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Synthesis and characterization of neutral oxorhenium(V) and nitridotechnetium(V) complexes with a tetradentate N_2S_2 unsaturated ligand derived from dithiocarboxylic acid

G. Cros [a],*, H. Belhadj Tahar [a], D. de Montauzon [a], A. Gleizes [b], Y. Coulais [c], R. Guiraud [c], E. Bellande [d], R. Pasqualini [d]

[a] *Laboratoire de Chimie de Coordination du CNRS, UP 8241 liée par convention à l'Université Paul Sabatier et l'Institut National Polytechnique, 205 route de Narbonne, 31077 Toulouse Cedex, France*

[b] *Laboratoire des Matériaux de l'Institut National Polytechnique, URA-CNRS 445, Ecole nationale supérieure de Chimie de Toulouse, 118 route de Narbonne, 31077 Toulouse Cedex, France*

[c] *Laboratoire de Biophysique et de Médecine Nucléaire, Faculté de Médecine Toulouse Purpan, 133 route de Narbonne, 31062 Toulouse Cedex, France*

[d] *CIS-Bio International, BP 32, 91192 Gif sur Yvette, France*

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Abstract

Neutral complexes of technetium(V) and rhenium(V) of the type TcN(L2) and ReO(L2)Cl, where L2 corresponds to the dianionic form of the tetradentate N_2S_2 ligand *N,N'*-ethylene bis(methyl 2-aminocyclopentane-1-dithiocarboxylate), were prepared by substitution reaction on the starting materials $^{99}TcNCl_2(PPh_3)_2$ and $ReOCl_3(PPh_3)_2$, respectively. The complexes were characterized by elemental analysis, IR, NMR spectroscopy and conductimetry. The molecular and crystal structure of the nitrido complex TcN(L2) was determined by single-crystal X-ray diffraction technique (monoclinic $P2_1/c$, $a = 13.380(6)$, $b = 9.945(2)$, $c = 15.839$ Å, $\beta = 113.91(3)°$). The electrochemical behaviour of the nitrido complex was investigated.

Keywords: Crystal structures; Rhenium complexes; Oxo complexes; Technetium complexes; Nitrido complexes; Unsaturated N_2S_2 ligand; Dithiocarboxylic acid derived ligand

1. Introduction

Since the preparation of the first nitrido technetium complexes in 1981 [1,2], the chemistry of the Tc≡N core has been widely developed and, so far, a large number of nitrido ^{99}Tc complexes has been prepared with various types of ligands, such as dithiocarbamates [3], arsines [4], phosphines [5], amines [6], dithiocarbazic derivatives [7], tetraazamacrocycles [8], bis-aminethiols [9], amino acids [10] and thiacrown ethers [11]. An additional interest for this new class of compounds has emerged recently due to the discovery of an efficient method for preparing the ^{99m}Tc≡N group at tracer level in sterile and apyrogenic conditions [12–14]. The method has been applied successfully to the labelling of dithiocarbamato ligands and the resulting complexes showed high myocardial uptake not only in animals but also in humans [15–18].

Recently we used this method to label two different classes of tetradentate unsaturated N_2S_2 Schiff bases whose parent ligands, *N,N'*-ethylene bis(thioacetonylideneimine) [19] and *N,N'*-ethylene bis(methyl 2-aminocyclopentene-1-dithiocarboxylate) [20] designated as H_2L1 and H_2L2, respectively, are represented in Fig. 1.

These ligands are of interest because: (i) during the past decade, extensive studies have proved that the technetium complexes of their N_2S_2 saturated analogues (e.g. bis-aminethiols) were potential brain perfusion agents [21–25]; (ii) the presence of N–H...S bridges stabilizes the S–H bonds and prevents their oxidation and the formation of S–S bridges; (iii) in the complexes of the related unsaturated N_2S_2 Schiff bases the presence of delocalized π electron systems on the six-membered

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*Corresponding author.

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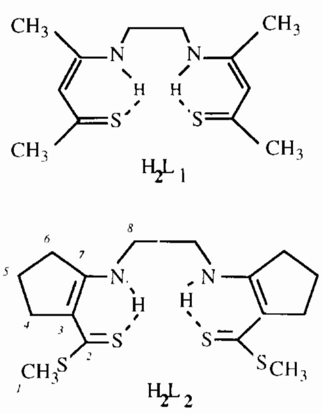

Fig. 1. Ligand structures and numbering schemes.

rings allows the transmission of electronic effects from the substituents to the metal and consequently enables modulation of the $E_{1/2}$ potential values of the redox couples [26].

Recent biodistribution studies in the rat, of neutral lipophilic ^{99m}Tc complexes with the ligands H_2L1 and H_2L2, have reported that while the complexes of related H_2L1 ligands cross only the blood brain barrier slightly, a significant heart uptake was observed for NTc(L2) [19,20].

In parallel with these previous studies and with the aim of checking whether any structural features might explain these unexpected differences of behaviour, in a preliminary work we prepared and fully characterized on a macroscopic scale, the complexes of H_2L1 with the long lived isotope ^{99}Tc [27]. In the present work we continue these investigations and report the preparation and the characterization of the nitrido ^{99}Tc complex of H_2L2 and its oxo rhenium analog. The structural features and electrochemical behaviour of complex TcN(L2) are compared with those of TcN(L1).

2. Experimental

2.1. Health precautions

Technetium 99 is a weak β emitter ($E_{max}=292$ keV, $t_{1/2}=2.12\times10^5$ years); handling was carried out in laboratories approved for low-level radioactivity using glove boxes under moderate vacuum for the synthesis and recovery operations. Normal safety procedures were followed at all times to prevent contamination.

2.2. Reagents

Unless otherwise stated, all chemicals were of reagent grade. The complex $ReOCl_3(PPh_3)_2$ was prepared from potassium perhenate (Aldrich) by a literature method [28]. ^{99}Tc as $NH_4{}^{99}TcO_4$ was obtained from Oak Ridge National Laboratory (USA) and purified [29]. $TcNCl_2(PPh_3)_2$ was prepared according to the literature procedure [30].

2.3. Synthesis of the ligand

The ligand H_2L2 was prepared as previously reported [20], following a procedure based on a transamination reaction of the methyl ester of 2-aminocyclopentene-1-dithiocarboxylic acid with an excess of ethylenediamine [31]. IR (cm^{-1}): ν(N–H...S) 3180(w); ν(C–H) 2980–2820(w); ν(C...C)+ν(C···N) 1580(s), 1565(s); δ(C–H) 1460(s); ν(S–CH_3) 1360(m); ν(S–H···N) 1280(s); ν($CSSCH_3$) 910(m). ^{1}H NMR (ppm): [H1] 2.6(s), [H4] 2.9(t), [H5] 1.7(qt), [H6] 2.9(t), [H8] 3.6(d+s), (N–H...S) 13.3 (m). ^{13}C NMR (ppm): [C1] 16.5, [C2] 199.5, [C3] 117.5, [C4] 32.7, [C5] 20.4, [C6] 30.4, [C7] 68.3, [C8], 45.5. (The numbering scheme is indicated in Fig. 1.)

2.4. Synthesis of the complexes

2.4.1. [ReO(L2)Cl]

To a sample of ligand H_2L2 (117 mg, 0.31 mmol) dissolved in a mixture of methylene chloride–toluene (3:1, 50 ml) were added $ReOCl_3(PPh_3)_2$ (267 mg, 0.31 mmol) and KOt–C_4H_9 (70 mg, 0.62 mmol). The reaction mixture was refluxed for 36 h under a closed atmosphere of argon. Upon cooling, the addition of 20 ml of pentane resulted in the formation of a reddish brown solid, which was filtered and washed with methanol and diethyl ether; yield 60%. *Anal.* Found: C, 32.9; H, 3.4; N, 4.3; S, 21.8; Cl, 6.1; Re, 31.0. Calc. for $C_{16}H_{22}N_2S_4OClRe$: C, 31.6; H, 3.6; N, 4.6; S, 21.1; Cl, 5.8; Re, 30.6%. IR (cm^{-1}): ν(C–H) 2990–2840(w); ν(C...C)+ν(C...N) 1535(s); δ(C–H) 1455(s). ν(S–CH_3) 1380(w); ν(Re–O) 940(m); ν($CSSCH_3$) 910(m); ν(Re–Cl) 380(m). ^{1}H NMR (ppm): [H1] 2.7(s), [H4], 2.9(t), [H5] 1.9(qt), [H6] 3.0(t), [H8] 3.9(m). ^{13}C NMR (ppm): [C1] 18.2, [C2] 200.0, [C3] 128.2, [C4] 34.4, [C5] 20.0, [C6] 37.6, [C7] 176.0, [C8] 62.3.

2.4.2. TcN(L2)

To a suspension of $TcNCl_2\cdot(PPh_3)_2$ in deaerated ethanol (30 ml) were added successively the ligand H_2L2 (37.2 mg, 0.1 mmol) and $KO_tC_4H_9$ (2.2 mg, 0.2 mmol). The mixture was refluxed for 36 h under an inert atmosphere. The resulting red–brown solution was slowly reduced to half volume under an argon stream. The brown solid was removed by filtration and washed several times with diethyl ether. Recrystallization from chloroform afforded orange crystals of TcN(L2) suitable for X-ray analysis; yield 40%. *Anal.* Found: C, 39.2; H, 4.2; N, 8.4; S, 27.0; Tc, 20.6. Calc. for $C_{16}H_{22}N_3S_4Tc$: C, 39.7; H, 4.6; N, 8.7; S, 26.5; Tc, 20.5%. IR (cm^{-1}): ν(C–H) 2980–2820(w); ν(C...C)+ν(C...N) 1560(s); δ(C–H) 1465(s); ν(S–CH_3) 1360(w); ν(Tc≡N) 1060(m);

ν(CSSCH$_3$) 910(m). ^{1}H NMR (ppm): [H1] 2.9(s), [H4] 2.9(t), [H5] 2.0(t), [H6] 3.0(t), [H8] 3.9(m). ^{13}C NMR (ppm): [C1] 17.4, [C2] 200.0, [C3] 126.2, [C4] 33.7, [C5] 20.6, [C6] 36.7, [C7] 178.3, [C8] 58.2.

2.4.3. TcN(L1)

The complex TcN(L1) was prepared readily by the same procedure with a shorter refluxing time (24 h) and without deprotonating agent; yield 60%. *Anal.* Found: C, 39.6; H, 5.2; N, 11.0; S, 17.8; Tc, 28.4. Calc. for $C_{12}H_{18}N_3S_4Tc$: C, 39.2; H, 4.9; N, 11.4; S, 17.4; Tc, 27.0%.

2.5. Physical measurements

Elemental analyses were performed using a Fisons EA1108/CHNS analyzer. Determinations of technetium were carried out on a Tricarb (4000 series) instrument, with Istagel, a ready-for-use xylene-based liquid scintillation cocktail (Packard Instrument, Zurich). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker WH 90 or WH 200 instrument using $CDCl_3$ as internal reference. IR spectra were run on a Perkin-Elmer model spectrometer using KBr discs. Magnetic measurements were performed on powdered samples using a Faraday type magnetometer. Conductivity measurements in solution were made at 298 K using a Consort K220 conductivimeter. Electrochemical measurements were carried out with a home-made potentiostat using an interfacing hardware with a PC compatible microcomputer – the positive feedback (scan rate >1 V s^{-1}) or interrupt (scan rate <1 V s^{-1}) method was used to compensate for incompensated resistance (*IR*) drop.

Electrochemical experiments were performed in an air-tight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge-compartment filled with a solution of the same supporting electrolyte in the same solvent as used in the cell. The counter electrode was a spiral of ~1 cm^2 apparent surface area, made of 8 cm long and 0.5 mm diameter platinum wire. The working electrode was a 2 mm diameter Pt/disk electrode.

The supporting electrolyte NBu_4BF_4 was obtained from the hydrogensulfate salt (Janssen) by treatment with $NaBF_4$ (Janssen) in water; it was recrystallized further from ethyl acetate.

2.6. Crystal structure determination for TcN(L2)

A crystal was mounted on an Enraf-Nonius CAD4 diffractometer. The crystal proved to be monoclinic. The cell dimensions (Table 1) were found by a least-squares refinement of the setting angles of 24 reflections that had been automatically centred.

Table 1
Crystal data for TcN($C_{16}H_{22}N_2S_4$)

Formula	$C_{16}H_{22}N_3S_4Tc$
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	13.380(6)
b (Å)	9.945(2)
c (Å)	15.839(9)
β (°)	113.91(3)
V (Å^3)	1927(2)
Z	4
Molecular weight	483.2
ρ_{calc} (g cm^{-3})	1.67
μ(λ Mo Kα) (cm^{-1})	10.62
Scan mode	θ–2θ
Take-off angle (°)	6
Max. Bragg angle (°)	24
Independent reflections	3031
Reflections used	2651 ($I>3\sigma(I)$)
Variables	227
Weighting scheme	unit weights
Max. (variable shift)/(e.s.d.)	0.11
$R=\Sigma(\lVert F_o\rvert-\lvert F_c\rVert)/\Sigma F_o$	0.057
$R_w=[\Sigma w(\lVert F_o\rvert-\lvert F_c\rVert)^2/\Sigma wF_o{}^2]^{1/2}$	0.060

Table 2
Final least-squares atomic parameters with e.s.d.s for TcN(L2)

Atom	x	y	z	B_{eq} (Å^2)
Tc	0.29957(5)	0.37606(6)	0.32716(5)	2.79(3)
N	0.2462(6)	0.3662(7)	0.2148(5)	3.7(3)
S1	0.4322(2)	0.2034(2)	0.3788(2)	3.5(1)
S2	0.2006(2)	0.2239(2)	0.3788(2)	3.8(1)
S3	0.6551(2)	0.1402(3)	0.3919(2)	5.8(1)
S4	−0.0185(2)	0.1954(3)	0.3835(2)	6.0(2)
C1	0.5521(7)	0.2605(8)	0.3766(6)	3.0(4)
C2	0.5793(7)	0.3884(8)	0.3657(6)	3.4(4)
C3	0.6916(8)	0.424(1)	0.3641(9)	6.2(6)
C4	0.7029(8)	0.569(1)	0.3776(8)	5.2(5)
C5	0.5961(7)	0.6279(9)	0.3733(6)	3.7(4)
C6	0.5237(7)	0.5096(8)	0.3649(5)	2.9(4)
N1	0.4224(5)	0.5201(6)	0.3592(5)	3.1(3)
C7	0.3867(9)	0.6580(9)	0.3687(9)	5.8(6)
C8	0.273(1)	0.665(1)	0.352(1)	9.6(9)
N2	0.2200(6)	0.5400(7)	0.3568(5)	3.5(3)
C9	0.1268(7)	0.5440(9)	0.3627(6)	3.5(4)
C10	0.0726(8)	0.676(1)	0.3718(7)	5.2(5)
C11	−0.0303(9)	0.639(1)	0.3784(8)	6.1(6)
C12	−0.0483(8)	0.489(1)	0.3624(8)	5.6(6)
C13	0.0590(7)	0.4343(9)	0.3651(6)	3.3(4)
C14	0.0841(7)	0.2968(9)	0.3752(6)	3.9(4)
C15	0.0357(9)	0.027(1)	0.3966(8)	6.4(6)
C16	0.5996(9)	−0.0177(9)	0.4044(8)	5.4(5)

Intensity data were collected at room temperature by the θ–2θ technique. The intensities of the three standard reflections measured every hour of X-ray exposure time showed no significant variations. A complete set of data was collected up to $\theta=24°$ in the octants hkl and $hk-l$. A total of 3031 reflections was measured of which 2651 were found to have $I>3\sigma(I)$.

No absorption correction was applied. Experimental details and crystal data are shown in Table 1.

The structure determination was carried out using the Patterson and Fourier map techniques, and refined by applying the full-matrix least-squares techniques, using the program SHELX-76 [32]. Hydrogen atoms were introduced at calculated positions. The final refinement on F_o included anisotropic thermal parameters for all non-hydrogen atoms and a riding model for the hydrogen atoms (227 variables, 2651 observations, max. (variable shift)/(e.s.d.) = 0.11) and resulted in $R = 0.057$ and $R_w = 0.060$. A final difference–Fourier map showed no unusual features. Final positional and thermal parameters are given in Table 2.

3. Results and discussion

As described in Section 2 the two complexes of the ligand H_2L2 were obtained with acceptable yields by an exchange reaction using $Re^{V}OCl_3(PPh_3)_2$ and $Tc^{V}NCl_2(PPh_3)_2$, respectively, as starting materials.

In the scope of this work we observed that, while the reaction between $TcNCl_2(PPh_3)_2$ and H_2L1 proceeded easily without deprotonating agent, in the case of H_2L2 the process was very slow requiring a long warming time and the presence of potassium tert-butoxide as deprotonating agent to achieve it.

The complexes we first characterized by elemental analysis. From the data reported in Section 2, the following formulations can be suggested: $Re^{V}O(L2)Cl$ and $Tc^{V}N(L2)$. The molar conductances in methanolic solutions ($\Lambda_{eq} = 40$–$50\ \Omega^{-1}\ cm^2\ mol^{-1}$) confirmed the non-electrolytic character of the two complexes and for the rhenium chelate indicate that the chlorine atom is probably bound to metal in the *trans* position to the oxo ligand. Susceptibility measurements indicate that in the solid state the two complexes are diamagnetic as expected for the d2 closed shell of a Tc(V) and Rc(V) oxidation state.

The X-ray crystal analysis confirmed definitively the structure of the nitrido complex. A perspective view of complex TcN(L2) with the atom numbering scheme is shown in Fig. 2. Table 3 lists the relevant bond distances and angles. In the complex the technetium has a slightly distorted penta coordination with the nitrido ligand located at the apex of a square pyramid. The four N_2S_2 donor atoms in the basal plane are nearly coplanar with a weak tetrahedral deformation, the mean deviation being less than 0.01 Å. The technetium is displaced 0.59(6) Å from the mean basal plane towards the nitrido ligand. The Tc–N distance 1.629(7) Å is indicative of a strong triple bond and is in accordance with the values reported for other five-coordinated nitrido complexes of technetium [3,6–10]. No significant dihedral angle (1.0(9)°) is observed between the two symmetric halves of the deprotonated ligand. Atom C(8) lies on the mean plane of the two N,S chelating units (atom-to-plane distance = 0.00(7) Å) while atom C(7) departs by 0.23(6) Å from it; thus on the ^{1}H NMR spectra the two corresponding methylene groups appear as non-equivalent.

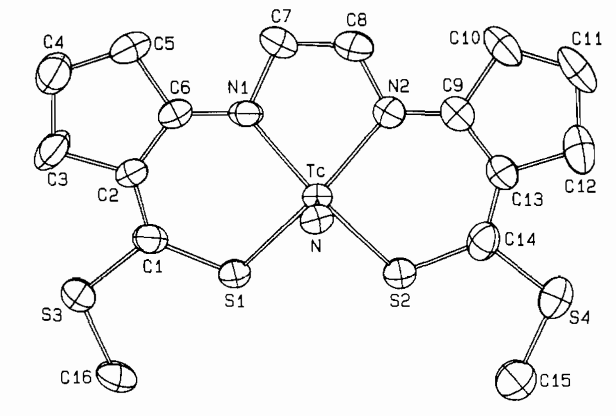

Fig. 2. ORTEP view of TcN(L2) (50% probable ellipsoids).

In the two six-membered rings containing the technetium atom the mean values of the C–N, C–C and C–S distances of 1.307, 1.400 and 1.707 Å, respectively, fall almost midway between the typical values of the corresponding single and double bonds. This confirms a certain degree of delocalization on these rings. The overall geometry of the ligand L2 including the pendant thio methyl groups is roughly planar: atom-to-mean plane deviations range from −0.15(5) to 0.24(6) Å. Finally it appears that the framework built by the atom set S1,C1,C2,C6,N1,C7,C8,N2,C9,C13,C14,S2 around the $Tc\equiv N$ core is very similar in the two complexes NTc(L1) and NTc(L2). For comparison some selected bond distances and angles [27] are given in Table 4.

A list of typical IR bands of the ligand H_2L2 and the two complexes is reported in Section 2. The assignments have been made on the basis of data published in a paper on the preparation and the properties of the complexes of ligand H_2L2 with Ni^{II}, Pd^{II}, Co^{II} and Cu^{II} ions [33]. Interestingly, the present IR data confirm, for ligand H_2L2 in the solid state, the structure with two typical N–H···S hydrogen bridges as represented in Fig. 1. Indeed no ν(S–H) stretching band was observed in the normal range 2600–2700 cm^{-1}; moreover one broad band at 3260 cm^{-1} and another very strong one at 1280 cm^{-1} were assigned straightforwardly to the ν(N–H···S) and δ(N–H···S) vibrations. These two bands disappeared when the ligand was coordinated to the metal and were characteristic of tetradentate unsaturated N_2S_2 Schiff bases [27]. It is interesting to note that the same type of vibrations were also observed in analogous unsaturated N_2O_2 Schiff bases with N–H...O bridges [34].

In the complexes, the Re=O and $Tc\equiv N$ bonds stretch at 945 and 1060 cm^{-1}, respectively, in accordance with

Table 3
Bond lengths (Å) and angles (°) for TcN($C_{16}H_{22}N_2S_4$)

Around Tc					
Tc–N	1.629(7)	N–Tc–N(1)	105.1(3)	N(1)–Tc–S(1)	90.45(19)
Tc–N(1)	2.082(7)	N–Tc–N(2)	104.6(3)	N(1)–Tc–S(2)	148.62(22)
Tc–N(2)	2.101(8)	N–Tc–S(1)	105.65(26)	N(2)–Tc–S(1)	149.68(19)
Tc–S(1)	2.3639(29)	N–Tc–S(2)	106.25(27)	N(2)–Tc–S(2)	90.81(23)
Tc–S(2)	2.3643(22)	N(1)–Tc–N(2)	80.38(28)	S(1)–Tc–S(2)	82.08(9)
Ligand					
S(1)–C(1)	1.716(10)	Tc–S(1)–C(1)	109.21(28)	N(2)–C(9)–C(10)	122.9(8)
C(1)–C(2)	1.353(12)	S(1)–C(1)–S(3)	117.2(5)	N(2)–C(9)–C(13)	128.4(8)
S(3)–C(1)	1.766(9)	S(1)–C(1)–C(2)	128.0(7)	C(10)–C(9)–C(13)	108.7(9)
S(3)–C(16)	1.782(10)	S(3)–C(1)–C(2)	114.8(7)	C(9)–C(10)–C(11)	106.6(9)
C(2)–C(3)	1.554(16)	C(1)–S(3)–C(16)	106.0(5)	C(10)–C(11)–C(12)	108.9(10)
C(2)–C(6)	1.414(12)	C(1)–C(2)–C(3)	121.9(8)	C(11)–C(12)–C(13)	105.4(9)
C(3)–C(4)	1.455(14)	C(1)–C(2)–C(6)	129.4(9)	C(9)–C(13)–C(12)	109.1(8)
C(4)–C(5)	1.522(15)	C(3)–C(2)–C(6)	108.3(8)	C(9)–C(13)–C(14)	128.5(9)
C(5)–C(6)	1.495(12)	C(2)–C(3)–C(4)	105.5(9)	C(12)–C(13)–C(14)	122.3(9)
N(1)–C(6)	1.326(12)	C(3)–C(4)–C(5)	109.6(9)	Tc–S(2)–C(14)	110.5(3)
N(1)–C(7)	1.480(12)	C(4)–C(5)–C(6)	105.2(7)	S(2)–C(14)–C(13)	126.5(8)
C(7)–C(8)	1.435(18)	C(2)–C(6)–C(5)	110.6(8)	S(2)–C(14)–S(4)	119.2(5)
N(2)–C(8)	1.450(14)	N(1)–C(6)–C(2)	125.9(8)	S(4)–C(14)–C(13)	114.3(8)
N(2)–C(9)	1.289(13)	N(1)–C(6)–C(5)	123.5(7)	C(14)–S(4)–C(15)	104.7(6)
C(9)–C(10)	1.530(14)	Tc–N(1)–C(6)	130.3(5)		
C(9)–C(13)	1.429(13)	Tc–N(1)–C(7)	114.0(6)		
C(10)–C(11)	1.470(18)	C(6)–N(1)–C(7)	115.4(7)		
C(11)–C(12)	1.510(16)	N(1)–C(7)–C(8)	112.9(8)		
C(12)–C(13)	1.521(15)	N(2)–C(8)–C(7)	116.9(9)		
C(13)–C(14)	1.402(13)	Tc–N(2)–C(8)	110.7(8)		
S(2)–C(14)	1.699(10)	Tc–N(2)–C(9)	129.3(6)		
S(4)–C(14)	1.751(11)	C(8)–N(2)–C(9)	119.0(9)		
S(4)–C(15)	1.807(11)				
van der Waals contacts					
C(3)–C(12)^{i}	3.552(17)	C(5)–C(16)^{ii}	3.556(12)		
C(4)–C(11)^{i}	3.632(17)	C(10)–C(15)^{ii}	3.569(15)		
C(4)–C(12)^{i}	3.524(17)	C(11)–C(15)^{ii}	3.942(15)		

Code of equivalent positions: ^{i}: $1+x, y, z$; ^{ii}: $x, 1+y, z$.

Table 4
Comparison of selected bonds lengths (Å) and angles (°) for TcN(L1) and TcN(L2)

	TcN(L1)	TcN(L2)
Tc–N	1.621(8)	1.629(7)
Tc–N(1)	2.105(8)	2.082(7)
Tc–N(2)	2.119(8)	2.101(8)
Tc–S(1)	2.347(3)	2.364(3)
Tc–S(2)	2.354(3)	2.364(3)
N–Tc–N(1)	102.8(4)	105.1(3)
N–Tc–N(2)	107.5(3)	104.6(3)
N–Tc–S(1)	106.3(3)	105.6(3)
N–Tc–S(2)	105.0(3)	106.3(3)
N(1)–Tc–N(2)	80.4(3)	80.4(3)
N(1)–Tc–S(1)	91.4(2)	90.4(2)
N(2)–Tc–S(2)	89.6(2)	90.8(2)
S(1)–Tc–S(2)	82.5(1)	82.1(1)

the frequency values observed up to now for this type of complex [6–10,27].

^{1}H and ^{13}C NMR data are given in Section 2. For the free ligand the N–$H \cdots$S resonances were characterized by a broad lowfield signal at 13.3 ppm which disappeared upon complexation. Due to the presence in solution of a tautomeric equilibrium the methylene protons $>$NCH_2– gave rise to two simultaneous signals: a singlet (thiol form) and a doublet (amine form) centred at 3.6 ppm. In the complexes, as seen from X-ray structure analysis, these two methylene groups were no longer equivalent and a typical A_2B_2 multiplet system was displayed. It is noteworthy that the same patterns were observed in the spectra of H_2L1 and its Tc and Re complexes [27]. Due to the high symmetry (close C_{2v}) of the ligand the ^{13}C NMR spectra exhibit only eight lines. All these resonances were conserved in the complexes but with a downfield shift, particularly strong for the carbon nucleus situated in the vicinity of the two nitrogen (N2 and N3) donor atoms. Such effects may be tentatively attributed to σ electron transfers from the L2 ligand towards the metal centre.

Recently published electrochemical studies on cobalt or copper complexes with a series of closely related tetradentate Schiff bases have shown that the $E_{1/2}$ value of potential of the metal redox couple could be correlated to the donor ability of these ligands [35,36]. Consequently, the fact that the $E_{1/2}$ value Cu^{II}/Cu^{I} for the Cu(L1) and Cu(L2) complexes (−1.07 [35] and −1.01 [37] V versus SCE, respectively) was very similar may suggest that the two ligands probably have the same ability to transfer electron density on (and/or from) the technetium centre. Thus, it seemed of interest to undertake an electrochemical study of these two nitrido Tc complexes. Cyclic voltammetry was carried out at room temperature, at a platinum wire electrode on an oxygen-free solution of the complex in dichloromethane (5×10^{-4} M) using $N(C_4H_9)_4BF_4$ (10^{-1} M) as base electrolyte. For the two complexes, the voltammograms displayed: (i) a first quasi-reversible one-electron oxidation wave at +1.03 V versus SCE (ΔE_p[1] $=90$ mV, $RI_p=0.35$ at 0.1 V s^{-1}) for TcN(L1) and at +1.04 V ($\Delta E_p=100$ mV, $RI_p=0.30$ at 0.1 V s^{-1}) for TcN(L2) (for ferrocene as internal standard $E_0=0.57$ V, $\Delta E_p=77$ mV, $RI_p=0.98$ at 0.1 V s^{-1}); as under the same conditions the voltammograms of the free ligands H_2L1 and H_2L2 showed one irreversible wave at +1.05 and at +1.03 V, respectively, it was suggested that ligand based orbitals could be involved in the first oxidation process of the two complexes; (ii) a second non-reversible wave at +1.56 V for TcN(L1) and at +1.50 V for TcN(L2); for the free ligands, no waves were observed in this region.

Although it seems difficult to reach a definite conclusion as to the nature of the electron transfer reaction involved, in the scope of our comparative analysis some significant information can be drawn from this preliminary electrochemical study: (i) the fact that the voltammograms of the two complexes are nearly identical confirms our previous remarks about the similarity of the chelating properties of the two ligands, (ii) the fact that no cathodic response was observed in the electroactive region of the solvent confirms that the nitrido group is a strong π donor [38] and stabilizes the Tc(V) state (with respect to the Tc(IV) state) while the sulfur atoms in this type of N_2S_2 ligand have been identified as π acceptors [26], (iii) because the first oxidaton process takes place at +1.03 it is expected that under physiological conditions the corresponding ^{99m}Tc complexes would be not oxidized. The importance of such behaviour has been recently highlighted in the case of nitrido complexes with dithiocarbamates [13].

Finally this electrochemical study, together with structural and spectroscopic analyses, confirms that in the two complexes TcN(L1) and TcN(L2) the coordination spheres around the technetium are basically similar and suggest that in the hypothesis of a structure-to-biodistribution relationship the difference of behaviour observed in vivo may be due principally to the presence of the two dithiomethylic ester groups in the TcN(L2) complex.

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