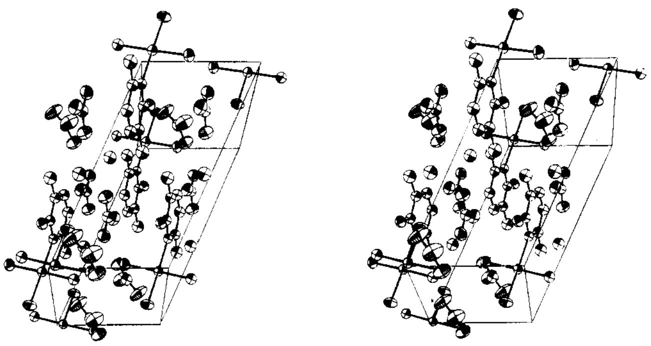

Figure 3. Packing in the unit cell of $[Pt(NH_3)_2(OH_2)(C_5H_7N_3O)](NO_3)_2\cdot H_2O$. **b** and **b** × **c*** are parallel to the bottom and side of the page, respectively, and the view is down **c***.

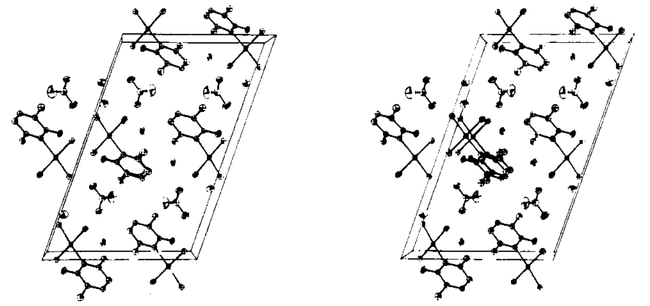

Figure 4. Packing in the unit cell of $[Pt(NH_3)_2(OH)(C_5H_7N_3O)](NO_3)\cdot 2H_2O$. **a** and **c*** are parallel to the bottom and side of the page, respectively, and the view is down **b**.

c direction through $N(5)\cdots O(82)^{iv}$, $N(6)\cdots O(82)^{v}$. Other hydrogen bonds stabilizing the structure and providing cation–anion links are $O(3)\cdots O(81)^{i}$ and $N(6)\cdots O(7)^{ii}$ and $O(7)\cdots O(72)$.

For II (Figure 3) the cations are arranged in layers centered in the planes $z = 0, {}^1/_2$. The anions lie in separating layers at $z = {}^1/_4, {}^3/_4$. Within a layer the cations are stacked up along the *b* direction and canted so there is some cytosine ring overlap; the rings are overlapped like tiles on a roof. This stack of cations is hydrogen bonded together through $O(3)\cdots O(7)^{vi}$, $O(7)\cdots N4)$, $N(5)\cdots O(2)^{i2}$, $N(6)\cdots O(8)^{vii2}$, and $N(6)^{vi}\cdots O(8)$. At the $x = {}^1/_2$ plane, cations in adjacent stacks are hydrogen bonded through $N(4)\cdots O(7)^{i}$, $N(4)^{i}\cdots O(7)$ giving a four centered system of two N(4) and two O(7) in a diamond shape. We have seen this type of hydrogen bonding involving cytosine before,[32] although the oxygen atoms were from nitrate groups. At $x = 0$ the hydrogen bonding between cation stacks is through $N(5)\cdots O(2)^{ii}$. Hydrogen bonding to the nitrate ion provides binding in the *c* direction, besides the ionic interactions, through $O(3)\cdots O(71)$, $O(7)\cdots O(71)$ and $N(5)\cdots O(73)^{vi2}$, $N(6)\cdots O(73)$,^{2x} and some binding in the *a* direction through the extra $O(8)\cdots O(73)^{x}$ hydrogen bonds. The large thermal motion of O(72) clearly arises because it is not involved in hydrogen bonding.

Acknowledgment. We thank the National Cancer Institute of Canada, the Natural Sciences and Engineering Research Council of Canada, the McMaster University Science and Engineering Research Board, Johnson, Matthey, Mallory Ltd., the Deutsche Forschungsgemeinschaft, EFG, and Technische Universität München for financial support of this work.

Registry No. I, 80662-72-2; Ib, 80662-74-4; II, 80662-77-7; IIa, 80662-76-6.

Supplementary Material Available: Tables of temperature factors, best planes and dihedral angles, hydrogen atom parameters, and moduli of observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

Contribution from the Institute for Materials Research,
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Preparation, Spectroscopic Properties, and Structure of 1-Oxo-2,3,6-(D-penicillaminato-*N*,*S*,*O*)-4,5-(D-penicillaminato-*N*,*S*)technetium(V)

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1-Oxo-2,3,6-(D-penicillaminato-*N*,*S*,*O*)-4,5-(D-penicillaminato-*N*,*S*)technetium(V), $TcO(C_5H_9NO_2S)(C_5H_{10}NO_2S)$, has been obtained as orthorhombic crystals: $P2_12_12_1$; $a = 21.878$ (5) Å, $b = 11.711$ (2) Å, $c = 5.924$ (1) Å; $Z = 4$. Data were collected with Mo Kα radiation and a Syntex P2$_1$ diffractometer. The crystal structure was solved by standard methods and refined to $R_1 = 0.0592$ and $R_2 = 0.0439$ on the basis of 3401 independent reflections. The technetium is six-coordinate, being bonded to oxygen (Tc–O = 1.657 (4) Å), the S, N, and O atoms of a D-penicillamine dianion deprotonated at S and O, and to the S and N atoms of a D-penicillamine anion deprotonated at S. The second Tc–O distance is longer (2.214 (4) Å), comparable to the Tc–N distances (2.185 (5), 2.209 (6) Å). Tc–S distances are normal (2.283 (2), 2.296 (2) Å). The molecules are strongly hydrogen bonded from carboxylic acid to carboxylate into a helical chain in the crystal. NMR, vibrational, and electronic spectra are reported.

Introduction

The nuclidic properties of technetium-99m (6-h half-life, 140-keV γ-ray, low radiation dosage) make this isotope an ideal radionuclide for the development of scanning agents in diagnostic medicine.[1] In fact, technetium-99m-labeled complexes have been a major contributing factor to the rapid growth of nuclear medicine.[2]

Relatively little is known, however, about the chemistry of technetium and its complexes,[3,4] and, thus far, serendipity has

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Table I. Crystal Data

compd	$TcO(C_5H_{10}NO_2S)(C_5H_9NO_2)$, $C_{10}H_{19}N_2O_5S_2Tc$
fw	410.30
crystal size, mm (cylinder)	$r = 0.05$, $l = 0.25$
systematic absences	$h00, h \neq 2n$; $0k0, k \neq 2n$; $00l, l \neq 2n$
space group	$P2_12_12_1$
unit cell parameters, Å	$a = 21.878$ (5), $b = 11.711$ (2), $c = 5.924$ (1)
V, Å^3	1517.9 (5)
Z	4
ρ(calcd), g cm^{-3}	1.80
ρ(obsd), g cm^{-3}	1.78 (1)
linear abs coeff, cm^{-1}	11.82
max 2θ, octant (55 °C)	$h,k,\pm l$
std reflctn (esd, %)	341 (1.30), 032 (1.37)
temp, °C	22
no. of independent reflctns	3401
no. with $I > 0$	3223[b]
no. with $I < 0$ rejected	178
no. of variables (last cycle)	188
final R_1,[a] R_2[a]	0.0592, 0.0439
final shift/error max (av)	
nonhydrogen atoms	0.130 (0.020)
all parameters	0.261 (0.035)
final difference map	
highest peak, e/Å^3; location	1.1; 0.40, 0.58, 0.01 and 0.36, 0.04, 0.14
lowest valley e/Å^3; location	−1.1; −0.06, 0.22, 0.08 and 0.42, 0.35, 0.52
weighting	$w = [(\sigma^2 + (0.0160F_O)^2]^{-1}$
error in an observn of unit wt	0.8453

[a] $R_1 = \Sigma(||F_O| - |F_C||)/\Sigma|F_O|$. $R_2 = [\Sigma w(|F_O| - |F_C|)^2/\Sigma wF_O{}^2]^{1/2}$. [b] 200 reflection was suppressed because of an uneven background (probably beam stop at low 2θ); thus only 3222 reflections were used in the refinement.

Table II. Atomic Positional Parameters ($\times 10^4$)

atom	x	y	z
Tc	4018 (0)	3051 (0)	971 (1)
O(3)	4564 (2)	3168 (4)	2894 (7)
S	4247 (1)	1452 (1)	−1107 (3)
C(1)	3747 (3)	371 (5)	294 (10)
C(2)	4120 (4)	−334 (7)	1915 (13)
C(3)	3484 (4)	−407 (7)	−1572 (13)
C(4)	3230 (3)	1019 (5)	1510 (10)
N(1)	3505 (2)	1850 (5)	3138 (9)
C(5)	2872 (3)	1782 (5)	−95 (10)
O(1)	3092 (2)	2766 (3)	−431 (6)
O(2)	2397 (2)	1412 (3)	−1003 (9)
S(a)	4287 (1)	4193 (1)	−1988 (3)
C(1a)	3990 (3)	5595 (4)	−1047 (10)
C(2a)	3902 (4)	6348 (7)	−3114 (13)
C(3a)	4441 (3)	6146 (6)	561 (11)
C(4a)	3356 (3)	5301 (5)	14 (11)
N(a)	3460 (3)	4519 (4)	1935 (9)
C(5a)	2982 (3)	6353 (5)	622 (10)
O(1a)	3185 (2)	6901 (4)	2354 (8)
O(2a)	2543 (2)	6631 (4)	−523 (8)

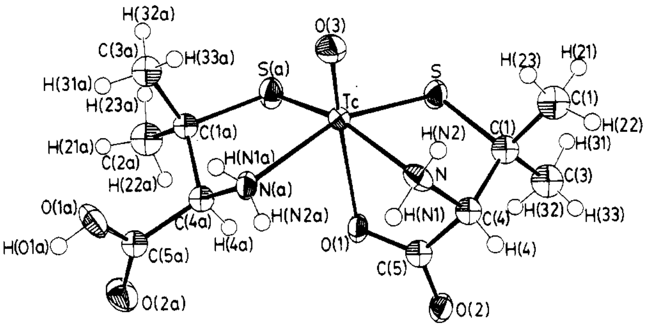

Figure 1. The molecule $TcO(C_5H_{10}NO_2S)(C_5H_9NO_2S)$ showing the atom numbering.

played a major role in radiopharmaceutical development.[5] In the future, the design of new and successful agents will be based on a better understanding of radionuclidic transport in vivo.[5] This understanding will, in part, involve correlating biodistribution with the structural features and chemical behavior of a number of complexes. We have undertaken to prepare and characterize complexes closely related to radiopharmaceuticals currently in use.

In the early days of radiopharmaceutical development, amino acids and their derivatives were widely used to complex various radionuclides. In particular, technetium-99m complexed by penicillamine was used as such, as well as a means of obtaining other labeled compounds.[6] It was soon discovered that a variety of complexes, each with different chemical, chromatographic, and physiological behavior, could be formed with relatively small changes in pH, temperature, or reactant concentrations.[6] Kits for the routine preparation of technetium-99m penicillamine complexes as liver[6] and kidney[7,8] scanning agents took advantage of this sensitivity to labeling conditions.

Since the concentrations of the above complexes were typically of the order of 10^{-9} M, chemical analysis was primarily based on chromatographic techniques, which meant that the detailed structures of these complexes remained unknown. With a view to a more complete characterization of technetium radiopharmaceuticals, we have determined the crystal structure of 1-Oxo-2,3,6-(D-penicillaminato-*S*,*N*,*O*)-4,5-(D-penicillaminato-*N*,*S*)technetium(V). We also report the analysis of the nuclear magnetic resonance, vibrational, and electronic absorption spectra.

Experimental Section

Preparation of $C_{10}H_{19}N_2O_5S_2Tc$. A solution of $NH_4(TcOCl_4)$ was prepared by dissolving 0.36 g (0.002 mol) of NH_4TcO_4 (Amersham) in 15 mL of concentrated hydrochloric acid. After 10 min at room temperature, 3 mL of the dark green solution was added to 0.12 g (0.0008 mol) of D(−)-Penicillamine (Aldrich) dissolved in 5 mL of water. On mixing the solution became dark reddish brown. It was allowed to evaporate to dryness in air, and crystals suitable for X-ray examination were obtained by recrystallizing the residue from water. Anal. Calcd for $C_{10}H_{19}N_2O_5S_2Tc$: C, 29.3; H, 4.4; N, 6.8. Found: C, 28.5, H, 4.1, N, 6.3. Infrared spectra were recorded on Perkin-Elmer Model 283 spectrophotometer. The samples were ground with KBr and pressed into disks. Spectra were calibrated with polyethylene. Raman spectra were excited with the green line (λ 5145 Å) of a Spectra-Physics Model 164 argon ion laser and recorded on a Spex 14018 double monochromator at both room temperature and liquid-nitrogen temperature. Samples were contained in glass melting point tubes. The electronic spectra were recorded on a Cary 14 recording spectrophotometer. The aqueous solutions were contained in 1-cm quartz cells. The ^1H NMR spectrum was recorded on a Bruker WP-80 spectrometer operating at 80 MHz, and the ^{13}C NMR spectra were recorded on the same instrument operating at 20.115 MHz. In both cases samples were dissolved in dimethyl-d_6 sulfoxide.

All manipulations were carried out in a fume hood whose environs were monitored routinely by the McMaster University Health Physics Group for radioactive contamination. All work involving ^{99}Tc was performed according to the regulations and recommendations of the Canadian Atomic Energy Control Board.

Collection of the X-ray Data. An acicular crystal, selected after examination under a polarizing microscope for homogeneity, was sealed to a glass fiber for X-ray examination. Precession photographs showed the crystal was orthorhombic, and unit cell parameters were obtained

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Table III. Selected Interatomic Distances (Å) and Angles (Deg)[a]

Tc-O(1)	2.214 (4)	Tc-N	2.209 (6)	Tc-S	2.296 (2)
Tc-O(3)	1.657 (4)	Tc-N(a)	2.185 (5)	Tc-S(a)	2.283 (2)
N-C(4)	1.497 (8)	C(4)-C(1)	1.541 (9)	C(1)-S	1.868 (7)
N(a)-C(4a)	1.478 (8)	C(4a)-C(1a)	1.563 (9)	C(1a)-S(a)	1.852 (5)
C(1)-C(2)	1.507 (10)	C(1)-C(3)	1.544 (10)	C(4)-C(5)	1.521 (9)
C(1a)-C(2a)	1.522 (10)	C(1a)-C(3a)	1.515 (9)	C(4a)-C(5a)	1.523 (9)
C(5)-O(1)	1.265 (7)	C(5)-O(2)	1.248 (7)		
C(5a)-O(1a)	1.289 (7)	C(5a)-O(2a)	1.220 (7)		
O(3)-Tc-S	106.2 (2)	O(3)-Tc-N	91.1 (2)	O(1)-Tc-S	82.9 (1)
O(3)-Tc-S(a)	107.0 (2)	O(3)-Tc-N(a)	99.1 (2)	O(1)-Tc-S(a)	92.1 (1)
O(1)-Tc-N	70.0 (2)	S-Tc-N	84.5 (2)	S-Tc-N(a)	154.7 (2)
O(1)-Tc-N(a)	72.9 (2)	S(a)-Tc-N(a)	83.3 (2)	S(a)-Tc-N	161.8 (2)
O(1)-Tc-O(3)	158.5 (2)	S-Tc-S(a)	90.55 (6)	N-Tc-N(a)	93.7 (2)
Tc-S-C(1)	100.8 (2)	S-C(1)-C(2)	109.7 (5)	S-C(1)-C(3)	107.5 (4)
Tc-S(a)-C(1a)	101.4 (2)	S(a)-C(1a)-C(2a)	108.5 (4)	S(a)-C(1a)-C(3a)	109.8 (4)
S-C(1)-C(4)	107.7 (4)	C(2)-C(1)-C(3)	109.6 (6)	C(2)-C(1)-C(4)	111.7 (5)
S(a)-C(1a)-C(4a)	103.7 (4)	C(2a)-C(1a)-C(3a)	110.0 (5)	C(2a)-C(1a)-C(4a)	109.7 (5)
C(3)-C(1)-C(4)	110.6 (6)	C(1)-C(4)-C(5)	112.0 (5)	C(1)-C(4)-N	109.1 (5)
C(3a)-C(1a)-C(4a)	114.8 (5)	C(1a)-C(4a)-C(5a)	113.2 (5)	C(1a)-C(4a)-N(a)	108.0 (5)
N-C(4)-C(5)	103.2 (5)	C(4)-N-Tc	104.1 (4)	C(4)-C(5)-O(2)	119.7 (5)
N(a)-C(4a)-C(5a)	113.7 (5)	C(4a)-N(a)-Tc	111.8 (4)	C(4a)-C(5a)-O(2a)	120.5 (5)
C(4)-C(5)-O(1)	115.9 (5)	O(2)-C(5)-O(1)	124.4 (6)	C(5)-O(1)-Tc	115.2 (4)
C(4a)-C(5a)-O(1a)	113.9 (5)	O(2a)-C(5a)-O(1a)	125.6 (6)		

[a] Possible hydrogen bonds (Å): O(2)-O(1a), 2.544 (6); O(2a)-N, 3.008 (7); O(2a)-N(a), 2.982 (7).

Table IV. ^1H and ^{13}C NMR Spectra of $C_{10}H_{19}N_2O_5S_2Tc$[a]

functional group	chem shift, ppm	
	^1H	^{13}C
$-CH_3$	1.44	24.32
	1.48	28.92
	1.71	30.10[b]
	1.84	
$-\overset{|}{\underset{|}{C}}-$		52.98[c]
		56.05[c]
$-\overset{|}{\underset{|}{C}}H$	3.19	66.94[c]
	3.55	71.77[c]
$-\underset{|}{N}H_2$	5.68[d]	
	6.52[d]	
$-COO^-$		171.87
		173.11

[a] Samples (0.09 M) were dissolved in Me_2SO-d_6. Chemical shifts are with respect to internal Me_4Si. [b] This resonance was approximately twice as intense as other peaks in the spectrum. [c] Assignments are based on an off-resonance spectrum. [d] Broad lines (no special precautions were taken to dry the solvent).

from a least-squares fit of χ, ϕ, and 2θ for 15 reflections in the range $17.3° < 2\theta < 25.2°$ recorded on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha_1$ radiation (λ 0.709 26 Å). Crystal data and other numbers related to data collection are summarized in Table I. The density was obtained by flotation in a carbon tetrachloride–bromoform mixture. Intensity data were also recorded on the Syntex $P2_1$ diffractometer using a coupled θ(crystal)–2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[9,10] Corrections were made for Lorentz–polarization effects but not for absorption. This will make a maximum error in F_0 of <1.5%.

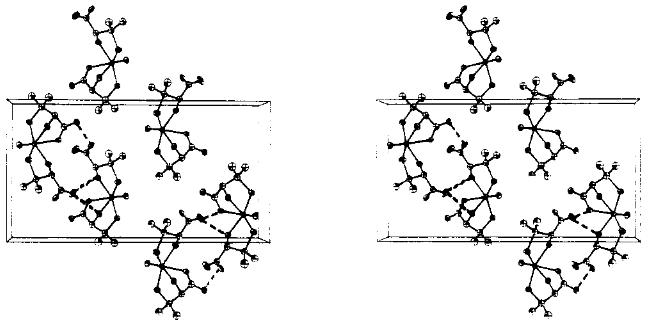

Figure 2. Packing of the molecules in the unit cell. The *a* and *b* axes are parallel to the bottom and side of the page, respectively, and the view is along *c*.

Solution of Structure. The acentric space group was chosen for structure solution because of the use of one enantiometer of a chiral ligand in preparing the compound. The choice is justified by the successful solution of the structure. The technetium atom was found from a three-dimensional Patterson synthesis, and a series of full-matrix least-squares refinements and electron density difference syntheses revealed all atoms. At this stage the temperature factors of the technetium, sulfur, nitrogen, and oxygen atoms were made sequentially anisotropic. Tests were made at each stage to show that the use of the increased parameters was justified.[11] Refinement using full-matrix least squares and minimizing $\sum w(|F_o| - |F_c|)^2$ was terminated when the maximum (average) shift/error was less than 0.13 (0.020) for nonhydrogen atoms and 0.26 (0.035) for all parameters. The residual indices were $R_1 = 0.0592$ and $R_2 = 0.0439$. The structure reported is consistent with the known chirality of the ligand. Nevertheless, the opposite chirality was tested by changing the signs of all positional parameters and refining until shift/error less than the above were achieved. The residual indices $R_1 = 0.0617$ and $R_2 = 0.0539$ indicate the reported structure is correct at the 99.5% confidence level.[11] Throughout, the scattering curves were taken from ref 12 and anomalous dispersion corrections from ref 13 were applied to the curves for all atoms. The positional parameters for nonhydrogen atoms are listed in Table II;[14] temperature factors and parameters for hydrogen atoms have been deposited.

Results and Discussion

The molecule is shown in Figure 1, and selected interatomic distances and angles are given in Table III. The structure comprises a distorted octahedron of ligand atoms about the technetium atom. There is a short Tc–O(oxo) bond (1.657 (4) Å), which is a characteristic feature of many Tc(V) and

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(13) Cromer, D. T. In ref 12; Table 2.3.1, pp 149–50.

(14) All calculations were carried out on CDC 6400 and Cyber 170–730 computers. Initial data treatment used the XRAY 76 package (Stewart, J. M. Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976). The structure was solved with SHELX (Sheldrick, G. M. Cambridge University, England, 1976). Diagrams were prepared with ORTEP II (Johnson, C. K. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976).

Table V. Vibrational Spectra (cm^{-1}) (Relative Intensities in Parentheses)

D-penicillamine		$C_{10}H_{18}N_2O_5S_2Tc$		
IR	Raman	IR	Raman (av of 3 spectra)	assignt
		3314 (44)		
		3244 (64)		$\nu(NH_2)$ asym
		3224 sh		
3162 (75)				$\nu(NH_3^+)$ asym
		3157 (21)		
		3135 sh		$\nu(NH_2)$ sym
3145 sh				$\nu(NH_3^+)$ sym
	3015 (19)			
	2980 (56)			
		2972 (25)		$\nu(CH_3)$ asym,
2958 (91)	2961 (27)			several components
2923 (90)	2929 (77)	2941 (17)		double
2903 sh	2902 (14)	2907 (5)		$\nu(CH) + 2 \times 1457$
2864 (33)	2862 (7)	2862 (11)		$\nu(CH_3)$ sym
2853 (32)				
2781 sh	2777 (4)			2×1397
2741 (24)				2×1373
2721 (22)				
2601 (11) br				
	2590 (10)			$\nu(S{-}H)$
2504 (8)	2511 (50) br			
2261 (5)				
2027 (30)				NH_3^+ comb band
		1677 (73) br		$\nu(C{=}O)$
1612 (38)	1626 (5) br			$\nu(CO_2^-)$ asym
1588 (98)	1596 (4) br	1589 (62)		$\delta(NH_3^+)$ asym (ligand),
1556 (38)				$\delta(NH_2^+)$(complex)
1518 (100)	1515 (7)			$\delta(NH_3^+)$ sym
1472 (11)	1471 (4)			
1457 (7)	1454 (21)	1457 (47)		$\delta(CH_3)$ asym
1437 (13)	1439 (21)	1437 (5)		
		1413 (72) br		$\nu(C{-}O)$
1397 (34)	1394 (19)			$\nu(CO_2^-)$ sym
1387 (15)	1386 (14)	1387 (22)		$\delta(CH_3)$ sym, in-phase,
1373 (12)		1372 (44)		and out-of-phase
1336 (25)	1336 (30)			$\delta(C{-}H)$
		1314 (14)		$\delta(C{-}H)$
		1303 (10)		
1278 (27)	1279 (6)			NH_3^+ twist
		1249 (20)		NH_2 twist
1208 (6)		1208 (16)		$\nu(C{-}N)$
1195 (28)	1192 (12)	1193 (10)		
1163 (33)	1159 (15)	1156 (18) br		CH_3 twists
1138 (8)				
	1119 (12) sh	1113 sh	1119 (10)	$\nu(C{-}C{-}N)$
1092 (38)	1090 (15)	1097 (34)		
1054 (43)	1052 (10)	1047 (33)		CH_3 wag
1012 (37)	1008 (9)	1002 (22)		$\nu(C{-}C)$
961 (33)	959 (24)	958 (100)	952 (100)	$\nu(Tc{=}O)$ complex
				NH_2 wag
	947 (16)	943 (26)		NH_2 wag
918 (24)	918 (24)	914 (32)		CH_3 rock
		896 (22)		NH_2 wag
885 (33)	883 (12)	883 (12)		$\nu(N{-}C{-}C)$
869 (54)	869 (23)			$\delta(SH)$
		824 (49)		NH_2 rock
754 (72)	754 (24)	763 (67)		CH_3 rock
		735		NH_2 rock
		724 (8)		
		709 (37)		$\delta(C{=}O)$
		698 (7)		$\pi(C{=}O)$
674 (37)	673 (26)			CO_2^- scissor
		609 (71)		
570 (67)	575 (33)			$\nu(C{-}S)$
		555 (39)		
540 (63)	546 (100)	489 (25)	491 (6)	$\delta(O{=}C{-}O)$
464 (54)	466 (6)	458 (42)		$\nu(Tc{-}N)$
		443 (29)	440 (11)	
405 (42)	402 (10)	412 (51)	406 (18)	$\delta(S{-}C{-}C{-}N)$
		384 (56)	386 (25)	$\nu(Tc{-}O)$
355 (25)	355 (24)	360 (33)		
321 (28) br	329 (11)	330 (5)		$\delta(C{-}C{-}S)$, CH_3 torsion
		293 (33)		$\nu(Tc{-}S)$
	281 (13)	286 (5)		
		272 (14)		

Table V (*Continued*)

D-penicillamine		$C_{10}H_{18}N_2O_5S_2Tc$		
IR	Raman	IR	Raman (av of 3 spectra)	assignt
246 (6)	252 (12)	249 (6)		
	208 (14)		208 w	δ(Tc-N)
	150 (37)			
	135 (13)		140 w	δ(S-Tc-S)
	114 (40)		114 (9)	
	100 (8)			

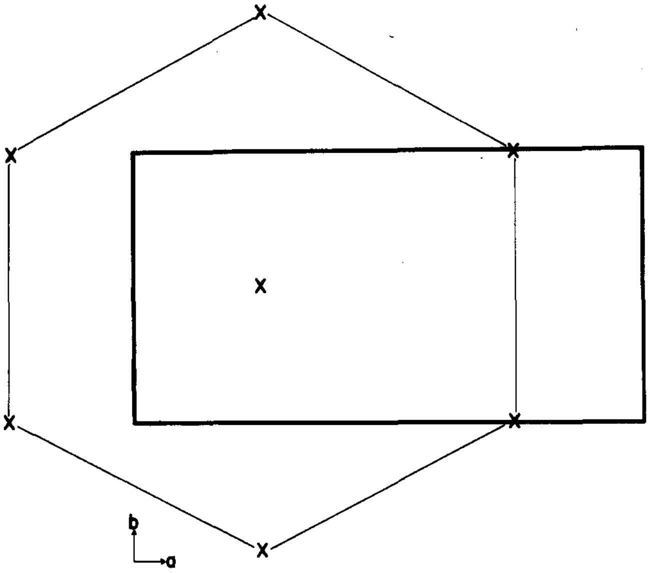

Figure 3. Arrangement of the spiral chains in the unit cell, showing the hexagonal net. × marks the spiral axis. The projection is the same as in Figure 2.

Re(V) complexes.[15,16] The S and N atoms of the two ligating D-penicillamine groups form a cis arrangement in the equatorial plane and are bent away from the oxo group in the usual manner. The reason the O(3)-Tc-N angle is smaller than O(3)-Tc-N(a) (91.1 (2) vs. 99.1 (2)°) appears to be because of the steric effects of the sixth coordinated oxygen atom O(1) of the ionized carboxylate group. Coordination angles involving this atom and other ligand atoms in the same D-penicillamine molecule are all smaller than between O(1) and corresponding atoms in the other D-penicillamine group (O(1)-Tc-S, 82.9 (1) vs. 92.1 (1)°; O(1)-Tc-N, 70.0 (2) vs. 72.9 (2)°). (The coordination of O(1) was unexpected and is at variance with a previous prediction of the structure of the D-penicillamine complex.[17]) The Tc-O(1) distance (2.214 (4) Å) is much longer than the Tc-O(3) distance but is comparable to the Tc-N distances and appears to indicate a relatively strong bond, in contrast to many bonds trans to an M═O group.[16,18] The reason for this argument is that the nonbonded O(1)···N, N(a), and O(1)···S distances (2.537 (7), 2.613 (6), 2.986 (4) Å) are generally considerably shorter than the sum of the van der Waals radii (2.90, 3.25 Å),[19] implying strong repulsion, which must be countered by strong bonding; and even O(1)···S(a) (3.238 (4) Å) is comparable to the O(3)···S distances and to the sum of radii. We have previously noted this effect when a coordinated oxygen atom is trans to an M═O group.[20]

The Tc-S distances are normal[15] as are most of the bond lengths and angles within the D-penicillamine molecule.[21,22] Angles in the bound ligands involving the coordinated atoms differ slightly from those in a free ligand,[21,22] and M-S-C(1), M-S(a)-C(1a), M-N-C(4), M-N(a)-C(4a), and M-O(1)-C(5) are all 2-3° bigger than corresponding angles in a cobalt complex (M = Tc or Co).[23,24] The Tc—N bonds (2.185 (5), 2.209 (6) Å) are longer than normal (range 2.07-2.16 Å)[25-27] and close to the value obtained for Tc—N trans to Tc═O (2.259 (4) Å),[26] where a structural trans effect is known to occur.[16] There is no such structural effect present here, and yet, as noted above, the Tc—N bonds are as long as Tc—O(1), which is trans to Tc═O. The lengthening of Tc—N must be caused by the steric interactions mentioned above.

The packing of the molecule within the unit cell is shown in Figure 2. The most important feature of the packing is a very strong hydrogen bond between O(2) of one molecule and O(1a) of a molecule related by the 2_1 axis at $^1/_4$, $^1/_2$, 0. The molecules thus form a spiral up the *c* direction. There are further, weaker hydrogen bonds between pairs of molecules in this spiral (O(2a)···N(a), 2.982 (7) Å; O(2a)···N, 3.008 (7) Å). Between spirals the interactions are solely van der Waals, and as a result the spirals pack in a hexagonal net, as shown in Figure 3. The electronic spectrum is shown in Figure 4 for reference purposes since Kramer[28] has suggested that the color of technetium complexes is very dependent on whether the pairs of N and S atoms in the equatorial planes are mutually cis or mutually trans.

The ^1H and ^{13}C NMR spectra of the complex are presented in Table IV. The resonances occur in the regions expected for each of the functional groups.[29,30] Because each region contains pairs of peaks, the solid-state structure appears to persist in solution. The doubling of the signals is shown schematically in Figure 5 for the ^{13}C NMR spectrum of $C_{10}H_{19}N_2O_5S_2Tc$. The ^{13}C NMR spectrum of a cobalt(III) complex in which penicillamine is N,S bonded to the metal is included for comparison.[31] There is no clear-cut correlation between these two spectra, so assignment of individual peaks to the tri- or bidentate D-penicillamine moieties was not at-

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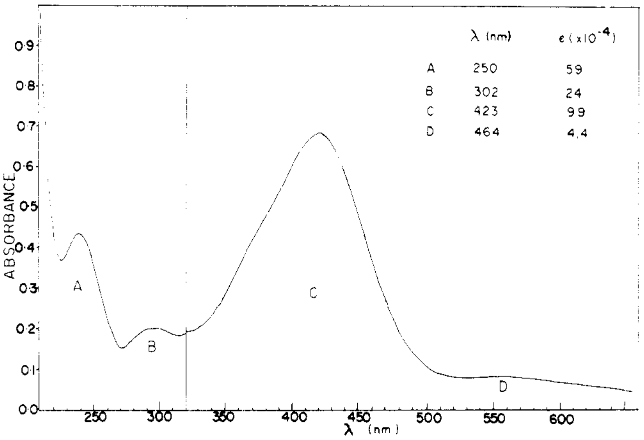

Figure 4. Electronic spectrum of $TcO(C_5H_{10}NO_2S)(C_5H_9NO_2S)$.

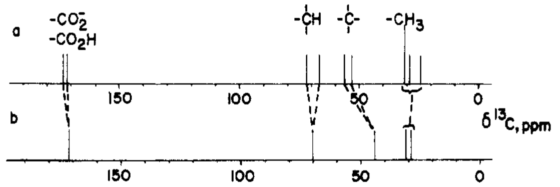

Figure 5. ^{13}C NMR spectra of (a) $C_{10}H_{19}N_2O_5S_2Tc$ and (b) $C_9H_{18}N_5O_2SCo$.

tempted. It is interesting to note that signals from the two carboxylate carbon atoms in the technetium complex are so close to each other.

The vibrational spectra of the technetium complex and D-penicillamine are given in Table V. Some assignments of the bands have been attempted based on comparisons with previous work[32-34] and the arguments contained herein.

The D-penicillamine ligand exhibits a typical Zwitterion spectrum in the infrared; that is, it has the vibrations of both an ionized carboxyl group (CO_2^-) and an amine salt (NH_3^+). The NH_3^+ asymmetric and symmetric stretching vibtations give rise to a broad, strong band over the range 3200–2400 cm^{-1}. There are several peaks on the low-frequency wing, which continues to 2200 cm^{-1}, and a prominent, isolated band at 2027 cm^{-1} (a combination band produced by NH_3^+ motions).

The NH_3^+ deformations are assigned as 1588 (asymmetric) and 1518 cm^{-1} (symmetric) (typical ranges 1665–1585 and 1530–1490 cm^{-1}). The CO_2 stretches are assigned as 1612 (asymmetric) and 1397 cm^{-1} (symmetric) (typical ranges 1605–1555 cm^{-1} and 1425–1393 cm^{-1}). The C–H and CH_3 vibrations occur virtually unshifted for both ligand and complex and fall in characteristic regions: the C–H deformation occurs at 1336 cm^{-1} (typical range 1340–1315 cm^{-1}). The bands at 1387 and 1373 cm^{-1} result from the in-phase and out-of-phase interaction of the symmetric deformations of the CH_3 group; the bands at 1457 and 1437 cm^{-1} result from the asymmetric deformations. CH_3 group twists, wags, and rocks are assigned to bands that follow the usual order of frequency and for which wags show greater intensity than twists. The NH_3^+ group (ligand) and NH_2 group (complex) twists, wags, and rocks fall in similar order.

The ligand can coordinate to a metal via the N, S, and O sites, and the Tc complex contains one ligand coordinated at all three sites and one ligand coordinated through N and S only. Neither retains the Zwitterion form.

The spectra of the Tc complex are therefore expected to show several major differences from those of the ligand: (1) presence of pairs of Tc—S, Tc—N, and single Tc=O, Tc—O stretching and deformation vibrations, (2) presence of two types of CO_2 group vibrations—carboxylic acid in one ligand and coordinated CO_2 groups of the other, (3) absence of S—H vibrations, and (4) absence of Zwitterion spectra and presence of NH_2 group vibrations.

In addition we may expect a general doubling of the other vibrations in the complex because of the presence of two ligands and some frequency shifting of vibrations in the complex.

(1) The region 760–300 cm^{-1} of both spectra contain several bands: some unique to the ligand, others unique to the complex. The C–S, Tc–S, Tc–O, and Tc–N stretches and the CO_2 deformations are all expected to fall in this region, and obviously there will be ambiguities; thus although we can make reasonable tentative assignments for these bands, positive assignments are not possible. The Tc=O stretch is assigned as the very intense 958-cm^{-1} band and happens to fall near the NH_2 wag (and NH_3^+ wag of the ligand). The Tc–N stretches are tentatively assigned as 458 and 443 cm^{-1}. The Tc–S stretch is assigned as the 293–286-cm^{-1} doublet.

(2) Two CO stretches are assigned for the complex. Only the C–O bond lengths of the carboxylic acid ligand are significantly different, and hence the C–O band may appear broadened rather than split. The CO_2 deformations are assigned at 709 and 698 (complex) and 674, 540, and 464 cm^{-1} (CO_2^- scissor, wag and rock, ligand). The 540-cm^{-1} band is broad and intense and could contain two components.

(3) The S–H stretching vibration occurs at 2511 cm^{-1} and the deformation at 869 cm^{-1} (for the ligand only); these bands are absent for the complex, as expected.

(4) The complex shows the presence of NH_2 vibrations, and the Zwitterion spectrum is absent, as expected.

Groups containing S tend to have bands that are more intense in the Raman than in the infrared region. Comparison with other thiols suggests that ν(C–S) should occur close to 585 cm^{-1} (similar to 2-methyl-2-propanethiol and *tert*-butyl sulfides). The bands at 570 and 540 cm^{-1} (ligand) and 609 and 555 cm^{-1} (complex) are likely candidates for ν(C–S). The C–S bond lengths are similar, and we do not expect a large ligand–complex frequency shift.

Metal–sulfur complexes exhibit bands in the range 250–360 cm^{-1} (ν(M–S)) and also one or two bands in the range 586–654; the origin of the latter is uncertain although they have the magnitude of ν(M–S) overtones and could result from Fermi resonance between such overtones and ν(C–S) modes. Also the ligand may show to ν(C–S) bands because of rotational isomerism. Deformations of the S–M–S unit occur at 145–155 cm^{-1}.

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Registry No. $TcO(C_5H_{10}NO_2S)(C_5H_9NO_2S)$, 80572-91-4; $(NH_4)(TcOCl_4)$, 80572-90-3; D-penicillamine, 52-67-5.

Supplementary Material Available: Listings of temperature factors for nonhydrogen atoms, hydrogen atom parameters, and structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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