Figure 1. Sound pressure level (S.P.L.) as a function of the frequency for one "crack" of the acoustic emission of crystallizing $ZnCl_2Pyr$.

possible explanation may be a phase transition in the crystal that damages the original crystal. Such a phase transition may be caused by a change in coordination geometry from initially formed, tetrahedrally coordinated Zn(II), with bridging pyrazines and terminal chloride ions, to octahedrally coordinated Zn(II), with both bridging pyrazines and chloride ions (the final product). A second possibility is the initial formation of relative short chains or dimers, followed by a rapid polymerization into infinite polymers. To investigate the nature of the acoustic emission, a frequency–intensity analysis has been performed. The sound pressure level (S.P.L.) of a single crack has been plotted as a function of the frequency in Figure 1. It is observed that the most intense sound emission is outside the region of the human hearing (which is up to $\sim$16 kHz). The maximum in the S.P.L. curve at $\sim$100 kHz is not accurately determined, owing to the use of a low-pass filter in the fast Fourier transform analysis. No measurements at all were possible above 160 kHz.

References and Notes

(1) Stoehr, C. *J. Prakt. Chem.*, **1895**, *51*, 449.
(2) Ferraro, J. R.; Wozniak, W.; Roch, G. *Ric. Sci.*, **1968**, *38*, 433.
(3) Ferraro, J. R. "Low Frequency Vibrations of Inorganic and Coordination Compounds", Plenum Press: New York, N.Y.; 1971.
(4) The authors are indebted to one of the referees pointing our attention to a paper[5] describing the crystalloluminiscence of $Ba(ClO_3)_2$ and of $KNa_3(SO_4)_2$. Acoustic signals registered by a hydrophone placed into the solution coincided with the luminescence.
(5) Belyaev, L. M.; Nabatov, V. V.; Martyshev, Y. N. *Soviet Phys. Crystallogr.*, **1963**, *7*, 464.
(6) A relationship with the well-known phenomenon of triboluminescence[7] was initially supposed. However, we were unable to detect any luminescence during or after the cracking.
(7) See, e.g., Zink, J. I. *Inorg. Chem.*, **1975**, *14*, 555; Hardy, G. E.; Baldwin, J. C.; Zink, J. I.; Kaska, W. C.; Liu, P. H.; Dubois, L. *J. Am. Chem. Soc.*, **1977**, *99*, 3552.

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Preparation and Crystal Structure of Oxotechnetium Bis(thiomercaptoacetate) and Its Relationship to Radiopharmaceuticals Labeled with ^{99m}Tc

Sir:

Because of the minute concentrations (typically 10^{-8} M) of technetium used in solutions of diagnostic imaging agents,[1-3] unambiguous identification of the chelated species present, or even of the oxidation state of the coordinated technetium, is difficult. Furthermore, the behavior[4,5] of technetium, partic-

Table I. Structural Parameters of $\{TcO[SCH_2C(O)S]_2\}^-$

	Distances, Å		
$Tc-S_1$	2.336 (3)	$S_1-S_2^1$	4.361 (4)
$Tc-S_2$	2.303 (3)	S_1-C_1	1.741 (12)
$Tc-O_1$	1.672 (8)	S_2-C_2	1.762 (13)
$S_1-S_1^1$	3.041 (5)	O_2-C_1	1.26 (2)
$S_2-S_2^1$	3.016 (6)	C_1-C_2	1.46 (2)
S_1-S_2	3.139 (4)		
	Angles, degree		
S_1-Tc-S_1	81.2 (1)	$Tc-S_1-C_1$	106.5 (5)
S_1-Tc-S_2	85.1 (1)	$Tc-S_2-C_2$	105.9 (4)
$S_1-Tc-S_2^1$	140.1 (1)	$S_1-C_1-O_2$	117 (1)
S_1-Tc-O_1	109.7 (3)	$S_1-C_1-C_2$	118.9 (9)
$S_2-Tc-S_2^1$	81.8 (2)	$O_2-C_1-C_2$	124 (1)
S_2-Tc-O_1	110.2 (3)	$S_2-C_2-C_1$	115.6 (8)

ularly in the V and VI oxidation states, has not been extensively investigated. Prior to this study no technetium coordination complexes had been isolated from aqueous solution close to physiological pH (7.4).

We report the synthesis and crystal structure of a novel five-coordinate Tc(V) compound, $(Bu_4N)[TcO(SCH_2COS)_2]$ (I).

The reaction of pertechnetate with thioglycolic acid ($HSCH_2COOH$) at pH 8.2 has been described as a colorimetric method for the quantitative determination of technetium.[6] In an attempt to isolate the technetium-containing species giving rise to the 655-nm absorption band described by Miller and Thomason,[6] complex I was obtained instead. Reagent thioglycolic acid (Fisher or MCB) was diluted to 10% v/v with distilled water and was adjusted to pH 7.5 with 50% w/w NaOH solution. Typically, 0.75 mL of 0.352 M NH_4TcO_4 solution (New England Nuclear) was added to 60 mL of the thioglycolate solution. After 10 min, 3 g of Bu_4NBr (Eastman) in 10 mL of distilled water was added, and a yellow-brown precipitate appeared. The precipitate was filtered, washed with water, and successively recrystallized from methanol–water and acetone–water mixtures.

The compound[7] crystallizes in the monoclinic space group C_m, confirmed by refinement.[8] The dimensions of the unit cell are $a = 10.451$ (5) Å, $b = 14.855$ (8) Å, $c = 9.927$ (7) Å, $\alpha = \gamma = 90°$, $\beta = 114.88$ (5)°, with two molecules per unit cell.

An Enraf–Nonius CAD4 diffractometer was used for the collection of intensity data on a crystal of dimensions $0.1 \times 0.3 \times 0.35$ mm, using a $\theta-2\theta$ scan employing graphite monochromatized Mo Kα radiation ($\lambda = 0.7103$ Å). The range of data collected was $0° < 2\theta$ (Mo Kα) $< 60°$. A total of 2207 independent reflections was collected.

Lorentz and polarization corrections were applied to the data, and an absorption correction was made using an empirical ψ scan correction.[9]

The structure was solved using the Patterson method. The Patterson map showed the position of the technetium atom, and the remaining nonhydrogen atoms were located in succeeding difference Fourier syntheses.

Only the 1248 reflections having $F_{OBS}^2 > 3\sigma(F_{OBS}^2)$ were used in the least-squares refinement, which resulted in final values of $R_1 = 0.082$ and $R_2 = 0.091$. The final difference Fourier map showed no residual electron density as high as 0.5 carbon atom on a previous difference Fourier map.

The anion was found to lie on a crystallographic mirror plane. The *n*-butylammonium cation was also found on the mirror plane and determined to be 50–50 disordered in all *n*-butyl chains. Anion bond lengths and bond angles are presented in Table I.

The technetium atom (Figure 1) is coordinated by an oxygen and four sulfur atoms in very nearly a square pyramid, with the sulfur atoms forming the basal plane and the oxygen atom
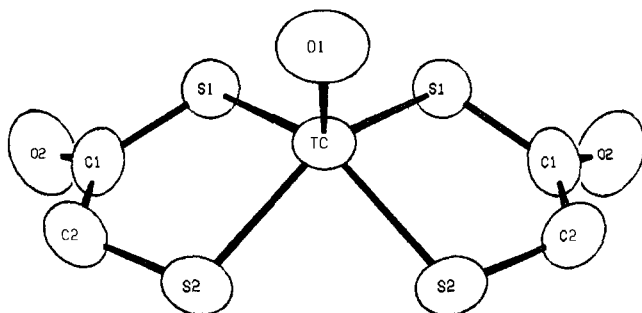
Figure 1. An ORTEP drawing of the {TcO[SCH$_2$C(O)S]$_2$}$^-$ ion; the numbering scheme is that used for the atoms in Table I.

the apex. The qualification is due to a slight difference in the length of the Tc–S$_1$ and Tc–S$_2$ bonds. The technetium atom lies 0.791 Å above the basal plane, and the Tc–O$_1$ 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^{V}OS$_4$ core of I to the isoelectronic Mo^{IV}OS$_4$ core[10] of MoO(*n*-Pr$_2$dtc)$_2$. 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 dithiocarbamato complexes MoO(Et$_2$dtc)$_2$[12] and MoO-(Me$_2$dtc)$_2$[13] (962 and 975 cm^{-1}, respectively) correspond to a band at 950 cm^{-1} in the IR and Raman spectra[14] 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 CH$_3$CN 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 d^2 configuration having local C_{4v} symmetry, where the ground state is expected to be $^1A_1$. 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 ^{99}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.

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

(1) P. Valk, J. McRae, A. J. Bearden, and P. Hambright, *J. Chem. Educ.*, **53**, 542 (1976).
(2) G. Subramanian, B. A. Rhodes, J. F. Cooper, and V. J. Sodd, Ed., "Radiopharmaceuticals", The Society of Nuclear Medicine, New York, N.Y., 1975.
(3) 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.
(4) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, N.Y., 1972, pp 972–990.
(5) R. D. Peacock in "Comprehensive Inorganic Chemistry", Vol. 3, J. C. Bailer, J. H. Emelaus, R. S. Nyholm, and A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973, pp 877–903.
(6) F. J. Miller and P. F. Thomason, *Anal. Chem.*, **32**, 1429 (1960).
(7) A detailed description of the characterization of this compound will be published separately.
(8) The X-ray structural determination was performed by Molecular Structure Corporation, College Station, Texas.
(9) The structure factor was divided by a correction factor varying from 0.727 to 1.000 with an average correction of 0.829.
(10) L. Ricard, J. Estienne, P. Karaglannidis, P. Toledano, J. Fischer, A. Mitschler, and R. Weiss, *J. Coord. Chem.*, **3**, 277 (1974).
(11) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965).
(12) R. N. Jowitt and R. C. H. Mitchell, *J. Chem. Soc. A*, 2632 (1969).
(13) E. I. Stlefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).
(14) We thank Dr. J. E. Smith of Union Carbide Research Labs, Tarrytown, N.Y., for obtaining the IR and Raman spectra so that we could make a comparison between the Tc–O stretch in I and those in the complexes [TcO(SXS)$_2$]$^-$, where X = CH$_2$CH$_2$, CH$_2$CH$_2$CH$_2$, and CH$_2$CH(CH$_3$), which he has recently isolated. Cf. J. E. Smith, E. F. Byrne, F. A. Cotton, and J. C. Sekutowski, *J. Am. Chem. Soc.*, following paper in this issue.
(15) W. P. Griffith, *Coord. Chem. Rev.*, **5**, 459 (1970).
(16) 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 ^{99}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 nonsurgical 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 ^{99}Tc (0.3-MeV β emitter with $t_{1/2}$ of 2.1 × 10^5 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 = CH$_2$CH$_2$, CH$_2$CH$_2$CH$_2$, and CH$_2$CH(CH$_3$), 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 SCH$_2$CH$_2$S compound, was investigated in order to establish the nature of this group of compounds.