Synthesis and Structure of Oxo(2-(1′-methyl-1′-mercaptoethyl)-3-(5″-methyl-5″-mercapto-3″-(dehydroaza)hexyl)thiazolidinato-N^3,$N^{3''}$,$S^{1'}$,$S^{5''}$)technetium(V), $TcO(C_{12}H_{23}N_2S_3)$: Unusual Formation of a Thiazolidine Ring

Hosen Alarabi, Russell A. Bell, Romolo Faggiani, Helen E. Howard-Lock, Colin J. L. Lock,* and Alfred V. Kramer[1]

Laboratories for Inorganic Medicine, Departments of Chemistry and Pathology, McMaster University, ABB-266A, Hamilton, Ontario L8S 4M1, Canada

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Others had attempted to synthesize the ligand *N*-(2-mercaptoethyl)-*N*,*N*′-bis(2-methyl-2-mercaptopropyl)-ethylenediamine and react the ligand with pertechnetate and a reducing agent. We showed that the product was the unexpected complex oxo(2-(1′-methyl-1′-mercaptoethyl)-3-(5″-methyl-5″-mercapto-3″-(dehydroaza)hexyl)-thiazolidinato-N^3,$N^{3''}$,$S^{1'}$,$S^{5''}$)technetium(V), $C_{12}H_{23}N_2OS_3Tc$, **1**. Crystals of **1** were orthorhombic, $P2_12_12_1$, with $a = 7.679(2)$ Å, $b = 11.993(4)$ Å, $c = 18.268(4)$ Å, and $Z = 4$ ($R = 0.053$ and $R_w = 0.043$ for 2841 independent reflections with $I > 0$). The complex had the usual square pyramidal structure associated with the $TcON_2S_2$ core with a Tc=O bond length of 1.665(5) Å. It was established that the synthesis was much more complicated than expected and, as a consequence, rather than the expected intermediate 3,3,10,10-tetramethyl-1,2-dithia-5,8-diazocyclodecane, **6**, 2,2,5,5-tetramethyl-3,4-dithia-7,10-diazabicyclo[5.3.0]decane, **5**, was obtained. Reaction of **5** with ethylene sulfide gave the thiazolidine-containing ligand 2,2,5,5-tetramethyl-3,4,13-trithia-7,10-diazabicyclo[8.3.0]tridecane as the hydrochloride salt, **7**, and the dimeric species 10,10′-(3,4-dithiahexane-1,6-diyl)bis(2,2,5,5-tetramethyl-3,4-dithia-7,10-diazabicyclo[5.3.0]decane), **8**. Crystals of **7**, $C_{12}H_{25}ClN_2S_3$, were triclinic, $P\bar{1}$, with $a = 6.921(2)$ Å, $b = 9.650(2)$ Å, $c = 13.712(2)$ Å, $\alpha = 106.88(2)°$, $\beta = 101.04(2)°$, $\gamma = 97.93(2)°$, and $Z = 2$ ($R = 0.095$ and $R_w = 0.068$ based on 2222 independent reflections). Bond lengths and angles were normal.

Introduction

We have undertaken a series of chemical and structural studies of the TcO^{3+} core attached to chelating ligands bound through N, O, or S atoms. In most cases a square pyramidal geometry was obtained; there was an axial oxo group, and atoms from the chelating ligands formed the base.[2−4] With D-penicillamine as a ligand, a six-coordinate species was obtained with a distorted octahedral geometry,[5] and a similar geometry was obtained with mixed *o*-phenanthroline, 1,2-ethylenediolato, chloro, and oxo ligands.[6]

Nitrogen atoms of ligands derived from 3,6-diazaoctane-1,8-dithiol are fairly reactive, and this led Kramer *et al.* to attempt to synthesize the ligand **2** (Chart 1), with five possible coordination sites.[7] It was hoped that a complex of type **3** would be obtained by reaction with the TcO^{3+} core, although our experience with this type of compound shows that exocyclic groups attached to the nitrogen atoms always point in the same direction as the oxygen atom and thus are in the wrong position to interact with any site trans to the oxygen atoms.[8] Subsequently a technetium compound was prepared and we determined the structure of this complex by single crystal X-ray diffraction. Much to our surprise, the expected product was not obtained; instead the additional mercaptoethyl group was joined to a carbon atom proximal to the nitrogen atom to give a thiazolidine ring. The ligand yielded a normal, square pyramidal, technetium complex, **1**. As a result we have attempted to repeat the synthesis of the thiazolidine-containing ligand and characterize it fully, in order to explain how it was formed. This work is described here.

Experimental Section

^{99}Tc is a weak β-emitter with a long half-life and has potential radiotoxicity, so all work that involved ^{99}Tc was performed according to the regulations and recommendations of the Canadian Atomic Energy Control Board. Transfers of radioactive materials, syntheses, and glassware washing were carried out in a fume hood with a high flow rate, and all samples for spectroscopic examination or X-ray crystallography were handled in sealed containers. All contaminated waste was sealed in appropriate containers and transferred to the McMaster Nuclear Reactor building for disposal.

Melting points were determined with a Gallenkamp apparatus and reported with no correction. Chemical ionization (CI) and electron impact (EI) mass spectra were determined with a VG Analytical ZAB-E spectrometer. Typical experimental conditions include the following: electron energy 70 eV; source temperature 200 °C; source pressure 2 × 10^{-6} mbar for EI and 4 × 10^{-5} mbar for CI. The IR spectra of samples as KBr pellets or Nujol mulls mounted between KBr plates were recorded with Perkin-Elmer 283 or BioRad FTS-40 spectrometers. For Raman spectroscopy crystalline samples were sealed in glass tubes and mounted on the stage of a microscope (80×). Spectra were excited

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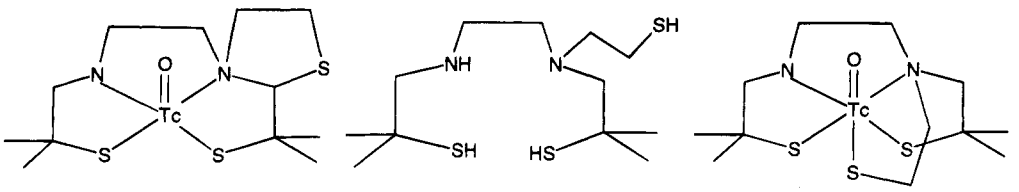
Chart 1



1 2 3

Table 1. Crystal Data

compd	$C_{12}H_{23}N_2OS_3Tc$, **1**	$C_{12}H_{25}ClN_2S_3$, **7**
fw	406.4	329.0
cryst color, habit	orange needle	colorless needle
size (mm)	0.10 × 0.13 × 0.30	0.15 × 0.20 × 0.40
systematic abs	$h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$	none
cryst system, space group	orthorhombic, $P2_12_12_1$	triclinic, $P\bar{1}$
unit cell (Å and deg)	$a = 7.679(2)$ $b = 11.993(4)$ $c = 18.268(4)$	$a = 6.921(2)$ $b = 9.650(2)$ $c = 13.712(2)$ $\alpha = 106.88(2)$ $\beta = 101.04(2)$ $\gamma = 97.93(2)$
V (Å^3)	1682.4(7)	841.7(3)
Z	4	2
d(calc) (g cm^{-3})	1.604	1.298
T (K)	295	296
abs coeff (mm^{-1})	1.185	0.586
abs corr	analyt,[a] $A^*_{min} = 1.10$, $A^*_{max} = 1.20$	DIFABS,[b] $corr_{min} = 0.83$, $corr_{max} = 1.16$
standard reflcns (esd)	102 (0.011), $0\bar{5}6$ (0.014)	−103 (0.014), $1\bar{1}1$ (0.014), 222 (0.017)
max 2θ (deg)	50	45
reflcns measd	$-8 \le h \le 9$, $0 \le k \le 14$, $0 \le l \le 21$	$0 \le h \le 7$, $-10 \le k \le 10$, $-14 \le l \le 14$
no. of reflcns measd	3390	2443
no. of unique reflcns	2841	2222
R_{int}	0.0201	0.0359
no. of reflcns, $I > 0$, used	2841	2222
F(000)	832	352
final R, R_w[e]	0.0533, 0.0425	0.0948, 0.0676
final Δ/σ max, av	0.114, 0.020	0.001, 0.000
final diff map: max, min (e Å^{-3})	0.87, −0.82	0.60, −0.54
no. of variables	173	264
secondary extinction, x	−0.00025	−0.0005
wtg function	$w^{-1} = \sigma_F^2 + 0.000336F^2$	$w^{-1} = \sigma_F^2 + 0.0009F^2$
goodness of fit	1.06	1.08
data-to-param ratio	16.4:1	8.4:1
diffractometer	Nicolet $P2_1$	Siemens P4, rotating anode
radiation	Mo Kα, $\lambda = 0.710\,73$ Å	Mo Kα, $\lambda = 0.710\,73$ Å
scan type	$\theta-2\theta$	$\theta-2\theta$
scan range	1° each side of Kα	0.6° each side of Kα
program package used	SHELX[c]	SHELXTL PC[d]
quantity minimized	$\sum w(\|F_o\| - \|F_c\|)^2$	$\sum w(\|F_o\| - \|F_c\|)^2$
absolute structure	yes, Hamilton test	not applicable
H atoms	included and refined	calculated position, riding on attached atom

[a] Siemens R3m/V Crystallographic Research System, Siemens Analytical X-ray Instruments, Madison, WI, 1989. [b] Walker, N.; Stewart, D. *Acta Crystallogr.* **1983**, *A39*, 158. [c] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. [d] Sheldrick, G. M. SHELXTL-PC. Siemens Analytical X-ray Instruments, Madison, WI, 1992. [e] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; $S = [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$.

with 60 mW of radiation from the 514.5 nm line of a Spectra Physics 2016 argon laser or 90 mW of radiation from the 647.1 nm line from a Lexel 3500 krypton laser and recorded with a Mole S 3000 spectrometer. NMR spectra were recorded with Bruker AM-500 and AC-200 spectrometers. Deuteriochloroform (99.8% D) was used as a solvent and reference for ^{13}C spectra, and tetramethylsilane or deuteriochloroform was used as an internal reference for ^1H spectra. Columns used for separation throughout this work were 8 mm diameter by 25 cm long and were filled with Fisher Scientific chromatographic silica gel, 100−200 mesh. Single crystal X-ray diffraction studies were conducted for **1** and **7**. Single crystals were selected by microscopic examination and sealed in a silica tube (**1**) or mounted on a glass fiber (**7**). Intensity measurements for **1** were made on a Nicolet P2 diffractometer, and those for **7**, on a Siemens P4 diffractometer with a rotating anode. Both diffractometers were fitted with graphite monochromators. Data were measured with $\theta-2\theta$ scans. Details of data acquisition and treatment are given in Table 1. For **1** only reflections with $I > 0$ were used in the structure solution, but for **7** the data were treated by the method of French and Wilson[9] and all independent reflections were used in the determination. The absolute configuration of **1** was determined by Hamilton's test.[10] The parameters for the alternative refinement were $R = 0.0537$, $R_w = 0.0458$, and $S = 1.070$. Scattering curves were taken from ref 11. Atomic coordinates and isotropic temperature factors for **1** and **7** are given in Tables 2 and 3.

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Table 2. Atomic Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$) for $C_{12}H_{23}N_2OS_3Tc$, **1**

atom	*x*	*y*	*z*	U_{eq}[a]
Tc	1886(1)	5973.3(5)	8759.0(3)	30.3
O	1528(7)	5309(5)	7976(3)	54
S(1)	511(2)	7683(2)	8842(1)	41
C(1)	1945(12)	8530(6)	8233(4)	40
C(2)	3788(9)	8235(6)	8481(4)	30
N(1)	4173(7)	7020(5)	8510(3)	31
C(3)	5511(10)	6785(7)	9103(4)	41
C(4)	5428(10)	5563(7)	9278(5)	55
N(2)	3594(7)	5275(6)	9363(4)	43
C(5)	3195(12)	4572(6)	9996(4)	48
C(6)	1345(9)	4113(7)	9952(4)	40
S(2)	23(2)	5302(2)	9623(1)	42
C(11)	1469(11)	8246(8)	7420(5)	60
C(12)	1570(12)	9771(7)	8394(5)	57
S(3)	5523(3)	8867(2)	7925(1)	53
C(21)	6258(12)	7555(8)	7556(4)	53
C(22)	4922(10)	6687(6)	7777(4)	43
C(61)	692(13)	3727(8)	10696(4)	56
C(62)	1208(13)	3163(7)	9408(5)	65

[a] U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $C_{12}H_{25}ClN_2S_3$, **7**

	x	*y*	*z*	U_{eq}
S(1)	6793(2)	4066(2)	4162(1)	49(1)
S(2)	4672(2)	2378(2)	3056(1)	49(1)
S(3)	10101(3)	7157(2)	2844(1)	59(1)
N(1)	8552(6)	4229(4)	2050(3)	35(2)
N(2)	7337(6)	1137(5)	1432(3)	41(2)
C(1)	7323(8)	5593(5)	3605(4)	37(2)
C(2)	9045(8)	5387(5)	3053(4)	36(2)
C(3)	10085(8)	3346(6)	1910(4)	47(2)
C(4)	9159(8)	1789(6)	1161(5)	52(3)
C(5)	7693(8)	929(6)	2476(4)	46(2)
C(6)	5776(9)	721(6)	2846(4)	48(3)
C(11)	8029(9)	6916(6)	4618(5)	56(3)
C(12)	5396(8)	5716(6)	2905(5)	55(3)
C(21)	9704(10)	6258(7)	1458(5)	62(3)
C(22)	8116(9)	4863(6)	1203(4)	54(3)
C(61)	6312(11)	389(7)	3881(5)	76(4)
C(62)	4116(9)	−499(6)	2044(5)	63(3)
Cl	6457(2)	−1978(2)	−129(1)	56(1)

[a] U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

2,2′-Dithiobis(2-methylpropanal). This compound was prepared as described previously.[12] Yield: 85%. ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 12H, 2 × $C(CH_3)_2$), 9.09 (s, 2H, CHO). EIMS: *m/z* 206 (20, $M^{\bullet+}$), 177 (26, $M^{\bullet+}$ − HC=O•), 149 ($M^{\bullet+}$ − $HCOCHCH_3$), 113 (12), 107 (40), 72 (100, $HCOCH(CH_3)_2^{\bullet+}$), 71 (86, $HCOC(CH_3)_2^+$).

3,3,10,10-Tetramethyl-1,2-dithia-5,8-diazacyclodeca-4,8-diene, 4. This compound was prepared according to the reported procedure[12] with a slight modification. To a solution of the dialdehyde (10.00 g, 0.048 mol) in heptane (400 mL) were added ethylenediamine (3.2 mL, 0.048 mol) and *p*-toluenesulfonic acid (0.20 g). The mixture was heated gently to boiling for 2 h. It was then concentrated *in vacuo*, and the residue was collected by filtration. The product was first washed with cold heptane (20 mL) and then with water (50 mL). Finally, it was recrystallized from ethyl acetate. Yield: 8.37 g, 75%. Mp: 162−164 °C, lit. mp 162 °C.[12] IR: 1655 cm^{-1}, $\nu_{C=N}$. CIMS: *m/z* 231 (100, $M^{\bullet+}$ + 1). EIMS: *m/z* 231 (6, $M^{\bullet+}$ + 1), 166 (44, $M^{\bullet+}$ − S_2), 156 (39, $M^{\bullet+}$ − $SC(CH_3)_2$), 151 (20, 166 − CH3), 98 (44), 84 (100, $C_4H_8N_2^+$), 82 (99, $C_4H_6N_2^+$), 68 (57). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 6H, 2 × CH_3), 1.41 (s, 6H, 2 × CH_3), 3.20 (d, 2H, ^2J = 6.40 Hz, H_{6A}, H_{7A}), 4.12 (d, 2H, ^2J = 6.15 Hz, H_{6B}, H_{7B}), 6.825 (s, 2H, H_4, H_9). ^{13}C NMR: δ 21.24 (2 × CH_3), 24.41 (2 × CH_3), 52.73 (C_3, C_{10}), 61.17 (C_6, C_7), 167.56 (C_4, C_9).

2,2,5,5-Tetramethyl-3,4-dithia-7,10-diazabicyclo[5.3.0]decane, 5, and 3,3,10,10-Tetramethyl-1,2-dithia-5,8-diazacyclodecane, 6. The reduction of **4** was carried out according to the procedure reported by Joshua *et al.*,[13] with slight modifications. To a suspension of the diimine **4** (2.02 g, 8.78 mmol) in absolute ethanol (50 mL) was added sodium borohydride (2.00 g, 52.6 mmol). The mixture was stirred at 25 °C for 24 h and then concentrated *in vacuo*. The residue was partitioned between water (50 mL) and methylene chloride (50 mL). The aqueous layer was washed with methylene chloride (3 × 10 mL). The combined organic extracts were washed with water (15 mL), dried over sodium sulfate, and concentrated *in vacuo*. The residue was chromatographed on silica gel. Elution with methylene chloride−methanol (95:5) gave 2,2,5,5-tetramethyl-3,4-dithia-7,10-diazabicyclo[5.3.0]decane, **5**. Yield: 1.18 g, 58%. TLC: R_f = 0.6, 80:20 CH_2Cl_2:CH_3OH; Mp: 66−67 °C, lit. mp 65 °C.[13] IR (KBr): 3298 cm^{-1}, ν_{N-H}. CIMS: 233 (2, $M^{\bullet+}$ + 1), 158 (20, $M^{\bullet+}$ − $SC(CH_3)_2$), 143 (3, 158 − CH_3), 125 (47, 158 − SH), 84 (100, $M^{\bullet+}$ − $(SC(CH_3)_2)_2$, $C_4H_8N_2^+$), 69 (24), 55 (22). ^{1}H NMR: δ 1.23 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 2.27 (s, 1H, exchangeable N−H), 2.61 (d, 1H, ^2J = 14.9 Hz, H_{6A}), 2.76 (t, 1H, J = 7.8 Hz, H_{8A}), 2.98 (m, 2H, H_{9A}, H_{9B}), 3.24 (m, 2H, H_{6B}, H_{8B}), 3.55 (s, 1H, H_1). ^{13}C NMR ($CDCl_3$): δ 18.56 (CH_3), 24.65 (CH_3), 26.59 (CH_3), 28.37 (CH_3), 66.37 (C_6), 51.90 (C_5), 53.01 (C_2), 46.29 (C_9), 58.34 (C_8), 91.34 (C_1). A second elution with methylene chloride−methanol−ammonium hydroxide (5:4:1) gave 3,3,-10,10-tetramethyl-1,2-dithia-5,8-diazacyclodecane, **6**. Yield: 0.72 g, 35%. TLC: R_f 0.01, CH_2Cl_2:CH_3OH (80:20). Mp: 56−58 °C. IR (KBr): 3290 cm^{-1}, ν_{N-H}. EIMS: 234 (21, $M^{\bullet+}$), 169 (6, M^+ − S_2H), 158 (100, M^+ − $HSCH(CH_3)_2$), 143 (8, 158 − CH_3), 125 (60, 158 − SH), 84 (70, $C_4H_8N_2^+$). ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 6H, 2 × CH_3), 1.35 (s, 6H, 2 × CH_3), 1.96 (s, 2H, 2 exchangeable NH protons), 2.54 (d, 2H, ^2J = 12.45 Hz, H_{4A}, H_{9A}), 2.78 (s, 4H, H_{6A}, H_{6B}, H_{7A}, H_{7B}), 2.98 (d, ^2J = 12.45 Hz, H_{4B}, H_{9B}). ^{13}C NMR ($CDCl_3$): δ 25.87 (2 × CH_3), 28.31 (2 × CH_3), 46.53 (C_6, C_7), 51.69 (C_3, C_{10}), 58.60 (C_4, C_9).

2,2,5,5-Tetramethyl-3,4,13-trithia-7,10-diazabicyclo[8.3.0]-tridecane Hydrochloride, 7, and 10,10′-(3,4-dithiahexane-1,6-diyl)-bis(2,2,5,5-tetramethyl-3,4-dithia-7,10-diazabicyclo[5.3.0]decane), 8. A solution of ethylene sulfide (0.39 mL, 6.47 mmol) in methylene chloride (5 mL) was added slowly to a solution of **5** (1.00 g, 4.31 mmol) in methylene chloride (10 mL). The mixture was stirred at 25 °C for 6 days under a nitrogen atmosphere. The mixture was then chromatographed on silica gel. Elution with methylene chloride−methanol (90:10) gave unreacted **5** (0.20 g, 20%), then product **7** (Yield: 0.47 g, 37%. Mp: 191−193 °C dec. EIMS: *m/z* 292 (18, $M^{\bullet+}$), 227 (8, M^+ − S_2H), 218 (89, M^+ − $SC(CH_3)_2$), 185 (40, M^+ − $(CH_3)_2CSSH$), 158 (14, M^+ − $(CH_3)_2CSSCHCH_3$)), 144 (54, M^+ − $(CH_3)_2CSSC(CH_3)_2$), 131 (100, M^+ − $SC(CH_3)_2CHSCH_2CH_2N$), 116 (47, $SC(CH_3)_2CH_2NCH_2^+$), 98 (49), 84 (35, $C_4H_8N_2^+$), 70 (22, $C(CH_3)CH_2N^+$). CIMS: 293 (100, $M^{\bullet+}$ + 1), 261 (8, M^+ + 1 − S), 259 (6, M^+ − SH), 233 (42, M^+ + 1 − CH_2CH_2S), 218 (20, M^+ − $SC(CH_3)_2$), 201 (7, M^+ − $S_2C(CH_3)$), 185 (11, M^+ − $HSSC(CH_3)_2$), 159 (9, M^+ − $(CH_3)_2CSSCCH_3$), 144 (11, M^+ − $(CH_3)_2CSSC(CH_3)_2$), 125 (8, 159 − SH_2). IR (KBr): 3390 ν_{N-H}. ^{1}H NMR ($CDCl_3$): δ (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 2.20 (d, 1H, ^2J = 11.35 Hz, H_{6A}), 2.44−3.23 (complex poorly resolved multiplet, 8H), 3.03 (d, 1H, ^2J = 11.34 Hz, H_{6B}); 3.50 (s, 1H, H_1). ^{13}C NMR ($CDCl_3$): δ 21.77 (CH_3), 24.40 (CH_3), 28.07 (CH_3), 30.24 (CH_3), 30.94 (C_{12}), 45.27 (C_8), 49.87 (C_9), 51.72 (C_5), 52.90 (C_2), 55.12 (C_{11}), 57.72 (C_6), 90.79 (C_1)), and finally the dimer **8** (Yield: 0.63 g, 25%. Mp: 97−100 °C. DCIMS: 583 (6, $M^{\bullet+}$ + 1), 293 (100; $^1/_2M^+$ + 2), 259 (49, $^1/_2M^+$ − S), 218 (18), 185 (6). DEIMS: no parent ion peak was observed, 83 (100, $C_4H_7N_2^+$). ^{1}H NMR ($CDCl_3$): δ 1.21 (s, 6H, 2 × CH_3), 1.26 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 2.85 (broad, poorly resolved multiplet, 10H), 3.50 (s, 1H, H_1). ^{13}C NMR: δ 19.15 (CH_3), 24.51 (CH_3), 26.67 (CH_3), 28.37 (CH_3), 39.04 (C_{12}), 52.09 (C_{11}), 53.11 (C_2,C_5), 54.28 (C_9), 57.79 (C_8), 66.39 (C_6), 98.90, (C_1). IR: no absorption in the 3000−3500 cm^{-1} region, ν_{N-H}.[14] Raman: no emission in the 2560−2580 cm^{-1}

(12) Kung, H. F.; Molnar, M.; Billings, J.; Wicks, R.; Blau, M. *J. Nucl. Med.* **1984**, *25*, 326.

(13) Joshua, A. V.; Scott, J. R.; Smith, S. M.; Ball, R. G.; Lown, W. J. *J. Org. Chem.* **1987**, *52*, 2447.

(14) Nakamoto, K. *Infrared and Raman spectra of inorganic and coordination compounds*, 3rd. ed.; Wiley-Interscience: New York, 1978; p 436.

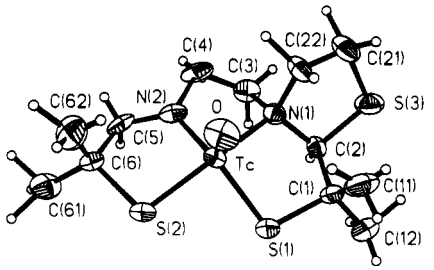


Figure 1. Technetium complex **1**, showing the atom numbering.

region from the exciting line, no ν_{S-H}[15]). Single crystals of **7** were obtained by the slow evaporation (at −15 °C) of a 50:50 methylene chloride and tetrahydrofuran solution. A satisfactory X-ray structure solution could only be achieved if it were assumed that the crystals were those of the chloride salt of **7**. Methylene chloride, which was used as a solvent in both the reaction and growing crystals, is believed to be the source of hydrochloric acid. The presence of chlorine in the crystal used for the X-ray structure determination was confirmed by X-ray energy dispersion analysis with use of a scanning electron microscope.

Oxo(2-(1′-methyl-1′-mercaptoethyl)-3-(5″-methyl-5″-mercapto-3″-(dehydroaza)hexyl)thiazolidinato-N^3,$N^{3''}$,$S^{1'}$,$S^{5''}$)technetium(V), 1. A solution of $Na_2S_2O_4$ (0.226 g, 1.3 mmol) in 2 N NaOH (8 mL) was added to a stirred solution containing NH_4TcO_4 (0.180 g, 1.0 mmol, Oak Ridge National Laboratories) and **7** (0.394 g, 1.2 mmol) in 3:1 water/ethanol (25 mL). The reaction mixture was stirred at room temperature for 3 h and then allowed to evaporate slowly overnight. The resulting yellow brown needles were removed by filtration, washed with petroleum ether, and air dried. Additional product was obtained by extraction of the filtrate with an equal volume of $CHCl_3$. The organic layer was washed with water (2 × 40 mL) and separated and dried over anhydrous sodium sulfate. Trituration with petroleum ether (100 mL) yielded additional product which was collected by filtration, washed with petroleum ether, and air dried. The products were combined and recrystallized by slow evaporation from 2:1 acetonitrile/water (30 mL). The yield of orange crystals, based on technetium, was 0.314 g, 70%. ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 2.09 (m, 1H, $^4J_{H_{3A}H_{22B}}$ = 1.8 Hz, $^3J_{H_{3A}H_{4A}}$ = 5.8 Hz, $^3J_{H_{3A}H_{4B}}$ = 11.7 Hz, $^2J_{H_{3A}H_{3B}}$ = 11.7 Hz, H_{3A}), 3.22 (m, 1H, $^3J_{H_{3B}H_{4A}}$ = 1.3 Hz, $^3J_{H_{3B}H_{4B}}$ = 4.1 Hz, $^2J_{H_{3B}H_{3A}}$ = 11.8 Hz, H_{3B}), 3.35 (m, 1H, $^2J_{H_{4A}H_{4B}}$ = 13.2 Hz, H_{4A}), 3.39 (m, 1H, H_{21A}), 3.40 (m, 1H, H_{21B}), 3.81 (d, 1H, $^2J_{H_{5A}H_{5B}}$ = 11.5 Hz, H_{5A}), 3.92 (d, 1H, $^2J_{H_{5B}H_{5A}}$ = 11.4 Hz, H_{5B}), 3.95 (s, 1H, H_2), 3.97 (m, 1H_{22B}), 4.32 (m, 1H, H_{4B}), 4.33 (m, 1H, H_{22A}). ^{13}C NMR ($CDCl_3$): δ 26.26 (CH_3), 27.98 (CH_3), 30.20 (CH_3), 30.91 (CH_3), 30.91 (C_{21}), 56.44 (C_6), 57.65 (C_1), 58.04 (C_{22}), 61.97 (C_4), 64.33 (C_3), 81.56 (C_5), 92.48, (C_2); the numbering scheme used for these NMR assignments is the same as that shown in Figure 1. Raman: 928 cm^{-1}, $\nu_{Tc=O}$. IR (Nujol): 929 cm^{-1}, $\nu_{Tc=O}$. The crystal structure was the same as that of the compound provided by Kramer *et al.*[7]

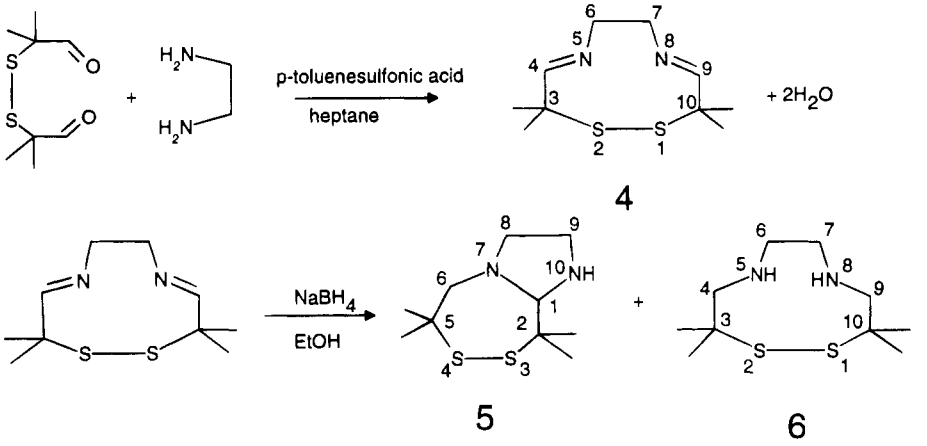
Results and Discussion

Kramer *et al.* attempted to make a six-coordinate technetium complex containing an oxo group and *N*-(2-mercaptoethyl)-*N*,*N*′-bis(2-methyl-2-mercaptopropyl)ethylenediamine, which, it was hoped, would be bound through the nitrogen and deprotonated sulfur atoms to give a $TcON_2S_3$ system.[7] We examined, by single crystal X-ray diffraction, the technetium complex prepared by them, and it is illustrated in Figure 1. Bond lengths and angles are given in Table 4. The complex clearly did not contain the expected ligand. Instead, the expected pendant mercaptoethyl group attached to N(1) had undergone an internal condensation to form a thiazolidine ring. We rejected the suggestion that the thiol group had attacked the CH_2 group proximal to the nitrogen atom directly, in the presence of the technetium atom,[16] and we sought, therefore, to examine the synthetic pathway used to prepare the ligand, in order to see where cyclization might have occurred.

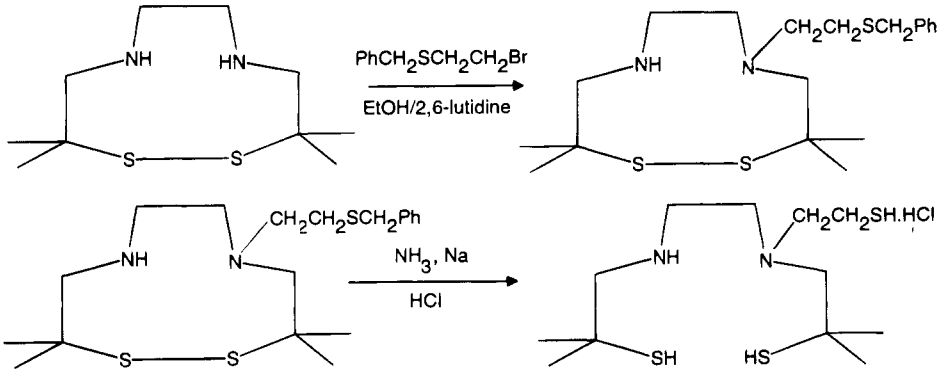
Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $C_{12}H_{23}N_2OS_3Tc$, **1**, and $C_{12}H_{25}ClN_2S_3$, **7**

	1	**7**		**1**	**7**
Tc−O	1.665(5)		Tc−S(1)	2.311(2)	
Tc−S(2)	2.278(2)		Tc−N(1)	2.207(5)	
Tc−N(2)	1.907(5)		S(1)−C(1)	1.860(7)	1.871(6)
C(1)−C(2)	1.53(1)	1.535(8)	C(2)−N(1)	1.486(8)	1.442(6)
N(1)−C(3)	1.510(8)	1.456(7)	C(3)−C(4)	1.51(1)	1.519(7)
C(4)−N(2)	1.458(9)	1.491(8)	N(2)−C(5)	1.469(8)	1.481(8)
C(5)−C(6)	1.52(1)	1.518(9)	C(6)−S(2)	1.850(7)	1.838(6)
C(1)−C(11)	1.56(1)	1.527(7)	C(1)−C(12)	1.54(1)	1.528(8)
C(2)−S(3)	1.835(6)	1.885(6)	S(3)−C(21)	1.792(8)	1.794(6)
C(21)−C(22)	1.52(1)	1.520(8)	C(22)−N(1)	1.513(8)	1.465(8)
C(6)−C(61)	1.528(9)	1.53(1)	C(6)−C(62)	1.51(1)	1.519(7)
S(1)−S(2)		2.040(2)			
O−Tc−S(1)	114.0(2)		O−Tc−S(2)	108.8(2)	
O−Tc−N(1)	103.2(2)		O−Tc−N(2)	113.7(3)	
S(1)−Tc−S(2)	89.0(1)		S(1)−Tc−N(1)	82.7(1)	
S(1)−Tc−N(2)	131.7(2)		S(2)−Tc−N(1)	147.6(1)	
S(2)−Tc−N(2)	82.9(2)		N(1)−Tc−N(2)	79.6(2)	
Tc−S(1)−C(1)	100.1(2)		S(1)−C(1)−C(2)	104.3(4)	110.3(4)
C(1)−C(2)−N(1)	114.9(5)	116.0(4)	C(2)−N(1)−C(3)	110.1(5)	113.7(4)
N(1)−C(3)−C(4)	107.4(6)	110.9(4)	C(3)−C(4)−N(2)	106.9(6)	111.4(5)
C(4)−N(2)−C(5)	115.6(6)	115.4(4)	N(2)−C(5)−C(6)	111.0(6)	112.6(4)
C(5)−C(6)−S(2)	104.6(5)	111.8(4)	C(6)−S(2)−Tc	98.7(2)	
S(1)−C(1)−C(11)	108.6(5)	100.1(4)	S(1)−C(1)−C(12)	107.7(5)	110.3(4)
C(2)−C(1)−C(11)	116.0(6)	110.1(4)	C(2)−C(1)−C(12)	110.2(7)	113.8(4)
C(11)−C(1)−C(12)	109.5(6)	111.5(5)	C(1)−C(2)−S(3)	114.5(4)	110.6(4)
N(1)−C(2)−C(3)	106.4(4)	107.3(4)	C(2)−S(3)−C(21)	94.2(3)	92.3(3)
S(3)−C(21)−C(22)	106.7(5)	105.0(5)	C(21)−C(22)−N(1)	107.9(5)	108.5(4)
C(2)−N(1)−C(22)	106.9(5)	109.6(4)	C(2)−N(1)−Tc	114.0(4)	
Tc−N(1)−C(3)	106.7(4)		C(22)−N(1)−C(3)	109.8(5)	111.2(5)
C(22)−N(1)−Tc	109.4(4)		C(4)−N(2)−Tc	119.6(5)	
Tc−N(2)−C(5)	124.3(5)		C(5)−C(6)−C(61)	111.7(6)	107.5(5)
C(5)−C(6)−C(62)	112.0(6)	112.9(5)	S(2)−C(6)−C(61)	110.1(5)	109.7(4)
S(2)−C(6)−C(62)	109.5(5)	104.1(4)	C(61)−C(6)−C(62)	108.9(6)	110.9(4)
S(2)−S(1)−C(1)		108.7(2)	S(1)−S(2)−C(6)		106.6(2)

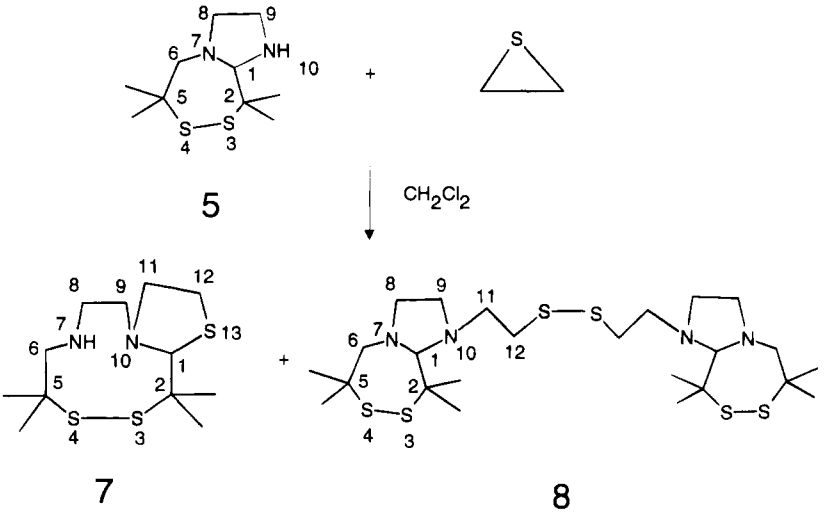
Scheme 1



Scheme 2



Scheme 3



The synthesis requires a multistep procedure outlined in the schemes below. Kung reported that the reaction of isobutyraldehyde with sulfur monochloride gave the dithiadialdehyde. Condensation of the dialdehyde with ethylenediamine led to the isolation of 3,3,10,10-tetramethyl-1,2-dithia-5,8-diazacyclodeca-4,8-diene (**4**). Subsequent reduction of **4** with $NaBH_4$ was reported to give 3,3,10,10-tetramethyl-1,2-dithia-5,8-diazacyclodecane (**6**) in 76% yield.[12] It was shown later by Joshua *et al.*[13] that **6** was only a minor product in the $NaBH_4$ reduction reaction. The major product was the bicyclic imidazolidine, **5**, as shown in Scheme 1. More recently, it has been shown that a considerably higher yield of **6** could be achieved if $NaBH_4$ were replaced by $NaBCNH_3$.[17] In the original work by the Kramer *et al.* it was assumed that subsequent steps in the supposed preparation of **2** had used **6**.[7] Reaction Scheme 2 outlines the synthetic sequence that was believed to have been followed. We believed that the formation of the thiazolidine ring could be explained if compound **5** had been used instead of **6**. C_1 in **5** is electron poor and hence susceptible to nucleophilic attack by the sulfur atom of the additional ethylenethiol group, with consequent formation of the thiazolidine ring. We decided, therefore, to investigate this hypothesis by examining the reaction of **5** with ethylene sulfide (reaction Scheme 3). The reaction was extremely slow in aromatic

(15) Freeman, S. K. *Applications of laser Raman spectroscopy*; Wiley-Interscience: New York, 1974; pp 204–206.

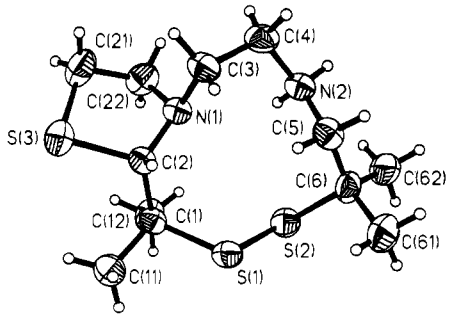


Figure 2. Molecular cation in **7**, showing the atom numbering.

solvents, such as benzene and toluene.[18,19] In halogenated solvents, chloroform and dichloromethane, the reaction was somewhat faster, although still relatively slow. Dichloromethane was chosen as the solvent for the reaction. A mixture of **5** and ethylene sulfide was stirred in CH_2Cl_2 under a nitrogen atmosphere for 6 days. Subsequent chromatographic separation led to the isolation of the target molecule, the thiazolidine-containing ligand **7**, and the dimer **8** (relative proportions by weight, 4:3). Although the ^{13}C NMR spectra were consistent with structural assignments, the ^1H NMR spectra were not very informative because of the overlap of signals corresponding to the methylene protons. Fortunately, we were able to isolate single crystals of **7**. The crystal structure shown in Figure 2 provided conclusive evidence for the formation of the thiazolidine ring before the addition of the metal. The assignment of a dimeric structure to compound **8** was based on the evidence provided by the mass spectrum. Also, the absence of any SH stretch in both the infrared and Raman spectra ruled out the monomer thiol.

NMR spectroscopy was used in the characterization of each of the intermediates involved in this synthesis. The ^1H and ^{13}C NMR for **4** were easily assigned. The singlet at 2.78 ppm in the ^1H NMR spectrum of **6** was assigned to the four protons on carbon atoms 6 and 7 because it split into a pattern corresponding to an A_2B_2 system when dimethyl sulfoxide (DMSO) was used as a solvent instead of $CDCl_3$. Once the ^1H spectrum was assigned for **6**, a $^{13}C/^1H$ correlation spectrum was obtained and used in the assignment of the ^{13}C spectrum. In the case of **5** the ^1H spectrum was more complex. $^1H/^1H$ and $^1H/^{13}C$ correlation spectra were needed for the assignment. The ^{13}C spectra of **7** and **8** were assigned by comparison with those of **5** and **6**. The ^1H and ^{13}C NMR spectra of the technetium complex **1** were assigned with aid of $^1H/^1H$ and $^1H/^{13}C$ correlation spectra and nuclear Overhauser effect (NOE) experiments. The chemical shifts of the carbon atoms changed considerably upon chelation of the ligand to technetium. In a comparison of equivalent atoms in **1** and **7** (numbering as **1**), it was evident that C(6), C(8), and C(9) were the atoms most affected by technetium chelation. C(6) and C(8) were bound to N(7) which underwent deprotonation upon reaction with metal and formed a strong Tc−N bond.

In **1** one of the protons on C(3) showed an unusually high field shift. The crystal structure showed this proton (H(3A)) was oriented beneath the base of the square pyramid toward the center. In this position the proton could experience the diamagnetic effects of the Tc−N(2) bond, which had at least some π character. In addition the anisotropic magnetic environment of the Tc=O bond, which was really a triple bond and should have, therefore, a deshielding region adjacent to the bond, but a shielding region at the ends, may have influenced the proton shift. Considering the position of H(3A) (Tc···H(3A) = 3.15 Å, H(3A)···Tc=O = 137°, H(3A)···N(2) = 2.72 Å, H(3A)···N(2)−Tc = 85°) both effects should be shielding. It was not clear which of the two shielding effects provided the greater contribution, although (H3A) was closer to the Tc−N(2) bond.

There were a number of interesting structural features in **7**, particularly when compared with the technetium complex **1**. Much of the general conformation of **7** was retained in the complex; torsional angles in the framework bonds were generally within about 10° in the two molecules. Only the torsional angles about N(2)−C(4) and N(2)−C(5) differed by much more than 20° in the two molecules. The new steric requirements of the coordination of N(2) to the technetium atom caused the change. N(2) went from a substituted ammonium ion to a coordinated amido group in the complex.

In **7** S(1),N(1),N(2),S(2) were not planar; they were twisted toward a very distorted tetrahedron, with the atoms lying 0.446(8) Å, S(1); −0.285(6) Å, N(1); 0.319(8) Å, N(2); and −0.480(6) Å, S(2) out of the best plane through the atoms. The requirement of square pyramidal geometry in the technetium complex forced the four atoms toward a plane but did not suppress the distortion completely, since the atoms were 0.096(7) Å, S(1); −0.119(8) Å, N(1); 0.130(8) Å, N(2); and −0.106(7) Å, S(2) out of the best plane through the four atoms. The technetium atom lay −0.735(5) Å out of this plane.

The deprotonation of N(2) meant that the atom was an excellent base and bound strongly to the technetium atom. The Tc−N(2) distance was 0.300 Å shorter than the Tc−N(1) distance, which lay in the normal range for Tc−N distances in this type of compound. The Tc−O distance of 1.665(5) Å lay in the normal range as did the Tc−S distances.[20] Equivalent bond distances in **1** and **7** generally did not differ significantly, but coordination of N(1) resulted in longer N(1)−C(2), N(1)−C(3), and N(1)−C(22) bonds in the complex by 0.026 Å, 4.4 σ; 0.054 Å, 5.1σ; and 0.048 Å, 4.2σ, respectively.[21] The longer (weaker) N(1)−C(2) bond resulted in a stronger C(2)−S(3) bond in the complex, which was shorter by 0.050 Å, 5.9 σ.

In thiazolidine rings the C−S bonds are rarely the same length. In previous compounds we have studied,[22−24] the lengths of the C−S bonds proximal to the nitrogen atom have varied from 1.816(5) to 1.885(6) Å, whereas the distal C−S bonds have varied from 1.784(5) to 1.869(6) Å. As we have noted, steric repulsion from bulky groups attached to the α and/or β carbon atoms caused long C−S bonds with consequent shortening of the C−S bond to the less sterically crowded carbon atom. Clearly the same effect is present here. In both **1** and **7** S(3)−C(2), where C(2) was adjacent to the bulky dimethylated C(1) atom, was longer than S(3)−C(21), where C(21) was adjacent to a CH_2 group. The S(3)−C(2) distance lay at the upper end of the previous range of equivalent distances, and the S(3)−C(21) distance lay at the lower end of its range. It should be noted that the steric effects were completely taken up in the bond lengths; the C(2)−S(3)−C(21) angles (94.2(3),

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92.3(3)°) lay within the small range of C−S−C angles observed previously (92.4(2)−95.4(3)°).

The changes in the torsional angles N(1)C(2)S(3)C(21) and C(2)S(3)C(21)C(22) from 15.1(4), 9.7(5)° in **1** to 2.5(4), 20.8(5)° in **7** meant that while the conformation of the thiazolidine ring in **7** was an open envelope, with C(22) 0.564 Å out of the plane through the other four atoms, the conformation of the ring in **1** was roughly a C_2 system with C(2), 0.372 Å, and N(1), −0.244 Å, out of the plane of the other three atoms. The former conformation has been observed in 2*R*,4*S*-2-(2′-methyl-3′-(hydroxymethylene)pyridine-$C^{4'}$)-5,5-dimethylthiazolidine-4-carboxylic acid[22] and the latter in *S*-2,2,5,5-tetramethylthiazolidine-4-carboxylic acid.[24]

In the solid state each cation in **7** was hydrogen bonded to two chloride ions, which were related by the inversion center at $^1/_2$, 0, 0. These chloride ions were, in turn, hydrogen bonded to another cation related to the first by the same inversion center, which gave (cation)$_2$Cl$_2$ units. One of the hydrogen bonds was quite strong (N(2)···Cl = 3.041(7) Å), but the other was weaker (N(2)···Cl = 3.223(7) Å). All other interactions were van der Waals, as was the case for the packing of **1** in the solid.

The infrared and Raman spectra of compounds **1**, **5**, **7**, and **8** have been measured. Tables of the wavenumbers, relative intensities, and assignments have been deposited (Table F).

The assignment of ν_{NH} was unambiguous with a broad, strong, single band at 3390 cm^{-1}, **7**, and a sharp, single band at 3302 cm^{-1}, **5**. There were no ν_{SH} bands (2500−2600 cm^{-1} region) in any of the compounds, as expected, and no ν_{NH} in the "dimer", **8**.

The most intense Raman band for **5** was at 476 cm^{-1} and was assigned as ν_{S-S}. In cyclic disulfides this band is usually between 490 and 550 cm^{-1}, and in acyclic disulfides, this band is between 450 and 550 cm^{-1}.[15] Compounds **5** and **8** had large enough rings that the S−S links might be considered as acyclic. Compound **8**, which contained two units of **5** joined by an bis-(ethylene) disulfide bridge, also had this band, but should have had an additional ν_{S-S} band typical of the acyclic, unsubstituted C−S−S−C group for the central link in the molecule. The band at 517 cm^{-1} was so assigned.

The ν_{C-S} bands were higher with Raman shifts in cm^{-1} of 554, 571, 634, 638, for **5**; 553, 574, 625, 647, for **8**; 548, 583, 606, 634, for **7**; and 541, 575, 620, 648 for **1**.

The relative intensities of ν_{S-S} to ν_{C-S} bands, $I_{SS/CS}$, are known to depend on structure; if a steric effect increases the CSSC torsional angle (normally about 90°), there is a decrease in $I_{SS/CS}$.[24] This ratio was 10:1 in cystine and 0.38 for *tert*-butyl disulfide. In **5** the CSSC torsional angle appears to be about 90° from a published diagram (although the angle is not tabulated, nor is it possible to derive it from the information given in the paper)[13] whereas in this work for **7** the CSSC angle was 123.4°. This effect could explain why in **5** ν_{S-S} at 476 cm^{-1} was the strongest band in the Raman spectrum while in **7** the ν_{S-S} band at 486 cm^{-1} had about half the intensity of the ν_{C-S} bands.

The thiazolidine ring in **7** and **1** had two unique ring deformations, δ_{CSC}, and δ_{CNS}, which were assigned to Raman bands at 190 and 299 cm^{-1}. A δ_{CNC} mode occurred in all four compounds at ~372 cm^{-1}. Deformations of the CSS groups should occur for **5**, **7**, and **8** but not **1**. The strong Raman bands at ~160 cm^{-1} in **5**, **7**, and **8** were so assigned. A strong deformation mode of the $(CH_3)_2CS$ group was assigned at ~330 cm^{-1} for tetramethylthiazolidine-4-carboxylic acid.[23] This correlated with ~340 cm^{-1} in **5**, **7**, **8**, and **1**.

For **1**, $\nu_{Tc=O}$ was unambiguous at 929 cm^{-1}, IR, and 928 cm^{-1}, Raman, the strongest band in both spectra. The ν_{Tc-N} and ν_{Tc-S} bands were less clear-cut, but were assigned as 481 cm^{-1}, IR, 440 cm^{-1}, Raman, for ν_{Tc-N}, and 363 cm^{-1}, Raman, for ν_{Tc-S}.

In conclusion, we have explained the unexpected formation of the thiazolidine ring that was found in the title compound.

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Supplementary Material Available: Tables of anisotropic temperature factors, hydrogen atom positions and U values, and least squares planes and torsional angles, diagrams of the packing in the unit cells for **1** and **7**, and a table of infrared and Raman spectral data for **1**, **5**, **7**, and **8** (12 pages). Ordering instructions are given on any current masthead page.

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