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Technetium and rhenium complexes of mercapto-containing peptides 1. Tc(V) and Re(V) complexes with mercaptoacetyl diglycine (MAG_2) and X-ray structure of $AsPh_4[TcO(MAG_2)]\cdot C_2H_5OH$

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Abstract

The reaction of mercaptoacetyl diglycine (MAG_2) with technetium(V) gluconate in aqueous solution produced $[TcO(MAG_2)]^-$. A single X-ray structure determination was carried out for the tetraphenylarsonium salt. The dark brown crystals are monoclinic, space group *P*2(1)/*n*, with $a=12.478(5)$, $b=14.922(5)$, $c=17.183(9)$ Å and $Z=4$. The $[TcO(MAG_2)]^-$ ion has a square pyramidal geometry with the technetium atom displaced by 0.756 Å towards the oxo ligand from the plane formed by the equatorial S,N,N,O atoms. The rhenium complex $AsPh_4[ReO(MAG_2)]$ was prepared analogously starting from Re(V) gluconate and characterized.

Introduction

Native or synthetic sulfur-containing amino acids and peptides are of great interest because of their considerable potential to provide access to novel technetium and rhenium tracers for nuclear medicine. A profound understanding of the course of reactions that lead to the Tc or Re complexes as well as knowledge of their structure and behaviour *in vivo* and *in vitro* is considered a prerequisite for making progress in radiotracer design.

With variable arrangements of different donor groups in amino acids/peptides, our studies also aim at generalizations that can be made about the interplay of these nitrogen (amine/amide), oxygen (hydroxy/carboxylic group) and sulfur (mercapto/thioether groups) donor groups in complexing metals. Our particular investigation of Tc/Re complexes of mercaptoacetyl glycines (MAG_n) is an extension to previous studies on the preparation of the renal function agent 99m-technetium mercaptoacetyl triglycine (MAG_3) [1–6]. The present article deals with preparation of Tc and Re complexes of the S,N,N,O-ligand mercaptoacetyl diglycine (MAG_2) and the X-ray structure of $AsPh_4[TcO(MAG_2)]\cdot C_2H_5OH$. The existence of a Tc–$MAG_2$ complex was postulated by Vandebrouck *et al.* [6].

Experimental

Methods and materials

Glycinanhydride (SERVA) and thiobenzoic acid (SIGMA) were of analytical grade.

Thin layer chromatography of the complexes was done on silica gel (Kieselgel 60/Merck) with ethanol as eluent. Thin layer chromatography for characterization of the ligands was carried out using Silufol® plates (Cavalier) and n-butanol/acetic acid/water (4/1/1) as solvent. Ninhydrine and iodine were used as spot markers.

UV–Vis spectra were recorded on a Specord M 40 from Carl Zeiss Jena. IR spectra were measured on KBr disks on a Specord M 80. ^1H NMR spectra were carried on a Bruker AM-250 device (solvent DMSO-d_6).

TLC and UV–Vis spectroscopy were used to investigate complexation and to characterize the products in solution. Crystalline complexes were identified by elemental analysis, ^1H NMR, IR spectroscopy and, in the case of the Tc–MAG_2 complex, by X-ray structure analysis.

Preparation of mercaptoacetyl diglycine (MAG_2)

Chloroacetyl diglycine

7.8 ml chloroacetyl chloride and 24 ml 5 N NaOH were added over 45 min to a solution of 10 g (90

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mmol) glycinanhydride dissolved in 50 ml 2 N NaOH while stirring in an ice bath. After acidification with 40 ml of 5 N hydrochloric acid while cooling, chloroacetyl diglycine crystallized. The product was separated, washed with ice-water and recrystallized from water. Yield 7.5 g, 41%; m.p. 174 °C; TLC r_f0.70 (iodine).

IR (KBr, cm^{-1}): 3350 NH; 1730 COOH, 1675, 1630 C=O; 1550 NH.

Benzoylmercaptoacetyl diglycine

5.7 g (40 mmol) thiobenzoic acid were dissolved in 20 ml methanol and neutralized with sodium methylate. This solution was dropped onto 5.2 g (25 mmol) of chloroacetyl diglycine in 11 dry methanol while stirring under nitrogen. After 12 h the reaction was stopped and the solvent was removed by rotary evaporation. 2 N HCl was added to the residue, the solid was separated and washed with warm water, then with chloroform, acetonitrile and diethyl ether to yield benzoylmercaptoacetyl diglycine. Yield 6.9 g, 89%; m.p. 194 °C; TLC r_f0.80 (iodine).

IR (KBr, cm^{-1}): 3450 NH; 1730 COOH; 1660, 1640, 1580 C=O; 1540 NH.

Mercaptoacetyl diglycine (MAG$_2$)

5.4 ml sodium methylate were dropped onto a solution of 4.8 g (15 mmol) benzoylmercaptoacetyl diglycine in 400 ml methanol over a period of 30 min while stirring under nitrogen. Stirring was continued for 1 h, and then the solution was neutralized with methanolic ion exchange resin DOWEX 50WX8. The resin was filtered off and the methanol was removed by rotary evaporation. The residue was dissolved in 150 ml water and extracted with 270 ml benzene. The aqueous layer was filtered and the product isolated by freeze drying. Yield 2.7 g, 84%; m.p. 148 °C; TLC r_f0.55 (ninhydrine).

Anal. Calc. for $C_6H_{10}N_2O_4S$: C, 34.95; H, 4.85; N, 13.59. Found: C, 34.92; H, 4.94; N, 13.51%.

IR (KBr, cm^{-1}): 3300 NH; 1735 COOH; 1655, 1645 C=O; 1565 NH.

^{1}H NMR (ppm): 2.75 (*1H*) *SH*, 3.8 (*4H*)–*CH*$_2$, 3.2 (2H)–CH$_2$–SH, 8.3 (2H)–NH.

Synthesis of Tc(V) and Re(V) complexes

Complexes were prepared by ligand exchange reactions starting from Tc(V) and Re(V) gluconate as precursors.

Technetium(V) gluconate

0.4 ml of a 0.25 M ammonium pertechnetate stock solution (0.1 mmol) was added to 2.0 ml 0.25 M sodium gluconate solution. 0.4 ml of a 0.25 M stannous chloride solution (stannous chloride dissolved in 0.1 M HCl) was added while stirring. The technetium gluconate solution obtained was ready for immediate use.

Rhenium(V) gluconate

26.8 mg (0.1 mmol) ammonium perrhenate were dissolved in 2.9 ml 0.1 M aqueous sodium gluconate solution. Nitrogen was bubbled through the solution for about 10 min and 0.1 ml 1 M (0.1 mmol) stannous chloride solution (stannous chloride dissolved in 1 M HCl) was added. The reduction was complete within 1 h. The rhenium gluconate solution obtained can be stored for several weeks as a frozen solution under nitrogen.

Tetraphenylarsonium(2-mercaptoacetyl diglycinato-S,N,N,O)oxotechnetate(V)·ethanol, $AsPh_4[TcO(MAG_2)]\cdot C_2H_5OH$

21 mg (0.1 mmol) MAG$_2$ dissolved in 1 ml 0.1 N NaOH were added to the above Tc gluconate solution (0.1 mmol). The colour of the reaction mixture changed to yellow–brown. After addition of 42 mg (0.1 mmol) tetraphenylarsonium chloride dissolved in water a dark coloured solid precipitated, which was collected and washed with ether/ethanol. Recrystallization from ethanol produced 45 mg (0.064 mmol = 64%) of a brown crystalline compound which contains one mole of ethanol per mole AsPh$_4$[TcO(MAG$_2$)], m.p. 190 °C.

Anal. Calc. for $C_{32}H_{32}N_2O_6SAsTc$: C, 51.55; H, 4.33; N, 3.75. Found: C, 51.57; H, 4.91; N, 3.21%.

IR (cm^{-1}); 960 ν(Tc=O). UV–Vis (ethanol) (λ_{max}(log ϵ)): 345 nm (3.16). ^{1}H NMR (ppm): 7.80 (m, 20 H) phenyl; 4.66/4.25 (AB, 2H) and 4.07 (s, 2H) 2×N-CH$_2$, 3.85/3.66 (AB, 2H) S-CH$_2$.

Tetraphenylarsonium(2-mercaptoacetyl diglycinato-S,N,N,O)oxorhenate(V), $AsPh_4[ReO(MAG_2)]$

21 mg MAG$_2$ (0.1 mmol) dissolved in 1 ml 0.1 N NaOH were dropped onto 3 ml (0.1 mmol) aqueous Re(V) gluconate solution while stirring. After standing for 15 min, 42 mg (0.1 mmol) tetraphenylarsonium chloride dissolved in 0.5 ml water were added. The reaction mixture was extracted with methylene chloride (3×2 ml), the combined extracts were dried over sodium sulfate and evaporated to dryness. The residue was recrystallized from acetone to give 54 mg (0.07 mmol = 70%) dark brown crystals, m.p. 203–205 °C.

Anal. Calc. for $C_{30}H_{26}N_2O_5SAsRe$: C, 45.74; H, 3.33; N, 3.56; S, 4.07. Found: C, 45.80; H, 3.31; N, 3.55; S, 3.86%.

^{1}H NMR (ppm): 7.80 (m, 20H) phenyl, 4.83/4.16 (AB, 2H) and 4.01 (s, 2H) 2×N–CH$_2$, 3.89/3.62 (AB, 2H) S–CH$_2$. IR (KBr, cm^{-1}): 976 ν(Re=O). UV–Vis (ethanol) (λ_{max}(lg ϵ)): 412 nm (2.15).

Structure determination and crystal data

The X-ray data of both complexes were collected at room temperature (296 K) with an ENRAF-NONIUS CAD 4 diffractometer, using graphite monochromatized

TABLE 1. Crystallographic data for $AsPh_4[TcO(MAG_2)]\cdot C_2H_5OH$

Crystal data	
Empirical formula	$C_{30}H_{25}N_2O_5SAsTc\cdot C_2H_5OH$
Formula weight	744.60
Crystal system	monoclinic
a (Å)	12.478(5)
b (Å)	14.922(5)
c (Å)	17.183(9)
α (°)	90.03(4)
β (°)	103.13(4)
γ (°)	90.02(3)
V (Å^3)	3115.9
Space group, No.	$P2(1)/n$; 1014
Z; $F(000)$; D_{calc}	4; 1380; 1.587
T (K)	296
Data collection	
Crystal size (mm)	0.62×0.44×0.35
λ (Mo Kα) (Å)	0.71073
μ (cm^{-1})	16.112
Data sphere (°)	$3<2\theta\leqslant 42$
Scan mode	ω–2θ
Scan rate (° min)	variable 1.1–4.8
Miller index range	h −12 to 12
	k 0 to 15
	l 0 to 16
Unique reflections measured	3650
Unique reflections used ($I_0\geqslant 3\sigma(I)$)	2715
Check reflections	0 −2 3
	−7 3 0
	−5 0 3
Absorption corrections	yes
$R=\Sigma[\|F_o\|-\|F_c\|]/\Sigma\|F_o\|$	0.033

Mo Kα radiation ($\lambda=0.71073$ Å). A summary of the crystallographic data is given in Table 1. The positions of the non-hydrogen atoms were determined by the heavy atom technique. After anisotropic refinement of the positions of these, the hydrogen positions were calculated according to ideal geometries. Empirical absorption corrections with the program DIFABS [7] were made at two stages during structure refinement. Most of the calculations were carried out in the ENRAF-NONIUS SDP system with some local modifications. The final atomic parameters are listed in Table 2. See also 'Supplementary material'.

Results and discussion

Reaction of MAG_2 with technetium(V) gluconate in neutral aqueous solution results in a spectrum of various compounds. The ratio of compounds changes with the metal to ligand molar ratio, which can be seen qualitatively in a change of colour after addition of various amounts of the ligand to the precursor (Fig. 1). The maxima in the UV spectrum of the reaction mixture are found as 345 nm for 1:1, 370 nm for 8:1, and 400

TABLE 2. Atomic positional parameters for $AsPh_4[TcO(MAG_2)]\cdot C_2H_5OH$ and their e.s.d.s

Atom	x	y	z	B (Å^2)^a
Tc	0.52386(6)	0.28603(5)	0.55782(4)	3.19(2)
As	0.28772(7)	0.53904(6)	0.86064(5)	2.63(2)
S	0.3396(2)	0.3105(2)	0.5212(2)	4.72(6)
O1	0.5528(5)	0.2145(4)	0.6325(4)	4.9(2)
O2	0.5131(5)	0.2218(4)	0.4531(4)	4.2(1)
O3	0.4403(5)	0.5295(4)	0.6403(4)	5.0(2)
O4	0.7815(5)	0.4456(4)	0.5432(4)	4.9(2)
O5	0.6059(6)	0.1804(5)	0.3623(4)	5.7(2)
O6	0.6168(5)	0.6335(5)	0.7436(4)	5.1
N1	0.5274(6)	0.4087(5)	0.6002(4)	3.3(2)
N2	0.6511(6)	0.3361(5)	0.5230(4)	3.5(2)
C1	0.3307(7)	0.4026(6)	0.5895(6)	4.2(2)
C2	0.4380(8)	0.4540(6)	0.6125(5)	3.8(2)
C3	0.6303(8)	0.4576(7)	0.6087(6)	4.4(2)
C4	0.6979(7)	0.4129(6)	0.5552(5)	3.8(2)
C5	0.6840(7)	0.2943(6)	0.4558(5)	3.9(2)
C6	0.5979(7)	0.2268(7)	0.4199(5)	4.1(2)
C7	0.3642(6)	0.6518(6)	0.8810(5)	3.0(2)
C8	0.3713(7)	0.7083(6)	0.8186(5)	3.9(2)
C9	0.4293(8)	0.7880(7)	0.8353(6)	4.7(2)
C10	0.4792(8)	0.8092(6)	0.9127(6)	4.7(3)
C11	0.4715(8)	0.7524(6)	0.9748(6)	4.4(2)
C12	0.4127(7)	0.6734(6)	0.9585(5)	3.5(2)
C13	0.2437(6)	0.5069(5)	0.9562(5)	2.8(2)
C14	0.2892(7)	0.4309(6)	0.9980(5)	3.2(2)
C15	0.2571(8)	0.4090(6)	1.0689(6)	4.1(2)
C16	0.1821(8)	0.4610(7)	1.0960(5)	4.3(2)
C17	0.1391(7)	0.5357(7)	1.0549(5)	4.3(2)
C18	0.1686(7)	0.5598(6)	0.9838(5)	3.8(2)
C19	0.3864(6)	0.4509(5)	0.8366(5)	2.7(2)
C20	0.3464(7)	0.3642(6)	0.8165(5)	3.7(2)
C21	0.4178(8)	0.3009(6)	0.7990(6)	4.4(2)
C22	0.5238(7)	0.3219(7)	0.8005(6)	4.4(2)
C23	0.5638(7)	0.4072(7)	0.8209(6)	4.5(2)
C24	0.4952(7)	0.4725(6)	0.8385(5)	3.5(2)
C25	0.1656(6)	0.5461(5)	0.7706(5)	2.6(2)
C26	0.0585(7)	0.5428(7)	0.7794(5)	4.2(2)
C27	−0.0253(7)	0.5476(7)	0.7115(6)	4.9(3)
C28	−0.0043(7)	0.5561(6)	0.6354(5)	3.9(2)
C29	0.1047(7)	0.5581(6)	0.6288(5)	3.8(2)
C30	0.1892(6)	0.5534(6)	0.6957(5)	2.9(2)
C31	0.675(1)	0.697(1)	0.7136(8)	8.1
C32	0.680(1)	0.785(1)	0.7451(9)	8.1
HO1	0.3079	0.3770	0.6423	5*
HO2	0.2653	0.4494	0.5587	5*
H6	0.5674	0.5865	0.7684	5*
H8	0.3301	0.6896	0.7560	5*
H9	0.4361	0.8340	0.7867	5*
H10	0.5284	0.8718	0.9258	5*
H11	0.5108	0.7711	1.0368	5*
H12	0.4031	0.6285	1.0075	5*
H14	0.3470	0.3882	0.9748	5*
H15	0.2962	0.3509	1.1045	5*
H16	0.1556	0.4415	1.1503	5*
H17	0.0794	0.5784	1.0776	5*
H18	0.1340	0.6201	0.9495	5*
H20	0.2573	0.3485	0.8143	5*
H21	0.3868	0.2317	0.7817	5*
H22	0.5793	0.2685	0.7876	5*

(continued)

TABLE 2. (*continued*)

Atom	x	y	z	B (Å^2)^a
H23	0.6521	0.4212	0.8238	5*
H24	0.5253	0.5409	0.8540	5*
H26	0.0405	0.5372	0.8389	5*
H27	−0.1127	0.5471	0.7164	5*
H28	−0.0725	0.5581	0.5824	5*
H29	0.1224	0.5649	0.5693	5*
H30	0.2760	0.5525	0.6893	5*
H31	0.6772	0.4555	0.6719	5*
H32	0.6149	0.5280	0.5921	5*
H51	0.7654	0.2622	0.4748	5*
H52	0.6914	0.3460	0.4107	5*
H311	0.7638	0.6731	0.7257	5*
H312	0.6471	0.6994	0.6482	5*
H321	0.7289	0.8335	0.7174	5*
H322	0.5939	0.8155	0.7322	5*
H323	0.7106	0.7892	0.8097	5*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of theisotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

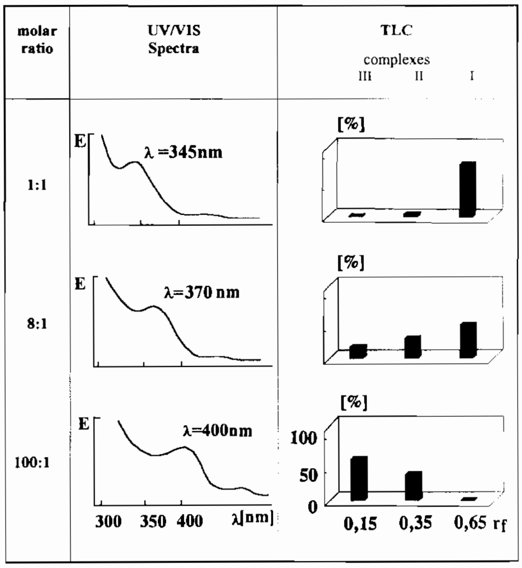

Fig. 1. UV absorption and TLC patterns of the reaction mixture of Tc(V) gluconate and various equivalents of MAG$_2$ (ligand to Tc ratio of 1:1, 8:1, 100:1).

nm for a 100:1 ligand/technetium molar ratio. In TLC, up to three species (I, II, and III, see Fig. 1) were detected at ratios greater than 1:1. The dependence of the product spectrum on the relative ligand supply as indicated by HPLC and the UV maxima is assumed to be due to the existence of complex species with different ligand to metal ratios 1:1, 2:1 and possibly 4:1.

If the reaction of MAG$_2$ with technetium(V) gluconate takes place in an alkaline medium, a pure component occurs regardless of the molar ratio. This species, which is identical with component I in the neutral medium, was isolated as tetraphenylarsonium salt. (Isolation of components II and III failed.) The dark brown crystals are stable in air and moisture. Elemental analysis, the IR spectrum (with the strong Tc=O absorption at 960 cm^{-1} and carbonyl stretching vibrations of the coordinated amido groups between 1657 and 1620 cm^{-1}), and the ^{1}H NMR spectrum (showing a ratio of aromatic to aliphatic protons of the complex anion of 20 to 6 and discrete signals for the methylene proton groups) resulted in the formulation as the oxotechnetium(V) complex AsPh$_4$[TcO(MAG$_2$)]·C$_2$H$_5$OH of the tetradentate S,N,N,O (carboxylic group) donor ligand. The structure and properties of the corresponding rhenium compounds proved to be analogous to the Tc complexes. As found for technetium, up to three species were detected in the reaction of MAG$_2$ with Re gluconate in neutral solution, whereas in an alkaline medium a single 1:1 complex is formed, which was isolated as the tetraphenylarsonium salt and identified to be AsPh$_4$[ReO(MAG$_2$)].

The structure of AsPh$_4$[TcO(MAG$_2$)]·C$_2$H$_5$OH was confirmed by X-ray crystallography. The crystal structure consists of discrete [TcO(MAG$_2$)]$^-$ anions, [AsPh$_4$]$^+$ cations and ethanol of crystallization, with no significant close contacts between any molecules. The geometries of the [AsPh$_4$]$^+$ cations and ethanol are normal and require no further discussion. A perspective view of the complex anion (Fig. 2) shows that the compound belongs to the well-known group [8] of square-pyramidal oxotechnetium(V) complexes. (Selected bond distances and angles are summarized in Table 3.) The Tc–O(1) bond length falls in the normal range observed for this structure element [8]. The complex exhibits an interesting structural feature in that the carboxylic group is bonded to the metal. Tc complexes including carboxylate groups in the coordination sphere in general and in the equatorial plane in particular as found in the [TcO(MAG$_2$)]$^-$ ion have been scarcely described so far.

The distance of the Tc–O(carboxylate) bond is relatively short (2.010 Å) compared to that in TcO(pen)$_2$(pen=penicillamine) (2.214 Å [9]), which is *trans*-coordinated to the oxo group, and to the rather long (2.16 and 2.03 Å) single bonded Tc–O distances associated with the carboxylate groups in the seven-coordinated ethylendiaminetetracetic acid complex Ba[TcO(EDTA)], where the carboxylate group bridges a Tc centre to a Ba centre [10]. A short Tc–O bond length (2.010 Å) was observed also for [*N*-(2-mercaptoacetyl)-*N*′-(4-(pentene-3-one-2))ethane-1,2-diaminato]-oxotechnetium(V), which has the same donor atom sequence S,N,N,O as [TcO(MAG$_2$)]$^-$ [11].

Tc–N(1)(amido) and Tc–N(2)(amido) bond distances differ slightly from each other (1.970 and 1.953 Å) due to the asymmetry in the chelate ring system but cor-

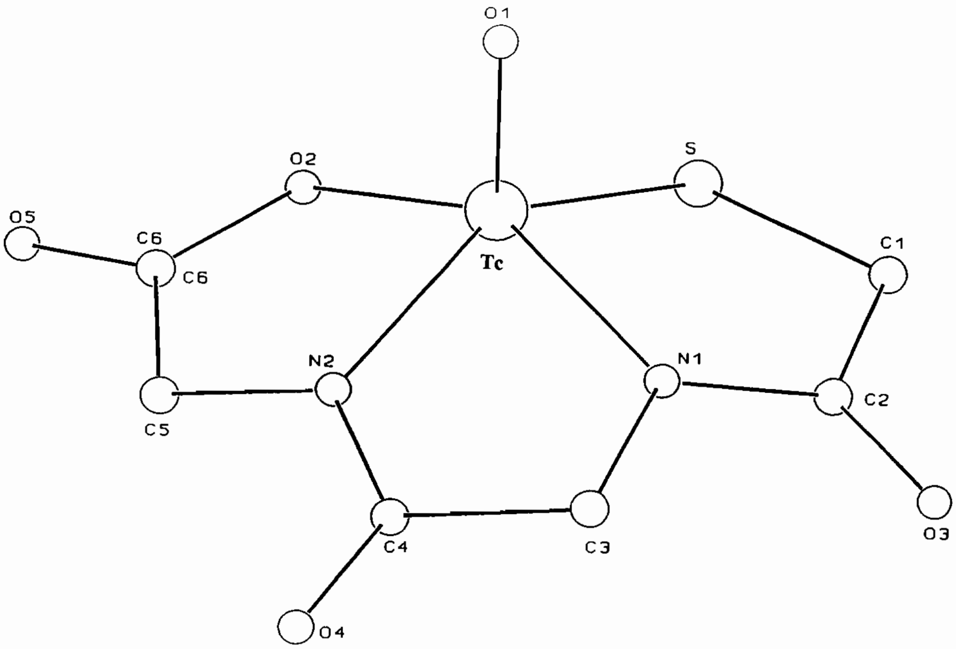

Fig. 2. CELLGRAF drawing of the $[TcO(MAG_2)]^-$ anion (the tetraphenylarsonium counterion has been omitted for clarity).

TABLE 3. Selected bond angles and distances for $[TcO(MAG_2)]^-$

Bond lengths (Å)					
Tc–O(1)	1.644	Tc–N(1)	1.968	C(1)–S	1.828
Tc–O(2)	2.016	Tc–N(2)	1.968	C(6)–O(2)	1.314
Tc–S	2.271			C(6)–O(5)	1.230

Bond angles (°)			
O(1)–Tc–S	110.4	S–Tc–N(2)	133.7
O(1)–Tc–N(1)	109.4	S–Tc–O(2)	88.3
O(1)–Tc–N(2)	115.8	N(1)–Tc–N(2)	78.9
O(1)–Tc–O(2)	110.2	Tc–S–C(1)	98.5
S–Tc–N(1)	83.6	Tc–O(2)–C(6)	117.6

respond in general to that found in [TcO(PIC)] where H_3PIC is *N*-(2-(mercaptoacetyl)amino)ethyl)-2-pyridinecarboxamide) (1.963 and 1.966 Å) [12].

$[TcO(MAG_2)]^-$ is related to the well-known technetium complex of MAG_3 $[TcO(MAG_3)]^-$ [3]. Unlike the latter compound in which the carboxylic group is free, coordination of the carboxylic group of MAG_2 is required as a substitute for the third amido group in MAG_3. Replacement of N- by O-donation does not seem to alter the stability of the complex.

The nature and occurrence of additional anionic complexes of MAG_2 in neutral media, predominantly with excess ligand over Tc, may be explained by the relative reactivity of the donor atoms in the ligand. These species are considered to be 2:1 (ligand/Tc) and, more speculatively, 4:1 complexes. It is hypothesized that the nucleophilic thiol predominates in the ligand in a first attack on the Tc(V)oxo core, causing it to react as a monodentate ligand. Due to the chelate effect the initial product may convert into the more stable 2:1 complex. These are only intermediate species, in alkaline solution they convert into the more stable 1:1 complex due to the increased reactivity of the deprotonated amide nitrogen.

Supplementary material

Additional X-ray structure data (thermal parameters, full lists of bond lengths and angles, and F_o/F_c values) can be obtained from Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-W-7514 Eggenstein-Leopoldshafen 2, Germany, quoting CSD No. 57135, authors' names as well as the title of the paper.

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