MO(L^n)Cl] (M = Tc or Re) and [TcN(L^n)(PPh_3)] in which H_2L^n are doubly deprotonated. All the compounds have been characterized by elemental analysis, IR and NMR spectroscopy and for [TcO(L^2)Cl] and [TcN(L^4)(PPh_3)] crystal structures determined. Both possess a distorted square-pyramidal geometry with the oxygen or nitrogen atom in the apical position, the tridentate ligand and a Cl^- ion or PPh_3 group forming the basal plane respectively. A study of reactivity shows that the formation of complexes can be related to the N-protecting groups, the alkyl substituent on the C_α atom and the metal precursors. Circular dichroism measurements on Re^V=O complexes have been performed in order to investigate possible conformational variations in solution. Finally, although the presence of isomers is possible, NMR spectroscopy has shown that they are absent at room temperature.

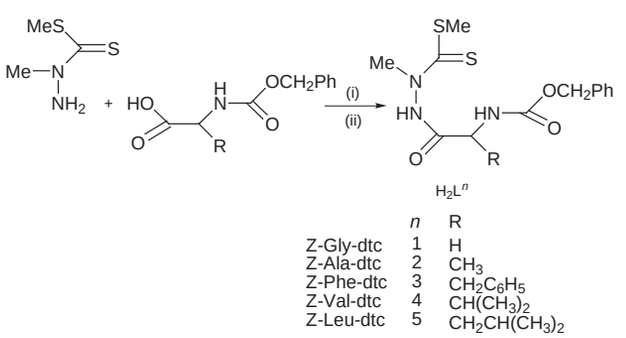
The studies of the inorganic chemistry of technetium and rhenium have undergone extensive developments due to the importance of the metastable γ-emitting isomer ^{99m}Tc in the field of diagnostic nuclear medicine and, more recently, the introduction of the β^- emitting isotopes ^{188}Re and ^{186}Re in radiotherapy.[1] Emphasis has been given to complexes of technetium(v) and rhenium(v) containing the $[M{=}O]^{3+}$ group and some years ago the first class of new ^{99m}Tc radiopharmaceuticals containing the $[Tc{\equiv}N]^{2+}$ core was proposed.[2]

In 1979 Davison and co-workers introduced a class of tetradentate ligands containing two thiolato and two nitrogen donor atoms, generally referred to as N_2S_2 ligands.[3] Since then, a great variety of bis(aminoethanethiol) (BAT) and diamide dithiol (DADT) complexes have been prepared.[3,4] Stable and neutral metal(v) oxo-complexes are obtained with BAT ligands, and although $^{99m}Tc^VO$(BAT) complexes were able to penetrate the blood–brain barrier, they showed poor brain retention.[5] Later, it was shown that BAT derivatives containing a side chain led to the formation of *syn* and *anti* $^{99/99m}Tc^V_{oxo}$ isomers, and the *syn* isomer displayed a brain uptake and retention time higher than the corresponding *anti* isomer in rats.[6]

The diamide dithiol ligand system forms anionic Tc^V_{oxo} compounds,[4b,7] and clinical evaluations of ^{99m}TcO(DADT) complexes have been shown to be good renal agents.[8] Stable and anionic complexes of both technetium(v) and rhenium(v) with N_3S (triamide monothiol) chelating agents have been structurally characterized.[9] In particular, the $[^{99m}TcO(MAG_3)]^{2-}$ (MAG_3 = mercaptoacetylglycylglycylglycine) is widely used as a renal radiopharmaceutical.[10] The corresponding derivatives of the two radionuclides $^{186/188}$Re are now being studied for use in cancer therapy.[9b,11]

Not long ago, a procedure for the synthesis of ^{99m}Tc-nitrido complexes was reported.[12] Technetium-99 nitrogen compounds containing N_2S_2 ligands were synthesized and structurally characterized,[13] but this class of complexes has not been further developed. For instance, it was demonstrated that oxotechnetium(v) complexes with dithiocarbamate ligands did not show a particular uptake for some organs; on the contrary, the corresponding nitrido compounds showed a good myocardial retention.[2,14]

Recently, we reported a study on the formation of the M≡N (M = Tc or Re) multiple bond and the characterization of Tc^V and Re^V complexes with the methyl ester of dithiocarbazic acid (dtc).[15] Our recent work has focused on the development of a new class of ligands obtained from the conjugation of simple N-protected amino acids with dtc useful for the preparation of oxo- and nitrido-complexes of Re^V and Tc^V. Here we describe the syntheses of these ligands (Scheme 1) and their metal(v) complexes (Scheme 2) their characterization and the preliminary conformational study in solution by circular dichroism spectroscopy. The crystal structures of [TcO(L^2)Cl] and [TcN(L^4)(PPh_3)] have been determined by X-ray crystallography.



	n	R
Z-Gly-dtc	1	H
Z-Ala-dtc	2	CH_3
Z-Phe-dtc	3	$CH_2C_6H_5$
Z-Val-dtc	4	$CH(CH_3)_2$
Z-Leu-dtc	5	$CH_2CH(CH_3)_2$

Scheme 1 (i) *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride anhydrous CH_2Cl_2, 0 °C; (ii) isobutyl chloroformate, *N*-methylmorpholine, anhydrous EtOAc, −15 °C

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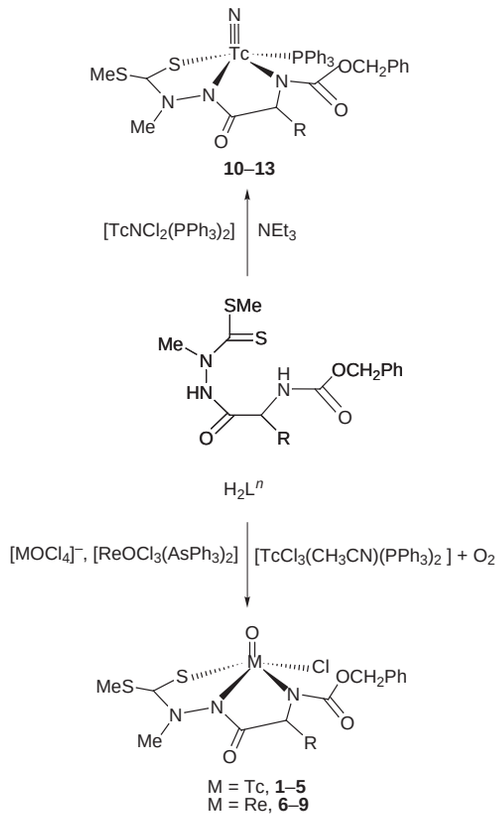

Scheme 2

Results and Discussion

Synthesis of ligands

The ligands were synthesized by coupling reactions between the carboxylic group of N-protected amino acids, in L configuration, with the NH_2 function of the chelating agent following standard methods of peptide chemistry. Although the ligands can be prepared following the two general procedures reported in the Experimental section, it was observed that condensation gave good results and yields *via* EDCI [*N*-ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide] rather than *via* MA (mixed anhydride) methods. The ligands have been characterized by melting point, polarimetric measurements, elemental analysis, IR and ^{1}H NMR spectra. They are stable in the solid state for several months.

Synthesis of oxotechnetium(V) and oxorhenium(V) complexes

The tetrachlorooxotechnetium(V) anion $[TcOCl_4]^-$ is a good starting material for preparation of the metal(V) complexes. It reacted rapidly and under mild conditions with H_2L^n (n = 1–5) ligands to form stable, neutral, purple complexes [TcO(L^n)Cl]. A difference in reactivity was observed in the formation of the complex **3** for which a longer reaction time was required. Although the formation of **3** occurred with poor yield, the corresponding oxorhenium complex was never isolated. This low reactivity of H_2L^3 could be attributable to the steric hindrance of the phenyl group in the C_α position. These complexes were also obtained, but in low yield, when the precursor was the Tc^{III} complex $[TcCl_3(CH_3CN)(PPh_3)_2]$. The reactions were carried out under reflux and the reaction mixture kept for a long time in air.

The corresponding oxorhenium(V) complexes were prepared by exchange reactions of Re^VO precursors such as $[ReOCl_3(AsPh_3)_2]$ and $[AsPh_4][ReOCl_4]$, while no reaction occurred with $[ReOCl_3(PPh_3)_2]$. No complex was obtained with the ligand H_2L^3 but rather only the starting compounds were recovered. A different behaviour was observed between the two oxorhenium(V) precursors. In fact, while the trichlorooxobis(triphenylarsine)rhenium(V) complex readily reacted with the $H_2L^{1,2,4,5}$ ligands, $[ReOCl_4]^-$ required a long reaction time indicating a lower exchange rate. In any case significant differences in yields were not observed.

These new oxometal(V) complexes were fully characterized by elemental analysis, IR and NMR spectroscopy, which are in agreement with the proposed formulations. In the case of [TcO(L^2)Cl], crystals suitable for X-ray diffraction analysis were grown from dichloromethane–ethanol.

Synthesis of nitridotechnetium(V) complexes

The nitridotechnetium(V) precursor $[TcNCl_2(PPh_3)_2]$ reacted with $H_2L^{1,2,4,5}$ ligands to form stable, yellow, neutral complexes [TcN(L^n)(PPh$_3$)]. The reactions were carried out in dichloromethane under reflux in the presence of NEt_3 because no reaction occurred in the absence of base. In addition, reactions with the ligand H_2L^3 did not give the desired product; the starting complex was recovered. Attempts to obtain the corresponding nitridorhenium complexes using $[ReNCl_2(PPh_3)_2]$ as precursor did not result in the desired products, giving a brown powder instead.

X-Ray diffraction analysis of the complex [TcN(L^4)(PPh$_3$)] confirmed the proposed formulations of this class of compounds.

Finally, no oxo- nor nitrido-metal(V) complexes were obtained when the corresponding precursors were made to react with *tert*-butoxycarbonyl (Boc)–N-protected ligands.

Spectroscopy

When compared with the spectra of the ligands $H_2L^{1–5}$, the infrared spectra of oxometal(V) complexes exhibit a strong M=O (M = Tc or Re) stretching vibration at 980–990 cm^{-1} for [TcO(L$^{1–5}$)Cl] and at 993–1001 cm^{-1} for the corresponding rhenium compounds. Differences in M=O stretching frequencies have been observed previously between analogous Tc and Re complexes.[6b,7,16] These values are at the high side of the range 900–1000 cm^{-1} generally observed for oxo-groups and are consistent with σ- and π-donating properties of the ligands in square-pyramidal structures. The absence of N–H stretching vibrations at 3200–3400 cm^{-1} is indicative of the presence of the two deprotonated and co-ordinated nitrogen atoms.

The IR spectra of the corresponding nitridotechnetium complexes differ from those discussed above in the presence of bands at 1065 and 1099 cm^{-1} attributed to the Tc≡N multiple bond and PPh_3 moiety, respectively.

The ^{1}H NMR spectra of both oxo- and nitrido-complexes are similar and comparable, but in comparison with those of the ligands they show marked differences. Besides the disappearance of the NH signals, we observed a downfield shift for the NMe and SMe protons, as has been previously discussed for technetium and rhenium complexes with the dithiocarbazate ligand.[15] Downfield shifts were also observed for $C_\alpha H$ and $C_\alpha H–CH$ protons, while the methyl protons of the alkyl group on C_α of $H_2L^{4,5}$ do not undergo a significant chemical shift, because they are located out of the co-ordination plane. The signals of the methylene protons of the Z-protecting group (Z = benzyloxycarbonyl) are of particular interest. They resonate as two doublets (δ 5.4–5.2) and a strongly deshielded broad singlet (*ca.* δ 7.0) in oxo- and nitrido-complexes, respectively. The observation at room temperature of these signals indicates that the methylene protons of the Z-group are not equivalent. It is known that this protecting group causes steric hindrance and its rotation can be impeded as a consequence of co-ordination. In order to verify this hypothesis, we collected ^{1}H NMR spectra of **1** and **13** in $(CD_3)_2SO$ over a range of temperatures from 25 to 120 °C. When the temperature was increased to 50 °C, the two doublets of the oxo-complex **1** collapsed to a broad single resonance, and at 100 °C it became a narrow singlet. The NMR

spectra of **13** showed that the broad singlet narrows somewhat at 50 °C and remains unchanged at 100 °C. Finally, the complexity of the spectra of both compounds at 120 °C precluded any assignment of the signals, and it was indicative of decomposition. The ^{31}P NMR signal in technetium complexes is not detectable or appears as a very broad line. This is attributed to a coupling of the ^{31}P nuclei with the quadrupole nucleus ^{99}Tc.[17,18] In the nitrido complexes reported here, the ^{31}P NMR spectra at room temperature showed a very broad signal in the range δ 45–47. The spectrum of the complex **13**, when collected at −80 °C, showed two broad peaks at δ 45.7 and 48.4. The molecules extend the Z-group away from the central core and the presence of two isomeric forms (*syn* or *anti* with respect to M≡N or M=O) could be expected. Isomers could be also expected for both oxo- and nitrido-complexes with H_2L^{2-5} ligands, differing in the orientation of the alkyl substituent on C_α with respect to M=O and Tc≡N. However, the presence of isomers in solution at room temperature was not observed by NMR spectroscopy.

Finally, the geometry about Tc and Re is, in all cases, distorted square pyramidal with oxygen or nitrogen in the apical position. The chelation proceeds by co-ordination of one neutral sulfur atom and two deprotonated NH groups which occupy three positions on the basal plane, the fourth being occupied by Cl^- or PPh_3 in the oxo- and nitrido-complexes, respectively.

In order to investigate a possible conformational variation in solution, induced in Z-Ala-dtc and Z-Val-dtc, by the formation of complexes **7** and **8**, some measurements of circular dichroism (CD) were performed at room temperature in 2,2,2-trifluoroethanol (TFE) solvent. This is often used to mimic the hydrophobic environment of the lipidic membrane.[19] Rhenium complexes were used because the experiments were performed in a laboratory not approved for handling radioactive products. In Fig. 1 the CD spectra in the far-UV region of Z-Ala-OH, Z-Ala-dtc and complex **7** are reported. A remarkable conformational variation is observed for the complex which is emphasized by the presence of a positive band at 245 nm ($[\theta]_M$ = +19 500 deg cm^2 dmol^{-1}), a very strong band at 202 nm ($[\theta]_M$ = +49 300 deg cm^2 dmol^{-1}) and a crossover point at 193 nm. The same profiles are observed in CD spectra of Z-Val-OH, Z-Val-dtc and the complex **8**. These data can be reasonably explained with a folded structure induced by a conformational rigidity and stability of the complexes in the solvent used.

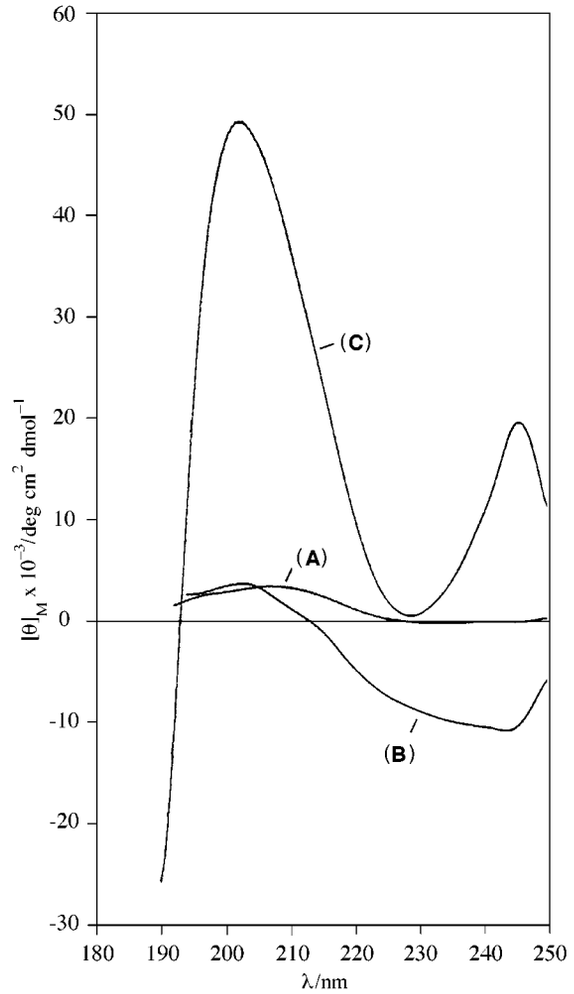

Fig. 1 Far-UV CD spectra in TFE of Z-Ala-OH (A), Z-Ala-dtc (B) and [ReO(L^2)Cl] (C)

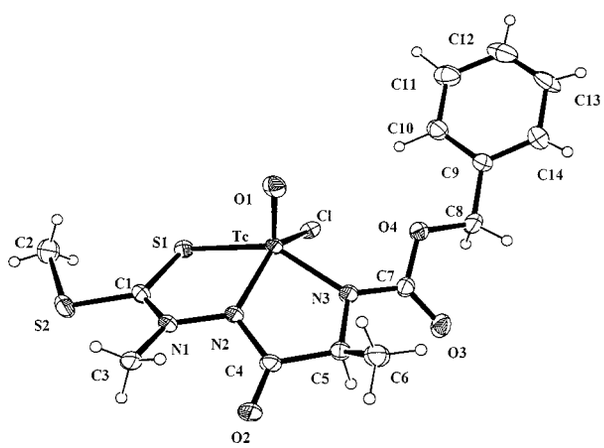

Fig. 2 An ORTEP view of compound **2** displaying the thermal ellipsoids at 30% probability

Description of the structures

Compound 2. The co-ordination around Tc^V is distorted square pyramidal with the oxo-oxygen atom at the apical position, and the tridentate S,N,N ligand and a Cl^- ion, *trans* to N2, forming the basal plane (Fig. 2). The Tc atom is displaced from the mean plane defined by Cl, S1, N2 and N3 by 0.7556(4) Å toward the oxo-atom O1. The Tc=O_{oxo} bond distance of 1.646(2) Å indicates a strong multiple bond character and is in agreement with the corresponding distances found in analogous square-pyramidal Tc^V complexes. The Tc–N (basal) bond distances of 1.960(2) and 1.983(2) Å, within the range 1.96–2.03 Å [8c,20–22] found in analogous compounds, are influenced both by the sp^2 hybridization of the nitrogens and by the delocalization of their negative charges on the N–C=O amidic groups. Accordingly, a significant shortening of the Tc–N bond distances to 1.90–1.92 Å [23,24] has been observed in compounds containing Tc$^V_{oxo}$–N (aminic) bonds, where the negative charges cannot be delocalized; and a significant lengthening of Tc–N to 2.13–2.21 Å [13,25,26] has been found in compounds containing Tc$^V_{oxo}$–N (aminic) bonds, where the nitrogen atoms are neutral.

Compound 12. The Tc–N complex **12**, structurally analogous to compound **2**, contains a similar basal ligand and a triphenylphosphine group in place of a Cl^- ion. The co-ordination around Tc^V is distorted square pyramidal with the nitrido-nitrogen atom at the apical position (Fig. 3). The Tc atom is displaced from the mean plane defined by the atoms S1, P1, N3 and N4 toward N1 by 0.6159(7) Å. The multiple Tc≡N bond distance of 1.621(9) Å, in agreement with other structural determinations,[27–29] is shorter than the corresponding Tc=O distance in **2**, in accord with the fact that the nitrido group is a 'harder' base than O_{oxo}. This Tc≡N shortening can be related to the lengthening of the Tc–X (basal) bond distances, with Tc–N = 1.960(2), 1.983(2) Å in **2** and 2.044(8), 2.054(8) Å in **12**, while Tc–S = 2.324(1) and 2.381(3) Å in **2** and **12**, respectively. This fact can be interpreted in terms of simple electrostatic considerations. The nitrido group is more effective in neutral-

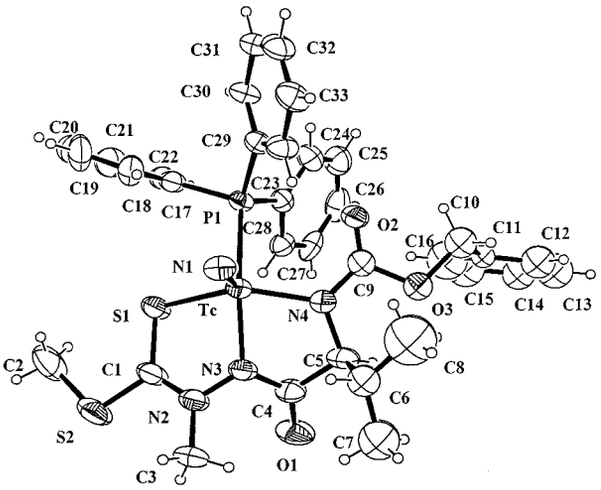

Fig. 3 An ORTEP view of compound **12** displaying the thermal ellipsoids at 30% probability

izing the charge at the Tc^{V} centre and accordingly the atoms of the basal ligand will be drawn less closely to $Tc^{V}_{nitrido}$ than to Tc in the Tc^{V}_{oxo} complexes. The other relevant difference is the ligand conformation around the corresponding N3–C7 and N4–C9 bonds of compound **2** and **12**, respectively. The *trans* conformation in **2** [torsion angle Tc–N3–C7–O3 = −151.4(2)°] and the *cis* conformation in **12** [Tc–N4–C9–O2 = 16(1)°] are probably determined both by the different steric requirements of Cl^{-} with respect to PPh_3, and of the methyl group bonded to C5 in **2** as compared to isopropyl in **12**.

Conclusion

Ligands have been prepared by facile coupling reactions between N-protected amino acids and the *N*-methyl ester of dithiocarbazic acid. We have synthesized the corresponding oxo- and nitrido-complexes [MO(L″)Cl] (M = Tc or Re, n = 1–5) and [TcN(L″)(PPh_3)] where H_2L'' is doubly deprotonated. They have been fully characterized by spectroscopic techniques, and the crystal structures of **2** and **12** have been determined. A comparison of the reactivity of the ligands has shown that protecting groups as well as substituents on C_a determine the formation of the metal complexes and their yields. An interesting difference amongst the reactivities of oxometal(V) precursors of the two elements has been observed, and it has been seen to follow the reactivity order: $[TcOCl_4]^{-} \gg [ReOCl_3(AsPh_3)_2] > [ReOCl_4]^{-}$.

All of the complexes reported here possess a square-pyramidal geometry in which the ligand occupies three of the four basal positions, offering a new possibility for designing oxo- and nitrido-complexes based on tridentate dianionic ligands and a monodentate coligand. In addition, CD measurements carried out on [ReO(L″)Cl] (n = 2 or 4) indicated that their structures were also retained in TFE solution, showing considerable stability in this solvent. We believe that this class of ligand may be an alternative to N_2S_2, N_3S, or NS_3 systems in the synthesis of Tc^{V} and Re^{V} complexes in the development of new radiopharmaceuticals.

This work constitutes the first part of a project to synthesize modified peptides and it demonstrates the viability of these ligands and their metal complexes.

Experimental

Materials and methods

CAUTION: Technetium-99 is a low-energy β^{-} emitter (E = 292 keV, *ca.* 4.67×10^{-14} J, $t_{\frac{1}{2}} = 2.12 \times 10^{5}$ years). When this material is handled, normal radiation safety procedures must be used to prevent contamination. All manipulation of solids or solutions were performed in a laboratory approved for low-level radioactivity.

Unless otherwise noted, all chemicals were reagent grade and used without further purification. Technetium-99 as solid $[AsPh_4][TcO_4]$ was obtained from the Radiochemical Centre, Amersham, UK. The compounds $[AsPh_4][TcOCl_4]$,[30] $[AsPh_4][TcNCl_4]$,[31] $[TcNCl_2(PPh_3)_2]$,[31] $[TcCl_3(CH_3CN)(PPh_3)_2]$,[32] $[ReOCl_3(AsPh_3)_2]$[33] and $[AsPh_4][ReOCl_4]$[34] were prepared according to literature methods. Protected amino acids, in L configuration, Z-Gly-OH, Z-Ala-OH, Z-Phe-OH, Z-Val-OH, Z-Leu-OH, and EDCI·*x*HCl were purchased from Inalco per la Nova Biochem, Milan, Italy; trifluoroacetic acid (TFA), isobutyl chloroformate (iBCF), *N*-methylmorpholine and 2,2,2-trifluoroethanol were obtained from Fluka. *S*-Methyl 2-methyldithiocarbazate (dtc) was prepared according to the literature method.[35]

High performance liquid chromatography (HPLC) analyses were performed on a Bruker LC 21-C chromatograph equipped with a UV/VIS LC 313 detector using a peptide and protein C-18 Vydac column with eluting system: (a) 10% v/v MeCN in water containing TFA 0.1%; (b) 60% v/v MeCN in water containing TFA 0.1% at a flow rate of 1.0 $cm^3\ min^{-1}$ monitored at 220 nm. Solvents used were purified by filtration on HOLV Millipore (0.45 μm) and degassed with helium prior to use. Analytical thin-layer chromatography (TLC) was performed using Merk silica gel 60 F-254 plates developed with EtOAc–pyridine–water–acetic acid (120, 40, 22, 12 cm^3) or CH_2Cl_2–MeOH–MePh (170, 20, 10 cm^3) and visualized by UV illumination at 254 nm and staining with hypochlorite–Starck–Jodine reagent.[36] Melting points were taken on a Reichert–Jung Thermovar apparatus and are uncorrected. Polarimetric measurements were recorded on a Perkin-Elmer model 241 polarimeter with a concentration c = 10 g dm^{-3} in MeOH at room temperature. Molecular weights of compounds were determined using a mass spectrometer Hewlett-Packard MALDI TOF model G2025A. Elemental analysis were performed using a Carlo Erba Instruments model EA1110; 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. Proton spectra of $(CD_3)_2SO$ and $CDCl_3$ solutions of the ligands and complexes were examined on a Varian Gemini 300 and Bruker AM 200 spectrometers with $SiMe_4$ as internal standard, ^{31}P-{^{1}H} NMR spectra on the same instruments in C_6D_6 and DMSO solutions with a 85% H_3PO_4 solution as external standard. Circular dichroism spectra were measured at room temperature using a Jasco model J-500A automatic recording dichrograph interfaced with an IBM AT computer. The instrument was calibrated with an aqueous solution of [$^{2}H_{10}$]camphorsulfonic acid and a 1,4-dioxane solution of epiandrosterone (5α-androstan-3β-ol-17-one).[37] Cylindrical fused quartz cells of 0.2 and 0.5 mm path lengths were used for CD measurements in the range 250–180 nm. The usual instrumental precautions were taken to avoid artefacts. The values are given in $[\theta]_M$ molar ellipticity (deg $cm^2\ dmol^{-1}$) using the molecular weight of the compounds. The concentration ranged from 3.7×10^{-3} to 1.2×10^{-3} M.

Synthesis of ligands

General procedures. The coupling reactions between N-protected amino acid and dtc were carried out by mixed anhydride (MA) and EDCI methods.[38] Here, the two general procedures are described for the ligand syntheses, the quantities of the reagents have to be adjusted accordingly.

Mixed anhydride. A solution of N-protected amino acid (3 mmol) in anhydrous EtOAc (25 cm^3) was stirred and cooled to −15 °C. *N*-Methylmorpholine (330 μl, 3 mmol) was added, followed by iBCF (394 μl, 3 mmol). After 5 min a solution of dtc (2 mmol) in dry EtOAc (25 cm^3) was added. Stirring was continued for 30 min at −15 °C and at room temperature overnight. The reaction mixture was diluted with EtOAc,

washed with water, K_2CO_3 (10%), brine and finally dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent evaporated at reduced pressure. Crystallisation from diisopropyl ether gave a white powder. Purity was determined by HPLC analysis and ligands were used without further purification.

EDCI. To an ice-cooled solution of the N-protected amino acid (10 mmol) and dtc (7 mmol) in anhydrous CH_2Cl_2 (50 cm^3) EDCI (10 mmol) was added. The mixture was stirred and allowed to warm to room temperature overnight. Solvent was removed under reduced pressure and the residue dissolved in EtOAc was washed with water, K_2CO_3 (10%) and brine. The organic phase was treated with anhydrous Na_2SO_4, filtered and concentrated to dryness. Crystallisation from diisopropyl ether provided white powders. The products were purified on a silica gel column, eluted with CH_2Cl_2, MePh and MeOH (85 : 5 : 10 v/v) and a white solid was isolated after recrystallisation from diisopropyl ether. Finally, purity was determined by HPLC analysis.

H_2L^1, Z-Gly-Dtc (yield 19%), m.p. 85–87 °C (Found: C, 47.6; H, 5.25; N, 12.8; S, 19.5. $C_{12}H_{17}N_3O_3S_2$ requires C, 47.7; H, 5.2; N, 12.8; S, 19.55%). FT-IR (KBr): 3389, 3318 [ν(NH)], 1705, 1686 [ν(C=O)], and 1246 cm^{-1} [ν(C=S)]. NMR [$(CD_3)_2SO$]: δ_H 2.4 (3 H, s, SCH_3), 3.45 (3 H, s, NCH_3), 3.73 (2 H, d, $C_\alpha H_2$), 5.04 (2 H, s, C*H*$_2$Ph), 5.68 (1 H, br s, $NHC_\alpha H_2$), 7.35 (5 H, m, Ph), 9.2 (1 H, br s, *H*$NNCH_3$).

H_2L^2, Z-Ala-Dtc (yield 82%, EDCI: 59%, MA), m.p. 147–149 °C. α(583 nm, 20 °C, 10 g dm^{-3} in MeOH, 10 cm path-length) = −65.7 ± 1° (Found: C, 49.75; H, 5.6; N, 12.25; S, 18.6. $C_{14}H_{19}N_3O_3S_2$ requires: C, 49.25; H, 5.6; N, 12.3; S, 18.8%). FT-IR (KBr): 3280 [ν(NH)], 1674 [ν(C=O)], and 1260 cm^{-1} [ν(C=S)]. NMR ($CDCl_3$): δ_H 1.45 (3 H, d, $C_\alpha HCH_3$), 2.45 (3 H, s, SCH_3), 3.6 (3 H, s, NCH_3), 4.4 (1 H, m, $C_\alpha HCH_3$), 5.18 (2 H, s, C*H*$_2$Ph), 5.28 (1 H, d, *H*$NC_\alpha H$), 7.3 (5 H, m, Ph), 9.0 (1 H, br s, *H*$NNCH_3$).

H_2L^3, Z-Phe-Dtc (yield 63%), m.p. 143–145 °C. α(583 nm, 20 °C, 10 g dm^{-3} in MeOH, 10 cm pathlength) = −35.35 ± 1° (Found: C, 57.7; H, 5.5; N, 10.0; S, 15.0. $C_{20}H_{23}N_3O_3S_2$ requires C, 57.5; H, 5.55; N, 10.05; S, 15.35%). FT-IR (KBr): 3290 [ν(NH)], 1678 [ν(C=O)], and 1265 cm^{-1} [ν(C=S)]. NMR ($CDCl_3$): δ_H 3.0–3.2 (2 H, m, $C_\alpha HCH_2$), 2.45 (3 H, s, SCH_3), 3.48 (3 H, s, NCH_3), 4.58 (1 H, m, $C_\alpha HCH_2$), 5.05 (2 H, s, C*H*$_2$Ph), 5.46 (1 H, br s, *H*$NC_\alpha H$), 7.25 (10 H, m, Ph), 9.0 (1 H, br s, *H*$NNCH_3$).

H_2L^4, Z-Val-Dtc (yield 65%), m.p. 180–183 °C. α(583 nm, 20 °C, 10 g dm^{-3} in MeOH, 10 cm pathlength) = −57.0 ± 1° (Found: C, 52.6; H, 6.55; N, 11.6; S, 17.3. $C_{16}H_{23}N_3O_3S_2$ requires C, 52.0; H, 6.3; N, 11.4; S, 17.35%). FT-IR (KBr): 3281 [ν(NH)], 1690–1672 [ν(C=O)], and 1252 cm^{-1} [ν(C=S)]. NMR [$(CD_3)_2SO$]: δ_H 0.98, 1.31 [6 H, 2d, $(CH_3)_2CH$], 2.22 [1 H, m, C*H*$(CH_3)_2$], 2.48 (3 H, s, SCH_3), 3.62 (3 H, s, NCH_3), 4.13 (1 H, m, $C_\alpha HCH$), 5.1 (2 H, s, C*H*$_2$Ph), 6.35 (1 H, br s, *H*$NC_\alpha H$), 7.35 (5 H, m, Ph), 10.83 (1 H, br s, *H*$NNCH_3$).

H_2L^5, Z-Leu-Dtc (yield 68%), m.p. 97–99 °C. α(583 nm, 20 °C, 10 g dm^{-3} in MeOH, 10 cm pathlength) = −56.0 ± 1° (Found: C, 53.8; H, 6.8; N, 11.1; S, 16.8. $C_{16}H_{25}N_3O_3S_2$ requires C, 53.2; H, 6.55; N, 10.95; S, 16.7%). FT-IR (KBr): 3240 [ν(NH)], 1686 [ν(C=O)], and 1263 cm^{-1} [ν(C=S)]. NMR ($CDCl_3$): δ_H 0.93, 0.96 [6 H, 2d, $(CH_3)_2CH$], 1.68 (3 H, m, $C_\alpha HCH_2CH$), 2.47 (3 H, s, SCH_3), 3.62 (3 H, s, NCH_3), 4.33 (1 H, m, $C_\alpha HCH_2$), 5.09 (2 H, s, C*H*$_2$Ph), 5.48 (1 H, br s, *H*$NC_\alpha H$), 7.25 (5 H, m, Ph), 9.33 (1 H, br s, H*N*NCH_3).

Synthesis of complexes

Oxotechnetuim(v) complexes [TcO(L^n)Cl] (n = 1–5). The salt [$AsPh_4$][$TcOCl_4$] (80 mg, 0.12 mmol) was dissolved in CH_2Cl_2–EtOH (2 : 1 v/v, 30 cm^3). Ligand (0.18 mmol) was added as a solution in CH_2Cl_2 (2 cm^3) causing an immediate colour change from pale green to dark violet. The reaction mixture was gently warmed for 15 min and through slow evaporation of the 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 based on the starting technetium complex.

Identical products were obtained when the reactions were carried out starting from the Tc^{III} complex [$TcCl_3(CH_3CN)(PPh_3)_2$]. To the orange solution of this compound (80 mg, 0.10 mmol) in CH_2Cl_2–MeCN (2 : 1 v/v, 30 cm^3) a solution of ligand (CH_2Cl_2, 2 cm^3) in stoichiometric ratio 1 : 2 was added. The reaction mixture was stirred and heated under reflux until it became brown (*ca.* 3 h). It was concentrated to small volume and allowed to stand for 3 weeks in air with addition of EtOH because the solvent did not evaporate. After this time, a purple solid was formed. Yields < 40% approximately.

Crystals of [$TcO(L^2)Cl$] suitable for X-ray analysis were grown using CH_2Cl_2 and EtOH as solvent and precipitant, respectively.

[$TcO(L^1)Cl$] **1**. Yield 90% (Found: C, 32.8; H, 3.2; N, 8.95; S, 13.1. $C_{13}H_{15}ClN_3O_4S_2Tc$ requires C, 32.8; H, 3.2; N, 8.8; S, 13.5%). FT-IR (KBr): 1709, 1668 [ν(C=O)], 1286 [ν(C=S)], 987 [ν(Tc=O)], and 966 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.60–7.30 (5 H, m, Ph), 5.40, 5.30 (2 H, 2d, C*H*$_2$Ph), 5.00, 4.62 (2 H, 2d, $C_\alpha H_2$), 4.18 (3 H, s, NCH_3), 2.98 (3 H, s, SCH_3). NMR [$(CD_3)_2SO$]: δ_H 5.25 (2 H, br s, C*H*$_2$Ph) (50 °C); δ_H 5.2 (2 H, s, C*H*$_2$Ph) (100 °C).

[$TcO(L^2)Cl$] **2**. Yield 90% (Found: C, 34.25; H, 3.5; N, 8.65; S, 13.05. $C_{14}H_{17}ClN_3O_4S_2Tc$ requires C, 34.3; H, 3.5; N, 8.6; S, 13.1%). FT-IR (KBr): 1707, 1670 [ν(C=O)], 1263 [ν(C=S)], 980 [ν(Tc=O)], and 968 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.60–7.10 (5 H, m, Ph), 5.40, 5.30 (2 H, 2d, C*H*$_2$Ph), 4.90 (1 H, q, $C_\alpha HCH_3$), 4.10 (3 H, s, NCH_3), 2.98 (3 H, s, SCH_3), 1.70 (3 H, d, $C_\alpha HCH_3$).

[$TcO(L^3)Cl$] **3**. This complex was obtained as above from [$AsPh_4$][$TcOCl_4$] but a reaction time of 1 h was required. Yield 60% (Found: C, 41.95; H, 4.0; N, 7.15; S, 11.1. $C_{20}H_{23}ClN_3O_4S_2Tc$ requires C, 42.3; H, 4.1; N, 7.4; S, 11.3%). FT-IR (KBr): 1695 [ν(C=O)], 1267 [ν(C=S)], 987 [ν(Tc=O)], and 964 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.60–7.20 (10 H, m, Ph), 5.50, 5.26 (2 H, 2d, C*H*$_2$Ph), 5.04 (1 H, m, $C_\alpha HCH_2$), 3.85 (3 H, s, NCH_3), 3.45 (2 H, m, C*H*$_2$Ph), 2.88 (3 H, s, SCH_3).

[$TcO(L^4)Cl$] **4**. Yield 65% (Found: C, 37.3; H, 4.2; N, 7.9; S, 12.0. $C_{16}H_{21}ClN_3O_4S_2Tc$ requires C, 37.1; H, 4.1; N, 8.1; S, 12.4%). FT-IR (KBr): 1701, 1674 [ν(C=O)], 1254–1230 [ν(C=S)], 980 [ν(Tc=O)], and 964 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.50–7.25 (5 H, m, Ph), 5.40, 5.22 (2 H, 2d, C*H*$_2$Ph), 4.73 (1 H, d, $C_\alpha HCH$), 4.09 (3 H, s, NCH_3), 2.96 (3 H, s, SCH_3), 2.42 [1 H, m, C*H*$(CH_3)_2$], 1.18, 1.11 [6 H, 2d, $CH(CH_3)_2$].

[$TcO(L^5)Cl$] **5**. Yield 40% (Found: C, 37.65; H, 4.30; N, 7.7; S, 11.8. $C_{17}H_{23}ClN_3O_4S_2Tc$ requires C, 38.4; H, 4.35; N, 7.9; S, 12.05%). FT-IR (KBr): 1700, 1676 [ν(C=O)], 1251 [ν(C=S)], and 966 (br) cm^{-1} [ν(Tc=O), ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.60–7.25 (5 H, m, Ph), 5.40, 5.25 (2 H, 2d, C*H*$_2$Ph), 4.90 (1 H, m, $C_\alpha HCH_2$), 4.05 (3 H, s, NCH_3), 2.98 (3 H, s, SCH_3), 2.00–1.80 [3 H, m, $CH_2CH(CH_3)_2$], 1.05, 0.95 [6 H, 2d, $CH(CH_3)_2$].

Oxorhenium(v) complexes [ReO(L^n)Cl] (n = 1,2,4,5). Addition of a solution of ligand (0.13 mmol) in CH_2Cl_2 (2 cm^3) at room temperature to the green complex [$ReOCl_3(AsPh_3)_2$] (100 mg, 0.11 mmol) dissolved in CH_2Cl_2–C_6H_6 (3 : 1 v/v, 40 cm^3) caused an immediate colour change from green to light brown. The reaction mixture was stirred and heated under reflux for 30 min, concentrated *in vacuo* and the residue was treated with Et_2O and *n*-hexane. Slow evaporation of the solvent provided a red-brown solid. Recrystallization from CH_2Cl_2–EtOH produced purple crystals.

Alternatively, [$AsPh_4$][$ReOCl_4$] (100 mg, 0.12 mmol) was dissolved in CH_2Cl_2–EtOH (1 : 1 v/v, 40 cm^3). The solution was heated to reflux, an excess of solid ligand was added and the

mixture was kept under reflux for 2 h, after which time the greenish yellow colour of the starting metal compound had been replaced by a brownish red colour. The solvent was removed under reduced pressure and the residue taken up in C_6H_6. Purple crystals formed upon the addition of diethyl ether were filtered off, washed with EtOH and dried with Et_2O. Yields were determined based on the starting metal compounds.

[ReO(L^1)Cl] **6**. Yield 90% (Found: C, 27.6; H, 2.75; N, 7.5; S, 11.2. $C_{13}H_{15}ClN_3O_4S_2Re$ requires C, 27.7; H, 2.7; N, 7.45; S, 11.4%). FT-IR (KBr): 1710, 1680 [ν(C=O)], 1280 [ν(C=S)], 993 [ν(Re=O)] and 964 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.55–7.25 (5 H, m, Ph), 5.45, 5.25 (2 H, 2d, CH_2Ph), 4.95, 4.60 (2 H, 2d, $C_\alpha H_2$), 4.28 (3 H, s, NCH_3); 2.98 (3 H, s, SCH_3).

[ReO(L^2)Cl] **7**. Yield 90% (Found: C, 30.1; H, 2.9; N, 7.1; S, 11.2. $C_{14}H_{17}ClN_3O_4S_2Re$ requires C, 29.15; H, 2.95; N, 7.3; S, 11.1%). FT-IR (KBr): 1715, 1676 [ν(C=O)], 1263 [ν(C=S)], 995 [ν(Re=O)], and 964 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.55–7.25 (5 H, m, Ph) 5.45, 5.25 (2 H, 2d, CH_2Ph), 4.88 (1 H, q, $C_\alpha HCH_3$), 4.20 (3 H, s, NCH_3), 3.00 (3 H, s, SCH_3), 1.66 (3 H, s, $C_\alpha HCH_3$).

[ReO(L^4)Cl] **8**. Yield 60% (Found: C, 31.9; H, 3.5; N, 6.7; S, 9.8. $C_{16}H_{21}ClN_3O_4S_2Re$ requires C, 31.7; H, 3.5; N, 6.9; S, 10.6%). FT-IR (KBr, cm^{-1}): 1709, 1678 [ν(C=O)], 1257 [ν(C=S)], 997 [ν(Re=O)], and 962 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.50–7.30 (5 H, m, Ph), 5.43, 5.24 (2 H, 2d, CH_2Ph), 4.72 (1 H, d, $C_\alpha HCH$), 4.19 (3 H, s, NCH_3), 2.97 (3 H, s, SCH_3), 2.38 (1 H, m, C$H(CH_3)_2$], 1.16, 1.09 [6 H, 2d, $CH(CH_3)_2$].

[ReO(L^5)Cl] **9**. Yield 60% (Found: C, 32.7; H, 3.7; N, 6.4; S, 10.1. $C_{17}H_{23}ClN_3O_4S_2Re$ requires C, 32.9; H, 3.7; N, 6.8; S, 10.3%). FT-IR (KBr): 1707, 1682 [ν(C=O)], 1253 [ν(C=S)], 1001 [ν(Re=O)], and 964 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.50–7.30 (5 H, m, Ph), 5.41, 5.25 (2 H, 2d, CH_2Ph), 4.88 (1 H, t, $C_\alpha HCH_2$), 4.18 (3 H, s, NCH_3), 2.97 (3 H, s, SCH_3), 1.88 [3 H, m, $CH_2CH(CH_3)_2$], 1.02, 0.95 [6 H, 2d, $CH(CH_3)_2$].

Nitrido technetium(v) complexes. [TcN(L^n)(PPh_3)] (n = 1,2,4,5). The pink compound [$TcNCl_2(PPh_3)_2$] (90 mg, 0.12 mmol) in CH_2Cl_2 (40 cm^3) was heated and stirred until all the solid dissolved. A solution of ligand (0.18 mmol, CH_2Cl_2 2 cm^3) was added and the reaction mixture was heated under reflux. Addition of 1–3 drops of NEt_3 produced a colour change from pink to bright yellow. After 1 h of heating, the solution was concentrated under reduced pressure and the residue taken up in Et_2O. Solid NEt_3·HCl was filtered off and washed with CH_2Cl_2 (2 × 25 cm^3). The organic solutions were combined and dried *in vacuo*. A yellow powder of the desired product was collected and washed with ethanol and diethyl ether. The solid was recrystallized twice from dichloromethane–ethanol mixture. Yields are based on the starting technetium complex. Crystals of [TcN(L^4)Cl] suitable for X-ray analysis were grown from CH_2Cl_2 and EtOH.

[TcN(L^1)(PPh_3)] **10**. Yield 80% (Found: C, 53.5; H, 4.4; N, 8.2; S, 9.4. $C_{31}H_{30}N_4O_3PS_2Tc$ requires C, 53.1; H, 4.3; N, 8.0; S, 9.15%). FT-IR (KBr): 1651 [ν(C=O)], 1292 [ν(C=S)], 1099 [ν(PPh_3)], 1065 [ν(Tc≡N)], and 997–939 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.60–7.10 (20 H, m, Ph), 6.88 (2 H, br s, CH_2Ph), 4.68, 4.27 (2 H, 2d, $C_\alpha H_2$), 4.05 (3 H, s, NCH_3), 2.58 (3 H, s, SCH_3). NMR (C_6D_6): δ_P 45.3 (br s).

[TcN(L^2)(PPh_3)] **11**. Yield 80% (Found: C, 54.2; H, 4.7; N, 7.65; S, 9.1. $C_{32}H_{32}N_4O_3PS_2Tc$ requires C, 53.75; H, 4.5; N, 7.8; S, 9.0%). FT-IR (KBr): 1719, 1661 [ν(C=O)], 1267 [ν(C=S)], 1097 [ν(PPh_3)], 1065 [ν(Tc≡N)], and 960 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.70–7.00 (20 H, m, Ph), 6.82 (2 H, br s, CH_2Ph), 4.65 (1 H, m, $C_\alpha HCH_3$), 4.02 (3 H, s, NCH_3), 2.55 (3 H, s, SCH_3), 1.72 (3 H, d, $C_\alpha HCH_3$). NMR (C_6D_6): δ_P 46.4 (br s).

[TcN(L^4)(PPh_3)] **12**. Yield 70% (Found: C, 55.1; H, 4.95; N, 7.7; S, 8.7. $C_{34}H_{36}N_4O_3PS_2Tc$: C, 54.95; H, 4.9; N, 7.5; S, 8.6%). FT-IR (KBr): 1713, 1657 [ν(C=O)], 1263 [ν(C=S)], 1099 [ν(PPh_3)] 1067 [ν(Tc≡N)], and 959 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.70–7.25 (20 H, m, Ph), 6.80 (2 H, br s, CH_2Ph), 4.45 (1 H, d, $C_\alpha HCH$), 4.00 (3 H, s, NCH_3), 2.60 (3 H, s, SCH_3), 2.50 (1 H, m, $C_\alpha HCH$), 1.25, 1.10 [6 H, 2d, $CH(CH_3)_2$]. NMR (C_6D_6): δ_P 46.8 (br s).

[TcN(L^5)(PPh_3)] **13**. Yield 90% (Found: C, 55.4; H, 5.05; N, 7.45; S, 8.3. $C_{35}H_{38}N_4O_3PS_2Tc$ requires C, 55.5; H, 5.05; N, 7.4; S, 8.5%). FT-IR (KBr): 1659 [ν(C=O)], 1285–1252 [ν(C=S)], 1099 [ν(PPh_3)], 1065 [ν(Tc≡N)], and 958 cm^{-1} [ν(NCSS)]. NMR ($CDCl_3$): δ_H 7.70–7.20 (20 H, m, Ph), 6.80 (2 H, br s, CH_2Ph), 4.75 (1 H, m, $C_\alpha HCH_2$), 4.00 (3 H, s, NCH_3), 2.60 (3 H, s, SCH_3), 2.10 [1 H, m, C$H(CH_3)_2$], 1.95 (2 H, m, $C_\alpha HCH_2$), 1.10, 1.00 [6 H, 2d, $CH(CH_3)_2$]. NMR [$(CD_3)_2SO$]: δ_H 6.85 (2 H, s, CH_2Ph) (50–100 °C). NMR (C_6D_6): δ_P 47.0 (br s); δ_P 45.7, 48.4 (2s), (−80 °C).

Table 1 Selected bond distances (Å) and angles (°) for complexes **2** and **12** with estimated standard deviations in parentheses

[TcO(L^2)Cl] **2**			
Tc–O1	1.646(2)	C1–N1	1.306(3)
Tc–C1	2.340(1)	N1–N2	1.418(2)
Tc–S1	2.324(1)	N2–C4	1.388(3)
Tc–N2	1.960(2)	C4–C5	1.508(3)
Tc–N3	1.983(2)	N3–C5	1.461(3)
S1–C1	1.718(2)		
O1–Tc–C1	113.76(7)	Cl–Tc–N2	134.43(6)
O1–Tc–S1	108.77(7)	Cl–Tc–N3	90.01(6)
O1–Tc–N2	111.57(9)	S1–Tc–N2	80.79(6)
O1–Tc–N3	108.65(9)	S1–Tc–N3	108.65(9)
C1–Tc–S1	80.73(2)	N2–Tc–N3	79.91(7)
[TcN(L^4)(PPh_3)] **12**			
Tc–N1	1.621(9)	C1–N2	1.294(14)
Tc–P1	2.437(2)	N2–N3	1.403(12)
Tc–S1	2.381(3)	N3–C4	1.352(10)
Tc–N3	2.044(8)	C4–C5	1.534(6)
Tc–N4	2.054(8)	C5–N4	1.496(9)
S1–C1	1.716(11)		
N1–Tc–P1	95.4(3)	P1–Tc–N3	154.2(2)
N1–Tc–S1	108.1(3)	P1–Tc–N4	95.4(2)
N1–Tc–N3	110.2(4)	S1–Tc–N3	79.5(2)
N1–Tc–N4	112.9(4)	S1–Tc–N4	137.8(2)
P1–Tc–S1	90.3(1)	N3–Tc–N4	77.5(3)

Crystallography

Crystal data. $C_{14}H_{17}ClN_3O_4S_2Tc$, **2**: M = 489.78, monoclinic, space group $P2_1$, a = 8.238(1), b = 14.169(1), c = 8.427(1) Å, β = 105.54(1)°, U = 947.7(2) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), Z = 2, D_c = 1.716 g cm^{-3}, μ = 11.44 cm^{-1}, F(000) = 492, crystal dimensions 0.40 × 0.26 × 0.15 mm.

$C_{34}H_{36}N_4O_3PS_2Tc$, **12**: M = 742.68, orthorhombic, space group $P2_12_12_1$, a = 10.040(1), b = 14.284(1), c = 24.256(3) Å, U = 3478.6(6) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), Z = 4, D_c = 1.418 g cm^{-3}, μ = 6.19 cm^{-1}, F(000) = 2528, crystal dimensions 0.38 × 0.24 × 0.19 mm.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, ω–2θ scan, graphite-monochromated Mo-Kα radiation: compound **2**, 2855 unique reflections measured ($2 \leqslant \theta \leqslant 30°$), giving 2688 with $I \geqslant 3\sigma(I)$, corrected for Lorentz-polarization and absorption effects (ψ-scan method, minimum transmission factor 0.952); compound **12**, 4659 unique reflections measured ($2 \leqslant \theta \leqslant 28°$), giving 3665 with $I \geqslant 2\sigma(I)$, corrected for Lorentz-polarization and absorption effects (ψ-scan method, minimum transmission factor 0.983).

Structure analysis and refinement. Solutions by Patterson and Fourier methods. For compound **2**: full-matrix least-squares

refinement on F, with all non-hydrogen atoms anisotropic and hydrogens isotropic. The weighting scheme $w = 4F_o^2/[\sigma^2(I) + (0.02F_o^2)^2]$ gave satisfactory agreement analyses. Final $R = 0.017$ and $R' = 0.021$. Goodness of fit = 1.33. Final difference map peaks in the range ± 0.34 e Å^{-3}. Programs used: MO1EN[39] and PARST.[40]

For compound **12**: full-matrix least-squares refinement on F^2, with the non-hydrogen atoms anisotropic, except C6, C7, C8, O3, C10, C11, C12, C13, C14, C15 and C16 which were found disordered and refined isotropically over two positions with occupancy 0.5; the hydrogens were placed at fixed, calculated positions. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0831P)^2 + 6.2133P]$ where $P = (F_o^2 + 2F_c^2)/3$ gave satisfactory agreement analyses. Final $R = 0.064$ and $R' = 0.180$. Goodness of fit = 1.18. Final difference map peaks in the range ± 0.53 e Å^{-3}. Programs used SHELXL 93[41] and PARST.[40]

For both compounds we chose to refine the enantiomer having the ligand in the same configurations as the L-amino acid from which it is derived.

A selection of bond distances and angles is reported in Table 1 and ORTEP[42] views in Figs. 2 and 3.

CCDC reference number 186/920.

See http://www.rsc.org/suppdata/dt/1998/1453/ for crystallographic files in .cif format.

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