

Investigations on Technetium and Rhenium Monothio- β -diketonate Complexes and X-ray Structure of Tris(monothiodibenzoylmethanato)technetium(III)

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(Received December 18, 1986)

Abstract

Six-coordinated tris(monothio- β -diketonates) of Tc(III) and Re(III) have been synthesized by the reaction of M(III) thiourea complexes with the appropriate monothio- β -diketone ligands in methanol. Characterization of the compounds by IR, UV-Vis, ^1H NMR and mass spectroscopy indicates that the ligands coordinate as bidentate. The ^1H NMR spectra of the paramagnetic substances are well resolved and the chelate ring protons show a large high-field shift of the Tc complexes and a low-field shift of the corresponding Re analogues. A complete crystal and molecular structure determination, performed on tris(monothiodibenzoylmethanato)technetium(III), is the first structural characterization of a Tc(III) compound with O and S chelate ligands.

Introduction

The coordination chemistry of technetium is of considerable interest owing to the widespread use of technetium-99m in diagnostic radio-imaging and there is an increasing demand for new Tc compounds as the basis of systematic chemical and radiopharmaceutical studies.

Complexes of Tc(V) with thiole ligands are well known [1] and tend to form square-pyramidal structures containing the technetyl group $(\text{Tc}=\text{O})^{3+}$, while coordination compounds of Tc(III) with sulphur donors are scarcely described. Although β -diketonates are known to form stable complexes with

Tc(III) [2–5], the corresponding Tc complexes of the sulphur analogue monothio- β -diketonates were unknown. Attempts to exploit the hexakis(thiourea)technetium(III) cation, which has been shown to be a good precursor of further low-valent Tc complexes, such as dichlorobis(1,2-bis(diphenylphosphino)ethane)technetium(III), hexakis(tert-butyl isocyanide)technetium(I), and hexakis(trimethylphosphine)technetium(I) [6], as starting material for the preparation of technetium chelate with monothiodibenzoylmethane led to the synthesis of tris(monothiodibenzoylmethanato)technetium(III) [7].

This work outlines the synthesis and spectroscopic characterization of further representatives of complexes of technetium and rhenium with monothio- β -diketonates and the characterization of tris(monothiodibenzoylmethanato)technetium(III) by X-ray diffraction.

Experimental

Materials

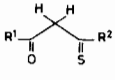

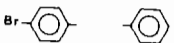




Hexakis(thiourea)technetium(III) trichloride tetrahydrate and the thiourea complex of rhenium were synthesized as reported in refs. 6 and 8. Monothio- β -diketonates were prepared by methods reported in refs. 9–11.

General procedure for the preparation of complexes 1–7

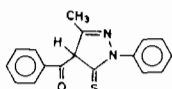
Hexakis(thiourea)technetium(III) trichloride tetrahydrate (50 μmol) (or the corresponding rhe-

nium analogue) and 150 μmol of the monothio- β -diketone in 5 ml of methanol were heated under reflux for 4 h. After cooling the solution, the dark microcrystalline precipitate was collected, washed twice with methanol, and dissolved in 5 ml of acetone. The dark blue solution was heated and 5 ml of methanol was added dropwise. The solution was allowed to stand overnight. Black crystals were collected and air-dried. No attempts were made to optimize the yield of complexes (see Table I).

TABLE I. Yields and Melting Points of Tc and Re Complexes (ML_3)

Compound	M	Ligand	Yield (%)	Melting point ($^{\circ}\text{C}$)
				
1	Tc		83	215–17
2	Tc		53	233–36
3	Tc		15	205–10
4	Tc		11	285–88
5	Tc	ligand ^a	64	217–23
6	Rc		52	210–15
7	Re		39	225–29

^aLigand HL:



Compound Characterization

All elemental analysis (except for ^{99}Tc) were performed by the Technical University of Dresden, Chemical Section. Technetium analysis was carried out by instrumental activation analysis as described in ref. 12 or by liquid scintillation counting.

Infrared spectra were taken on a UR 20 spectrometer in the range 3600–400 cm^{-1} in KBr pellets. UV–Vis spectra were obtained on a Beckmann Dk-2A spectrometer. Mass spectra were taken on a Hewlett-Packard 5995 A mass spectrometer.

^1H NMR spectra were measured on a Bruker Spectrospin WH 90 DS spectrometer. All spectra were recorded at room temperature in acetone.

Structure Determination

Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of an acetone/propanol solution.

Crystal data

$\text{C}_{45}\text{H}_{33}\text{O}_3\text{S}_3\text{Tc}$: molecular weight = 816.8, monoclinic, $a = 21.638(6)$, $b = 17.520(5)$, $c = 10.188(4)$ Å, $\beta = 100.24(5)^{\circ}$, $U = 3800.7(2.2)$ Å³, $F(000) = 1672$, $Z = 4$, $D_c = 1.43$ g cm^{-3} , space group $P2_1/n$, $\mu(\text{Mo K}\alpha) = 5.7$ cm^{-1} . Intensity data were recorded at room temperature on an automatic Philips PW1100 diffractometer with graphite filtered Mo $\text{K}\alpha$ radiation ($\lambda = 0.7107$ Å), using the ω - 2θ scan procedure, with a scan rate of $0.03^{\circ} \text{s}^{-1}$ and a scan width of 1.1° . A total of 5963 reflections was measured up to $2\theta = 48^{\circ}$; of these only 2701 unique reflections were considered observed [$I > 3\sigma(I)$] and were used for the structure analysis. The integrated intensities were corrected for Lorentz and polarization effects, but not for absorption. In fact, a series of ψ -scans at $\chi \approx 90^{\circ}$ showed that the relative transmission coefficient was nearly one and therefore the absorption correction was judged to be unnecessary.

Structure determination and refinement

The structure was solved by the heavy atom method. The position of the technetium atom was derived from a three-dimensional Patterson map, and subsequent difference Fourier syntheses revealed the positions of all 51 non-hydrogen atoms of the complex. Full-matrix least-squares refinement with anisotropic temperature factors assigned to the 'inner core' atoms converged with a reliability index $R = \Sigma\Delta F/\Sigma|F_o|$ of 0.063 (289 variables). The function minimized was $\Sigma w(\Delta F)^2$, where w was one. Refinement with weights based on $\sigma(F_o)$ did not improve the model. The maximum parameter shift-to-error ratios at convergence was 0.29:1 for the z/c of C(12)c and 0.26:1 for the z/c of C(13)c. All other shift-to-error ratios were 0.10:1. The largest peak on a final difference synthesis was of height $0.6 \text{ e } \text{Å}^{-3}$, near to the heavy atom (at 1.0 Å).

Final atomic positional coordinates, with e.s.d.s. in parentheses, are listed in Table II. Thermal parameters, and observed and calculated structure factors are available (see 'Supplementary material').

Structure determination and refinement were performed with the SHELX 76 program system [13].

Results and Discussion

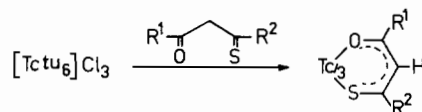
The utility of hexakis(thioureato)technetium(III) trichloride as starting material for the preparation of the first technetium complex of a monothio- β -diketone has been demonstrated previously

TABLE II. Final Atomic Positional Coordinates ($\times 10^4$) (with their e.s.d.s in parentheses)^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Tc	3840(0)	2390(1)	1925(1)
S <i>a</i>	3038(1)	2364(2)	66(3)
O <i>a</i>	4439(4)	2878(4)	767(8)
C(1) <i>a</i>	3239(5)	2872(7)	-1233(10)
C(2) <i>a</i>	3789(5)	3224(7)	-1278(12)
C(3) <i>a</i>	4355(5)	3237(7)	-344(12)
C(4) <i>a</i>	2707(5)	2957(7)	-2413(12)
C(5) <i>a</i>	2826(6)	3058(8)	-3702(13)
C(6) <i>a</i>	2329(7)	3154(9)	-4750(15)
C(7) <i>a</i>	1732(7)	3167(9)	-4523(15)
C(8) <i>a</i>	1599(7)	3064(9)	-3272(15)
C(9) <i>a</i>	2091(6)	2962(7)	-2194(12)
C(10) <i>a</i>	4900(6)	3674(7)	-585(12)
C(11) <i>a</i>	4835(6)	4322(7)	-1396(13)
C(12) <i>a</i>	5363(7)	4739(8)	-1566(14)
C(13) <i>a</i>	5940(7)	4520(9)	-977(16)
C(14) <i>a</i>	6015(7)	3885(9)	-171(16)
C(15) <i>a</i>	5490(7)	3476(8)	62(14)
S <i>b</i>	3527(2)	3598(2)	2543(3)
O <i>b</i>	4564(4)	2395(5)	3460(8)
C(1) <i>b</i>	3957(6)	3857(7)	4044(12)
C(2) <i>b</i>	4469(6)	3492(8)	4782(12)
C(3) <i>b</i>	4768(5)	2822(6)	4478(12)
C(4) <i>b</i>	3741(6)	4596(7)	4590(12)
C(5) <i>b</i>	3110(7)	4816(8)	4266(14)
C(6) <i>b</i>	2932(8)	5524(10)	4761(17)
C(7) <i>b</i>	3343(8)	5953(9)	5601(15)
C(8) <i>b</i>	3944(8)	5732(9)	5956(16)
C(9) <i>b</i>	4171(6)	5056(8)	5425(13)
C(10) <i>b</i>	5375(5)	2560(7)	5260(11)
C(11) <i>b</i>	5637(6)	1898(8)	4832(14)
C(12) <i>b</i>	6251(7)	1688(9)	5484(15)
C(13) <i>b</i>	6569(6)	2085(8)	6523(14)
C(14) <i>b</i>	6297(7)	2719(9)	6972(13)
C(15) <i>b</i>	5706(7)	2950(8)	6256(15)
S <i>c</i>	3163(2)	1882(2)	3219(3)
O <i>c</i>	4191(4)	1320(5)	1629(8)
C(1) <i>c</i>	3403(6)	985(6)	3736(11)
C(2) <i>c</i>	3849(7)	555(7)	3324(13)
C(3) <i>c</i>	4226(6)	715(7)	2296(12)
C(4) <i>c</i>	3044(6)	649(7)	4697(12)
C(5) <i>c</i>	3026(6)	1054(8)	5893(13)
C(6) <i>c</i>	2713(7)	730(8)	6838(14)
C(7) <i>c</i>	2423(7)	39(8)	6596(14)
C(8) <i>c</i>	2443(6)	-353(8)	5443(14)
C(9) <i>c</i>	2751(6)	-40(7)	4508(13)
C(10) <i>c</i>	4691(6)	138(7)	2048(13)
C(11) <i>c</i>	4617(7)	-639(9)	2216(15)
C(12) <i>c</i>	5071(8)	-1153(10)	1942(17)
C(13) <i>c</i>	5603(8)	-884(10)	1555(16)
C(14) <i>c</i>	5699(8)	-118(10)	1419(16)
C(15) <i>c</i>	5251(7)	400(8)	1675(14)

^aEach symbol for an atom of an [SC(Ph)CHC(Ph)O]⁻ ligand carries a number to distinguish between atoms of the same element within the same ligand and a letter to identify the particular ligand (*a*, *b*, or *c*).

[7]. In this study it is shown that the ligand exchange reaction on hexakis(thioureato)technetium(III) is applicable to further representatives of monothio- β -diketones, such as *p*-bromobenzoylthiobenzoyl-methane, thiobenzoylacetone, thiothenoyltrifluoroacetone and 1-phenyl-3-methyl-4-benzoyl-5-thione, giving solid Tc(III) chelates 1–5 according to Scheme 1. Furthermore, complexes of Re(III) 6 and 7 can also be obtained in a similar way as the corresponding Tc analogues with a rhenium thiourea complex as precursor [8].



Scheme 1.

The yields of compounds obtained were not optimized, but seem to depend on the thermic stability of the ligands under the reaction conditions. Complexes which are partially substituted by aliphatic groups are formed in smaller yields in comparison to those with aromatic substituents. Gray, insoluble solids are formed as by-products when aliphatic substituted ligands are used.

Attempts to synthesize the Tc chelates by direct reduction of technetate(VII) with stannous chloride in ligand/methanol solution proved unsuccessful.

Characterization

The dark coloured complexes, compounds 1–4 and 6 and 7 are quite lipophilic, as is indicated by their solubility in acetone and diethyl ether. They are only slightly soluble in methanol and insoluble in water. In accordance with this, these compounds migrate on TLC plates with acetone as eluent as sharp, blue spots with R_f values of 0.8–0.9, but do not migrate in more polar solvents. Compound 5 is only slightly soluble in acetone and practically insoluble in methanol.

The results of the chemical analysis of the complexes obtained are summarized in Table III. These data as well as the results of the determination of the metal content in Tc compounds indicate that the complexes contain three monothio- β -diketone ligands per metal atom.

Infrared spectra show absorptions at 950 cm^{-1} , which is a typical region for Tc=O bonds [1]. However, the formation of oxotechnetium(V) compounds is not expected from the reaction route and can be excluded by the results of mass spectra and the X-ray analysis of compound 1 (both will be discussed below). Other absorptions for the coordinated ligand were also observed. The C=O vibration in the complexes is bathochromic shifted compared to the

TABLE III. Analytical Data of Complexes ML₃

Compound	Formula	Analytical Data (%) ^a			
		C	H	S	Tc
1	C ₄₅ H ₃₃ O ₃ S ₃ Tc	66.01 (66.16)	3.92 (4.07)	12.37 (11.77)	12.31 (12.12)
2	C ₄₅ H ₃₀ O ₃ S ₃ Br ₃ Tc	51.58 (51.30)	2.81 (2.87)	9.49 (9.12)	9.14 (9.40)
3	C ₃₀ H ₂₇ O ₃ S ₃ Tc	— (57.13)	— (4.31)	— (15.25)	15.76 (15.70)
4	C ₂₄ H ₁₂ O ₃ S ₆ F ₉ Tc	— (35.56)	— (1.49)	— (23.73)	11.87 (12.21)
5	C ₅₁ H ₃₉ N ₆ O ₃ S ₃ Tc	62.92 (62.56)	4.02 (4.02)	9.98 (9.82)	9.22 (10.11)
6	C ₄₅ H ₃₃ O ₃ S ₃ Re	60.44 (59.78)	4.61 (3.68)	10.10 (10.64)	—
7	C ₄₅ H ₃₀ O ₃ S ₃ Br ₃ Re	48.22 (47.38)	3.20 (2.65)	8.90 (8.43)	—

^aCalculated values are in parentheses.

TABLE IV. UV-Vis Spectral Parameters of Tc and Re Complexes (ML₃) (in Methylene Chloride)

Complex	λ_{\max}	(nm)	(log ϵ)			
1	294sh	321 (4.71)	435sh	500br (4.16)	560 (4.17)	675sh
2	296sh	325 (5.03)		500br (4.44)	565 (4.43)	675sh
3	261sh	321 (4.40)	410sh	456 (3.73)	522 (3.68)	620sh
4		375 (4.64)	450sh	483 (4.44)	560sh	680sh
5		279 (4.86)	460sh	491 (4.19)		6.37sh
6	290sh	323 (4.81)	485sh	515 (4.24)	540sh	630 (4.09)
7	294sh	331 (5.03)	483sh	523 (4.43)	555sh	637 (4.29)

br = broad absorption

non-coordinated C=O group (1638 cm⁻¹) for the disulphide of monothiodibenzoylmethane [14], confirming the coordination of oxygen and sulphur to the metal atom.

The UV-Vis absorptions of the technetium and rhenium complexes are summarized in Table IV. All compounds show three groups of absorptions: an intensive absorption in the ultraviolet part, a group of three intensive bands in the region of 400–560 nm, and an additional band at 620–670 nm. In technetium complexes, two bands in the 450–560 nm region are not resolved and appear as a broad maximum at about 500 nm, whereas the third band is well separated; the longwave absorption is observed as a shoulder. Unlike the Tc complexes, the rhenium compounds 6 and 7 show the maximum at about 520 nm, accompanied of two shoulders and the long-wave absorption is observed as a separated maximum at about 630–640 nm. The intensity of the bands suggest charge-transfer transitions of the ligand and ligand-to-metal transitions.

Mass Spectra

The mass spectra of the tris(monothio- β -diketonato) chelates of technetium(III) 1–4 and of rhenium(III) 6 were measured in the temperature region from 150 to 250 °C.

In the case of the technetium(III) chelates 1 and 3, the molecular ions Tc^{III} L₃Γ⁺ (*m/e* 816, 2% and *m/e* 630; 2%) were observed. The mass spectrum of the chelate 4 exhibits besides the ligand ion LΓ⁺ (*m/e* 237; 18%) the metal containing fragmentation ions Tc^{II}L₂SΓ⁺ (*m/e* 605; 24%) and Tc^{II}L₂Γ⁺ (*m/e* 573; 5%).

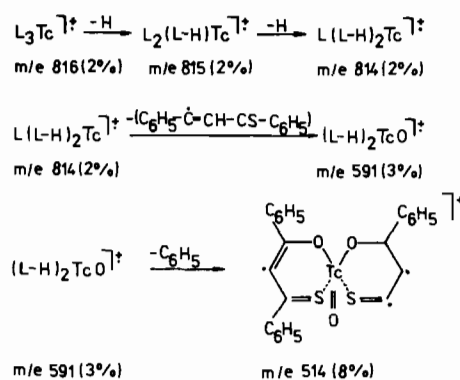
Because of the low volatility of the chelates 2 and 6, composition reactions occur in the mass spectrometer at high temperatures. The mass spectrum of 2 shows the metal-containing fragmentation ions Tc^{II}L₂Γ⁺ (*m/e* 733) and Tc^{II}LΓ⁺ (*m/e* 416) with very low intensities besides the dimer ligand (disulphide of the ligand L₂Γ⁺ (*m/e* 634; 0.4%) and the fragment C₇H₅Br⁺ (*m/e* 168 100%).

TABLE V. ^1H NMR Data of Complexes TcL_3 and ReL_3 ^a

Complex		R ¹		R ²		Chelate ring	
1	phenyl	<i>o</i>	9.50br,s	phenyl	<i>o</i>	15.58d	-12.85br
		<i>m</i>	5.74d		<i>m</i>	6.02t	
		<i>p</i>	8.47t		<i>p</i>	11.83t	
2	<i>p</i> -bromo-phenyl	<i>o</i>	9.50br,s	phenyl	<i>o</i>	15.46d	-13.17br
		<i>m</i>	5.87s		<i>m</i>	6.11t	
		<i>p</i>	—		<i>p</i>	11.63t	
3	methyl		-6.07s	phenyl	<i>o</i>	15.34d	-20.09br
					<i>m</i>	6.00t	
4	trifluoro methyl		—	thienyl	3	11.16d	-12.52br
					4	1.50t ^b	
					5	2.80d	
5	phenyl	<i>o</i>	5.35br,d	phenyl	<i>o</i>	7.15d	—
		<i>m</i>	6.98t		<i>m</i>	8.69t	
		<i>p</i>	6.46t		<i>p</i>	6.36t	
6	phenyl			methyl		-2.84s	+20.80br
		<i>o</i>	2.23d		<i>o</i>	11.11d	
		<i>m</i>	6.35t		<i>m</i>	8.80t	
7	<i>p</i> -bromo-phenyl	<i>p</i>	4.57t	<i>p</i>	7.31t	+20.75br	
		<i>o</i>	2.18d	<i>o</i>	10.89d		
		<i>m</i>	6.57d	<i>m</i>	8.85t		
		<i>p</i>	—	<i>p</i>	7.20t		

^aValues in ppm, solvent acetone, at room temperature. ^b $J_{3,4} = J_{4,5}$; br = strongly broadened, s = singlet, d = doublet, t = triplet.

In the mass spectrum of the rhenium(III) chelate **6** only the metal species $\text{Re}^{\text{III}}\text{L}^+\text{Tc}^{\text{III}}\text{L}^+$ (m/e 424; 1%) is observed, whereas the basic peak is produced by the ligand ion $\text{L}^+\text{Tc}^{\text{III}}\text{L}^+$ (m/e 239; 100%). The results are in accordance with the monomeric behaviour of the chelates. The fragmentation of the technetium chelates with monothio- β -diketones depends on the substituents R¹ and R² of the chelate ring. In the case of tris-(thiobenzoylacetonato)technetium(III) the mass spectrum exhibits the species $\text{Tc}^{\text{III}}\text{LS}^+\text{Tc}^{\text{III}}\text{L}^+$ (m/e 485; 23%) and $\text{Tc}^{\text{III}}\text{L}_2^+\text{Tc}^{\text{III}}\text{L}^+$ (m/e 453; 19%) which results by splitting off the ligand fragment (L-S) or the ligand L. The fragment ions L-S (m/e 145, 30%) and L (m/e 177, 32%) are also observed in the mass spectrum of the ligand. The occurrence of an ion L^+ can be explained by the reduction reaction $\text{Tc}^{\text{III}}\text{L}_3 \rightarrow \text{Tc}^{\text{II}}\text{L}_2 + \text{L}^+$. On the contrary, the technetium(III) chelates of symmetrically substituted monothio- β -diketones split off the γ -hydrogen atom of the ligand in the first step. For compound **1** typical fragmentations are given in Scheme 2.

Scheme 2. Fragmentation of compound **1**.

^1H NMR Spectra

The ^1H NMR data of the paramagnetic Tc and Re chelate complexes **1**–**7** are listed in Table V. As was already found [7], compound **1**, for example, leads to seven characteristic signals, which are distributed

over an uncommonly wide range from -13 ppm to $+16$ ppm (at room temperature), as against the chemical shifts of the diamagnetic ligand protons. The well separated and broadened signals result in first-order spectra, whereby the linewidth decreases with increasing distance from the paramagnetic central ion. Only in the case of *ortho*- and *meta*-protons of R^1 (O adjacent) in **1** and **2** are unexpected splitting patterns observed. The signal of the *ortho*-protons is a considerably broadened singlet, which shows no coupling with the *meta*-protons. Thus, a doublet for the *meta*-protons is caused by coupling with the *para*-proton. The assignment of the protons within the same aromatic ring was proved by decoupling experiments for all compounds. Comparing spectra of different chelate complexes, the protons of different rings may be assigned. Thus, for instance, on comparing **1** and **2** it is evident that the protons of phenyl adjacent to the S atom are strongly shifted downfield as against those adjacent to the O atom. In the thienyl complex **4** the proton in position 3 is also considerably shifted downfield, but generally the chemical shifts of the thienyl protons deviate from the shifts of the phenyl protons in **1**, **2** or **3**.

From the extent of these differences it is supposed that electronic influences at the π -ring system predominate, whereas steric effects are of minor importance.

A methyl group introduced instead of the phenyl group (compound **3**) results in a significant high-field shift to -6 ppm. This chemical shift is comparable to the extreme values of the chelate ring protons in **1** to **4**. These two types of protons (methyl and chelate ring, respectively) have similar distances from the central ion.

In compound **5**, the methyl group is less shifted to high-field (-2.84 ppm) because of its greater distance from the central ion. The phenyl protons adjacent to the O atom were assigned from the fact that the signals of *ortho*-protons in **1** and **2** are also broadened.

Substitution of Tc by Re(III) results in quite different spectra. The sequence of chemical shifts at R^1 is inverted and the chemical shifts at R^2 move together. The most interesting fact is observed for the chelate ring protons, which are shifted extremely downfield by 33 ppm.

All spectra are not influenced significantly by the nature of the solvent, indicating the high stability of the complexes. In general, the ^1H spectra show that ligands in their deprotonated form are coordinated with Tc(III) and Re(III) via the heteroatoms oxygen and sulphur. Presumably, the chemical shifts are caused by the contact interaction between the paramagnetic central ion and the ligands.

It should be noted that paramagnetic β -diketonate complexes of Tc(III) [5] and of some other transition metals [15] show also well-resolved spectra,

whereas from Tc(III) chelates with the O and S donor ligands benzoylthioureas [16] no reasonable ^1H NMR spectra could be observed.

Further investigations are required to explain in detail the chemical shift effects observed with the paramagnetic Tc and Re complexes.

Crystal Structure of Tris(monothiodibenzoylmethano)technetium(III) (**1**)

The molecular geometry and atom numbering of the complex are shown in Fig. 1, where the three bidentate ligands are designated with *a*, *b* and *c*. Interatomic bond distances and angles, with e.s.d.s derived from the refinement, are given in Table VI. Other geometrical entities (planes of best fit for the ligands, deviations of atoms from the planes, dihedral angles between them and some torsion angles) are listed in Table VII.

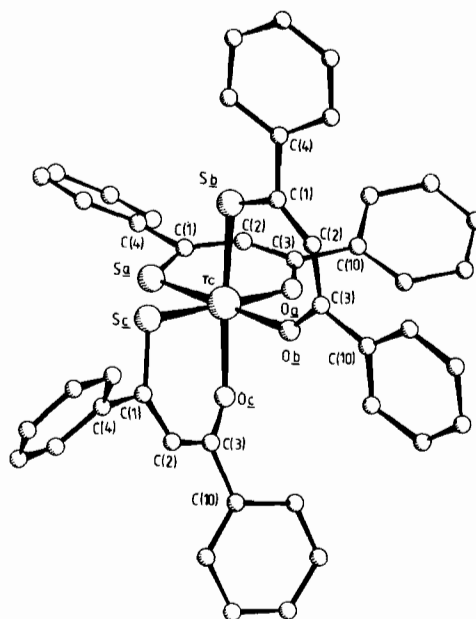


Fig. 1. Model in perspective showing the $\text{Tc}(\text{SC}(\text{Ph})\text{CHC}(\text{Ph})\text{O})_3$ molecule. The three bidentate ligands are designated *a*, *b* and *c*.

The structures of tris(monothiodibenzoylmethano)metal(III) complexes with Fe(III) [17] and In(III) [18] have already been determined. This is the first structure determination dealing with the TcS_3O_3 core. The structure consists of discrete molecules of $\text{Tc}(\text{SC}(\text{Ph})\text{CHC}(\text{Ph})\text{O})_3$, in which the technetium coordination environment is essentially octahedral. Figure 2 shows the TcS_3O_3 octahedron along with the various distances. In effect, the average twist angle between the upper and lower triangular faces (Fig. 2) ($\theta = 28.8^\circ$), the normalized bite ($b = 1.420$) and the compression ratio ($s/h = 1.167$) indicate very little trigonal distortion from the

TABLE VI. Selected Interatomic Bond Distances (Å) and Angles (°) (with their e.s.d.s. in parentheses)

		Ligand <i>a</i>	Ligand <i>b</i>	Ligand <i>c</i>	
Tc-S		2.331(3)	2.343(4)	2.316(4)	
Tc-O		2.085(9)	2.008(8)	2.065(9)	
S-C(1)		1.71(1)	1.70(1)	1.71(1)	
C(1)-C(2)		1.35(2)	1.38(2)	1.35(2)	
C(2)-C(3)		1.41(2)	1.41(2)	1.46(2)	
O-C(3)		1.28(2)	1.27(1)	1.25(2)	
C(1)-C(4)		1.52(1)	1.51(2)	1.48(2)	
C(3)-C(10)		1.46(2)	1.49(2)	1.48(2)	
C _{ph} -C _{ph}	mean	1.38(1)	1.39(1)	1.38(1)	
Sa-Tc-Sb	91.5(1)	Oa-Tc-Sb	91.1(2)	Sb-Tc-Sc	87.2(1)
Sa-Tc-Ob	176.8(3)	Oa-Tc-Ob	87.7(3)	Sb-Tc-Oc	172.4(3)
Sa-Tc-Sc	90.0(1)	Oa-Tc-Sc	178.4(3)	Ob-Tc-Sc	92.5(3)
Sa-Tc-Oc	96.0(3)	Oa-Tc-Oc	90.5(3)	Ob-Tc-Oc	82.0(4)
		Ligand <i>a</i>	Ligand <i>b</i>	Ligand <i>c</i>	
S-Tc-O		89.8(3)	90.6(3)	91.2(3)	
Tc-S-C(1)		111.3(4)	110.1(5)	109.9(5)	
S-C(1)-C(2)		127.6(9)	128.5(1.0)	127.8(1.0)	
C(1)-C(2)-C(3)		130.6(1.1)	127.8(1.1)	129.5(1.2)	
C(2)-C(3)-O		123.9(1.1)	124.9(1.1)	124.2(1.1)	
C(3)-O-Tc		134.3(8)	137.2(8)	132.6(8)	
S-C(1)-C(4)		113.7(8)	113.7(9)	113.8(9)	
C(4)-C(1)-C(2)		118.6(1.0)	117.8(1.1)	118.3(1.1)	
C(2)-C(3)-C(10)		121.6(1.1)	121.1(1.1)	118.3(1.1)	
O-C(3)-C(10)		114.5(1.1)	114.0(1.0)	117.5(1.1)	
C _{ph} -C _{ph} -C _{ph}	mean	120(1.0)	120(1.0)	120(1.0)	

TABLE VII. Other Geometrical Entities in Tc(SC(Ph)CHC(Ph)O)₃

		<i>a</i>	<i>b</i>	<i>c</i>						
(1) Deviations (Å) from the mean planes										
$\left\{ \begin{array}{l} \text{S} \\ \text{O} \\ \text{C(1)} \\ \text{C(2)} \\ \text{C(3)} \\ \text{Tc} \\ \text{C(4)} \\ \text{C(10)} \end{array} \right.$	S	0.00	0.00	0.00						
	O	0.01	-0.02	0.00						
	C(1)	0.04	-0.03	0.02						
	C(2)	-0.01	-0.01	-0.01						
	C(3)	-0.04	0.06	-0.01						
	Tc	-0.30	-0.20	-0.47						
	C(4)	0.07	-0.04	0.15						
C(10)	-0.13	0.26	-0.05							
		<i>a</i>	<i>b</i>	<i>c</i>	C(4)-(9) <i>a</i>	C(10)-(15) <i>a</i>	C(4)-(9) <i>b</i>	C(10)-(15) <i>b</i>	C(4)-(9) <i>c</i>	C(10)-(15) <i>c</i>
(2) Dihedral angles between the planes (°)										
<i>a</i>	0									
<i>b</i>	87.6	0								
<i>c</i>	66.0	106.9	0							
*C(4)-(9) <i>a</i>	29.2	116.7	59.3	0						
*C(10)-(15) <i>a</i>	27.2	75.1	50.3	47.5	0					
*C(4)-(9) <i>b</i>	87.3	27.0	82.2	112.7	65.2	0				
*C(10)-(15) <i>b</i>	90.7	13.6	96.2	118.8	72.9	14.2	0			
*C(4)-(9) <i>c</i>	118.9	96.7	54.4	111.4	95.9	73.3	83.5	0		
*C(10)-(15) <i>c</i>	70.0	76.3	31.2	78.4	44.1	51.0	65.0	52.5	0	

(continued)

TABLE VII. (continued)

	Ligand <i>a</i>	Ligand <i>b</i>	Ligand <i>c</i>
(3) Some torsion angles (°)			
Tc–S–C(1)–C(2)	3.1	7.2	–10.1
S–C(1)–C(2)–C(3)	4.7	1.7	–3.2
C(1)–C(2)–C(3)–O	1.1	–8.4	1.5
C(2)–C(3)–O–Tc	–17.5	2.9	18.7
C(3)–O–Tc–S	19.6	5.1	–25.6
O–Tc–S–C(1)	–10.1	–8.1	17.5

*Phenyl groups are designated as the ligands to which they belong.

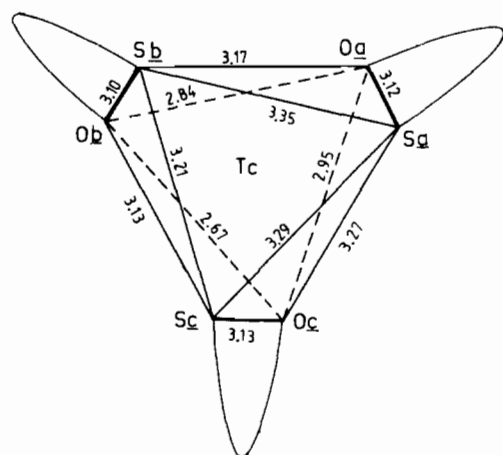


Fig. 2. Polyhedron edge lengths in $\text{Tc}(\text{SC}(\text{Ph})\text{CHC}(\text{Ph})\text{O})_3$. The thick edges refer to the 'bite' distances.

regular octahedral shape [$\theta = 30^\circ$, $b = 1.414 (\sqrt{2})$ and $s/h = 1.225 (\sqrt{3/2})$] [19]. It is well known [17–21] that in $\text{M}(\text{bidentate})_3$ complexes with a large six-membered chelate ring, where the angle about the metal atom subtended by the bidentate ligand is close to 90° (Table VI), the expected stereochemistry is close to octahedral. Moreover, the dihedral angles between the top and the bottom trigonal faces are 2.5, 12.0, 9.0 and 6.0° and no tetragonal elongation of the octahedron is observed.

Unlike monomeric tris(monothiodibenzoylmethanato)iron(III) [17] and tris(dithiolato)metal(III) complexes [19, 20], in this molecule two of the three ligands (*a* and *b*), excluding of course phenyl groups, are not planar, as confirmed by the significant atomic deviations (up to 0.06 Å) from the least-squares fitted mean planes (Table VII).

Within the TcSOC_3 six-membered rings, the Tc–S distances (2.32–2.34 Å) are substantially equal, while those of the Tc–O vary between 2.01 and 2.08 Å and the remainder of the ligand system distances and angles are normal compared with those found in related systems [17–20]. The short Tc–O_b

distance (2.01 Å) is not easy to explain and it remains obscure, at least in the absence of a tetragonal elongation; within the coordination polyhedron the O_b atom participates in the O_b...O_c contact (2.67 Å) which is less than 2.80 Å, the van der Waals diameter of oxygen [21]. But, even with this difference at the O_b donor atom, all bond angles subtended at the Tc atom are within 1.2° of the idealized 90° value.

The three symmetrically substituted chelate rings of tris(monothiodibenzoylmethanato)technetium(III) exhibit the nonequivalence of the C–C distances observed for analogous complexes with Fe(III) and In(III) (Table VI). The technetium(III) chelate shows a similar structure to the corresponding iron(III) compound, only the structural details are different. This means that the Tc–S bond is 0.02 Å shorter than the Fe–S distance, whereas the Tc–O distance is 0.03 Å longer than the Fe–O bond. This fact can be explained by a stronger interchange of the technetium with the soft sulphur donor atom.

Supplementary Material

Thermal parameters and observed and calculated structure factors are available from the authors on request.

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