

Figure 1. An ORTEP drawing of the $\{\text{TcO}[\text{SCH}_2\text{C}(\text{O})\text{S}]_2\}^-$ ion; the numbering scheme is that used for the atoms in Table I.

the apex. The qualification is due to a slight difference in the length of the Tc-S₁ and Tc-S₂ bonds. The technetium atom lies 0.791 Å above the basal plane, and the Tc-O₁ line is perpendicular to the least-squares plane formed by the four sulfur atoms. There is nothing remarkable about the bond lengths and angles within the ligands.

It is interesting to note the similarity of the Tc^{VO}S₄ core of I to the isoelectronic Mo^{IV}O₄ core¹⁰ of MoO(*n*-Pr₂dtc)₂. The molybdenum atom in the latter compound is coordinated in the same square-pyramidal fashion as I, and corresponding bond lengths are similar (Mo-O = 1.664 (8) Å, average Mo-S = 2.414 (2) Å), as is the elevation of the molybdenum above the basal plane (0.83 Å). Referring to Cotton and Wing's correlation,^{10,11} the Mo-O bond order has been assigned as 3, and the IR stretching frequencies for the Mo-O bond of the dithiocarbamate complexes MoO(Et₂dtc)₂¹² and MoO(Me₂dtc)₂¹³ (962 and 975 cm⁻¹, respectively) correspond to a band at 950 cm⁻¹ in the IR and Raman spectra¹⁴ of I, assigned to the Tc-O stretch.

I has two moderately intense bands in its optical spectrum: λ_{max} (nm) 325, 415 (ε (L mol⁻¹ cm⁻¹) 3100, 3700), respectively, in CH₃CN solution. It is weakly paramagnetic in the solid state. The effective moment, which is field strength dependent, lies in the range of 1.2-1.5 μ_B (295 K). Similar behavior is found for some oxomolybdenum and oxorhenium complexes, with a d² configuration having local C_{4v} symmetry, where the ground state is expected to be ¹A₁. This has been suggested^{13,15,16} to be due to temperature-independent paramagnetism.

The formation of this novel compound demonstrates the possibility of stabilizing the +5 oxidation state of technetium by the appropriate choice of ligand.

The avidity of the ^{99m}Tc in this experiment for an impurity of manufacture in thioglycolic acid, or an equilibrium species in alkaline thioglycolate solutions, suggests caution be exercised in assuming that a particular ^{99m}Tc-labeled radiopharmaceutical is simply a complex of technetium with the intended ligand.

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Supplementary Material Available: A list of bond distances, angles, positional and thermal parameters, and a table of structure factors (11 pages). Ordering information is given on any current masthead page.

References and Notes

- P. Valk, J. McRae, A. J. Bearden, and P. Hambright, *J. Chem. Educ.*, **53**, 542 (1976).
- G. Subramanian, B. A. Rhodes, J. F. Cooper, and V. J. Sodd, Ed., "Radiopharmaceuticals", The Society of Nuclear Medicine, New York, N.Y., 1975.
- J. A. Siegel and E. Deutsch in "Annual Reports in Inorganic and General Syntheses—1975", H. Zimmer and K. Niedenzu, Ed., Academic Press, New York, N.Y., 1976.

- F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, N.Y., 1972, pp 972-990.
- R. D. Peacock in "Comprehensive Inorganic Chemistry", Vol. 3, J. C. Bailar, J. H. Emelius, R. S. Nyholm, and A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973, pp 877-903.
- F. J. Miller and P. F. Thomason, *Anal. Chem.*, **32**, 1429 (1960).
- A detailed description of the characterization of this compound will be published separately.
- The X-ray structural determination was performed by Molecular Structure Corporation, College Station, Texas.
- The structure factor was divided by a correction factor varying from 0.727 to 1.000 with an average correction of 0.829.
- L. Ricard, J. Estienne, P. Karaglannidis, P. Toledano, J. Fischer, A. Mitschler, and R. Weiss, *J. Coord. Chem.*, **3**, 277 (1974).
- F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965).
- R. N. Jowitt and R. C. H. Mitchell, *J. Chem. Soc. A*, 2632 (1969).
- E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).
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- W. P. Griffith, *Coord. Chem. Rev.*, **5**, 459 (1970).
- D. E. Grove and G. Wilkinson, *J. Chem. Soc.*, 1224 (1966).

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A Thiol Complex of Technetium Pertinent to Radiopharmaceutical Use of ^{99m}Tc

Sir:

Recently, new impetus to explore the chemistry of ^{99m}Tc has been provided by the utility of ^{99m}Tc, a 140-keV γ emitter with a half-life of 6 h. The ready availability and ideal nuclear properties of ^{99m}Tc have led to its widespread use in the non-surgical diagnostic examination of internal organs by radioactive imaging.^{1,2} Chemical forms of ^{99m}Tc are presently the most widely used radiopharmaceuticals for imaging of the brain, liver, lung, and skeleton.²

The chemical nature of the ^{99m}Tc imaging agents at present is only speculative. By working with long-lived ⁹⁹Tc (0.3-MeV β emitter with *t*_{1/2} of 2.1 × 10⁵ years) rather than short-lived ^{99m}Tc (*t*_{1/2} of 6 h), macroscopic amounts of technetium compounds can be isolated and characterized by conventional chemical and spectroscopic methods.

Since several ^{99m}Tc labeled radiopharmaceuticals appear to involve technetium-sulfur coordination,³⁻⁹ the complexation of technetium with dithiols was investigated. It has been shown that 1,2- and 1,3-dithiols react with technetium to form oxotechnetium(V) bis(dithiolate) complexes.

In this paper we describe three new oxotechnetium(V) bis(dithiolate) compounds and give a definite X-ray crystallographic characterization of the structure of one of them.

Three oxotechnetium(V) bis(dithiolate) complexes, [Tc(O)(SXS)₂]⁻, where X = CH₂CH₂, CH₂CH₂CH₂, and CH₂CH(CH₃), have been synthesized by reducing ammonium pertechnetate in ethanol with sodium borohydride in the presence of the appropriate 1,2- or 1,3-dithiol. All three complexes are bright orange in solution and were conveniently precipitated upon addition of the tetraphenylarsonium ion.¹⁰ Since it appeared likely that very similar complex anions were present in each case, the crystal structure of one of them, viz., the SCH₂CH₂S compound, was investigated in order to establish the nature of this group of compounds.

Table I. Some Bond Distances (Ångstroms) and Angles (Degrees)^a

Tc-S(1)	2.299 (4)	S(1)-C(1)	1.84 (2)
Tc-S(2)	2.283 (4)	S(2)-C(2)	1.83 (2)
Tc-S(3)	2.305 (4)	S(3)-C(3)	1.82 (2)
Tc-S(4)	2.313 (4)	S(4)-C(4)	1.83 (2)
Tc-S, av	2.300 (13)	S-C, av	1.83 (2)
Tc-O	1.64 (1)	C(1)-C(4)	1.50 (2)
		C(2)-C(3)	1.44 (2)
S(1)-Tc-S(3)	82.4 (2)	S(1)-Tc-O	110.1 (4)
S(1)-Tc-S(4)	84.8 (1)	S(2)-Tc-O	111.3 (4)
S(2)-Tc-S(3)	84.4 (2)	S(3)-Tc-O	109.4 (4)
S(2)-Tc-S(4)	83.5 (1)	S(4)-Tc-O	106.3 (3)
S(1)-Tc-S(2)	138.5 (2)	S(1)-C(1)-C(4)	111 (1)
S(3)-Tc-S(4)	144.4 (4)	S(2)-C(2)-C(3)	113 (1)
		S(3)-C(3)-C(2)	116 (1)
Tc-S(1)-C(1)	107.2 (5)	S(4)-C(4)-C(1)	108 (1)
Tc-S(2)-C(2)	109.5 (5)		
Tc-S(3)-C(3)	104.0 (6)		
Tc-S(4)-C(4)	102.7 (5)		

^a Figures in parentheses are esd's in the least significant digit.

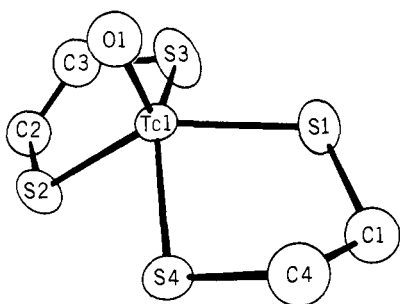


Figure 1. An ORTEP drawing of the $[\text{Tc}(\text{SCH}_2\text{CH}_2\text{S})_2\text{O}]^-$ ion. Each atom is represented by its thermal ellipsoid scaled to enclose 50% of its electron density. The atom numbering scheme used in Table I is defined.

The structure of $(\text{Ph}_4\text{As})[\text{TcO}(\text{SCH}_2\text{CH}_2\text{S})]$ was solved in the space group $Pbca$, with unit cell dimensions of $a = 19.669$ (3) Å, $b = 18.745$ (4) Å, $c = 15.122$ (3) Å, and $Z = 8$. Intensity data were collected on a Syntex PI counter diffractometer using Mo $K\alpha$ radiation monochromated with a graphite crystal in the incident beam. Using 2555 unique reflections with $I > 1\sigma(I)$ the structure was refined by full-matrix least squares to convergence using anisotropic temperature factors for the technetium, arsenic, and sulfur atoms, isotropic temperature factors for the oxygen and carbon atoms, and omitting hydrogen atoms. The final residuals are $R_1 = 0.089$ and $R_2 = 0.087$ with the error in an observation of unit weight equal to 1.34. A final difference Fourier had no peaks of higher intensity than $1.1 \text{ e}/\text{Å}^3$.

The structure of the oxotechnetium anion, $[(\text{C}_2\text{H}_4\text{S}_2)_2\text{TcO}]^-$, is shown in Figure 1, and bond distances and angles for the oxo anion are listed in Table I. The tetraphenylarsonium ion has no unusual features and a complete list of bond lengths and angles is available as supplementary material, along with a table of all atomic positional and thermal parameters and a table of structure factors.¹¹

The coordination geometry around the technetium approximates closely to square pyramidal, although no crystallographic symmetry is imposed. The four sulfur atoms form the square base with the technetium atom 0.761 (2) Å above the mean plane. The average Tc-S bond distance is 2.30 (1) Å. An oxygen atom constitutes the apex of the square pyramid, with a Tc-O bond distance of 1.64 (1) Å.

There appears to be no prior report of a technetium sulfur bond length. The Tc=O bond distance in this compound may be compared with those in the technetium(VII) compound Tc_2O_7 , 1.649 (4) Å,¹² and in TcOF_4 , 1.66 (3) Å.¹³ It is slightly

shorter than that recently found in the closely similar compound¹⁴ $[(n\text{-C}_4\text{H}_9)_4\text{N}][(\text{SC}(\text{O})\text{CH}_2\text{S})_2\text{TcO}]$, 1.672 (8) Å.

The observed square-pyramidal coordination of Tc(V) is similar to that found in several Re(V) species such as the ReBr_4O^- ion,¹⁵ but the Tc-O distance appears significantly shorter than the Re-O bonds which are 1.71 (4) Å^{15a} and 1.73 (6) Å.^{15c} In the case of the rhenium anion, however, there are weakly coordinated molecules trans to the oxygen atom, which may tend to weaken the Re=O bond slightly.

Supplementary Material Available: A list of bond distances and angles of the tetraphenylarsonium ion, positional and thermal parameters, and a table of structure factors (14 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) J. A. Siegel and E. Deutsch, *Annu. Rep. Inorg. Gen. Synth.*, **4**, 311 (1975).
- (2) W. C. Eckelman and S. M. Levenson, *Int. J. Appl. Radiat. Isot.*, **25**, 67 (1977).
- (3) I. Ikeda, O. Inoue, and K. Kurata, *J. Nucl. Med.*, **18**, 1222 (1977).
- (4) A. K. Tonkin and F. H. DeLand, *J. Nucl. Med.*, **15**, 539 (1974).
- (5) T. H. Lin, A. Khentigan, and H. S. Winchell, *J. Nucl. Med.*, **15**, 613 (1974).
- (6) F. C. Hunt, D. J. Maddalena, and M. G. Yeates, *Proc. World Cong. Nucl. Med.*, 1st, 1974, 869 (1974).
- (7) B. A. Rhodes, H. S. Stern, J. A. Buchanan, I. Zolle, and H. N. Wagner, Jr., *Radiology*, **99**, 613 (1971).
- (8) J. A. Stelgman, H. P. Williams, and N. A. Solomon, *J. Nucl. Med.*, **16**, 573 (1975).
- (9) H. Burns, P. Worley, H. N. Wagner, Jr., and L. Marzilli, First International Symposium on Radiopharmaceutical Chemistry, Brookhaven National Laboratory, Sept. 21-24, 1976.
- (10) Details of the syntheses as well as chemical and spectroscopic properties of these compounds will be reported later. Satisfactory elemental analyses were obtained for all compounds.
- (11) See paragraph at end of paper regarding supplementary material.
- (12) B. Krebs, *Angew. Chem. Int. Ed. Engl.*, **8**, 381 (1969).
- (13) A. J. Edwards, G. R. Jones, and R. J. C. Sills, *J. Chem. Soc. A*, 2521 (1970).
- (14) B. V. DePamphilis, A. G. Jones, M. A. Davis, and A. Davison, *J. Am. Chem. Soc.*, preceding paper in this issue.
- (15) (a) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **4**, 1621 (1965); (b) *ibid.*, **5**, 9 (1966); (c) *ibid.*, **5**, 416 (1966).

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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 17. Synthesis and Electrical Properties of the First Homologous Series of 1-Dimensional (Pt-Pt) Metals Containing the (FHF)⁻ and F⁻ Anions¹

Sir:

The study of one-dimensional inorganic metals of the partially oxidized tetracyanoplatinate (POTCP) series has been severely restricted by the scarcity of new materials.² In an effort to obtain new compounds with improved electrical transport and materials properties over that of the prototype $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.30} \cdot 3\text{H}_2\text{O}$ (KCP(Br)), we have undertaken a program of new materials synthesis which involves incorporation of complex anions other than Cl^- or Br^- in the TCP crystal lattice. In many cases totally new structure types are produced and recently we reported the syntheses³ and structures^{4,5} of $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$ ($\text{CsCP}(\text{FHF})_{0.39}$) (Pt-Pt = 2.833 (1) Å)⁵ and $\text{Rb}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.40}$ ($\text{RbCP}(\text{FHF})_{0.40}$) (Pt-Pt = 2.798 (1) Å),⁴ which are the first anhydrous POTCP salts and which have the shortest Pt-Pt