

(3,6-Dimethyl-3,6-diazaoctan-1,8-dithiolato-*S*¹,*N*³,*N*⁶,*S*⁸)oxotechnetium(V) Pertechnetate

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Abstract. [TcO(C₈H₁₈N₂S₂)]TcO₄, $M_r = 484.2$, monoclinic, $P2_1/c$, $a = 7.447(2)$, $b = 16.952(8)$, $c = 12.236(3)$ Å, $\beta = 99.63(2)^\circ$, $V = 1523(1)$ Å³, $Z = 4$, $D_x = 2.112$, $D_m = 2.09(1)$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.06$ mm⁻¹, $F(000) = 952$, $T = 295(1)$ K, final $R = 0.071$ for 2496 significant reflections and 173 parameters. The Tc atom is bound to the oxo group and the N and S atoms of the complex ligand in a rough square pyramid. The Tc atom lies 0.770(3) Å out of the S,N,N',S' plane. This plane is significantly distorted such that N and N' lie nearly 0.25 Å out of the plane on opposite sides. The Tc–S bonds [2.238(3), 2.266(3) Å] are short but other bond lengths and angles are normal.

Introduction. We have prepared and examined a number of complexes of technetium with substituted 3,6-diazaoctan-1,8-dithiols because the complexes are lipophilic and may find use as radio-imaging agents. One has shown potential as a brain scanning agent (Lever *et al.*, 1985). Because of deprotonation and protonation reactions on the ligand N atoms, characterization of these complexes has sometimes proved difficult, except by X-ray diffraction. The compound described here is the first which is methylated at both N atoms. The ligand was prepared by the method of Karlin & Lippard (1976). The complex was prepared by the direct reaction of the ligand and ammonium pertechnetate in sulfuric acid solution.‡

Experimental. Red–brown needles; crystal used: right parallelepiped 0.16 × 0.20 × 0.30 mm, preliminary

data from precession photographs. Density by suspension in carbon tetrachloride–dibromomethane mixture. Unit-cell parameters refined by least-squares fit of χ , ψ and θ of 15 strong independent reflections measured on a Nicolet P3 diffractometer for $20.3 \leq 2\theta \leq 28.1^\circ$, with use of graphite-monochromated Mo $K\alpha$ radiation. Intensities of $h = 0 \rightarrow 8$, $k = 0 \rightarrow 20$, $l = -14 \rightarrow 14$ measured by $\theta/2\theta$ step scans, scan rate 4.88 to 29.30° min⁻¹ in 2θ , max. $2\theta = 50^\circ$. Ratio of total background time to scan time is 1.0. Two standard reflections monitored every 48 scans showed no correction for instrument instability or crystal decay required. 3032 measured reflections gave 2699 unique reflections, $R_{\text{int}} = 0.0393$. 2496 reflections with $I > 0$ were used in structure solution. Corrections made for L_p but not absorption (absorption correction factors, $A^* = 1.31\text{--}1.65$), max. error in F_o 6%. Structure solved by heavy-atom method. Anisotropic full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma_F^2 + 0.002654F_o^2)^{-1}$. Final $R = 0.0714$, $wR = 0.0811$ (for all reflections with $I > 0$). Correction for secondary extinction, x (Sheldrick, 1976), was applied (-0.00026). In the final refinement cycle $(\Delta/\sigma)_{\text{max}} = 0.002$, $(\Delta/\sigma)_{\text{ave}} = 0.001$, $S = 1.0644$. Hydrogen atoms were located from the difference map: positional and temperature factors were refined for two cycles only, and were not refined further. Final refinements on scale, secondary extinction, positional and anisotropic temperature factors for non-hydrogen atoms, 173 parameters. Final difference maps were essentially featureless except for a peak of $1.4 \text{ e } \text{Å}^{-3}$ near Tc2, valley $-1.0 \text{ e } \text{Å}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974). Corrections for anomalous dispersion were made for Tc and S (Cromer & Ibers, 1974). Calculations employed *SHELX76* (Sheldrick, 1976), *SNOOPI* (Davies, 1983) and *XTAL* (Stewart & Hall, 1983).

Discussion. The complex is shown in Fig. 1. Table 1 lists the final atomic parameters for non-hydrogen

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‡ Lists of structure factors, anisotropic temperature factors, H-atom positions, bond lengths and angles involving hydrogen atoms, least-squares planes and torsional angle data and a detailed method of preparation have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44728 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atoms, and bond lengths and angles are given in Table 2. The ligand atoms bonded to Tc form a rough square pyramid such that the Tc atom lies 0.770 (3) Å above the best S1, N1, N2, S2 plane. The plane is quite distorted, however, with the two N atoms lying about one quarter of an ångström on either side of this plane [Si, -0.029 (4); N1, 0.23 (1); N2, -0.24 (1); S2, 0.035 (4), Tc2, -0.770 (3) Å]. The *R,S* (or *S,R*) configuration of the molecular cation means the N-methyl bonds lie roughly at right angles to the basal plane with the methyl groups on the same side as the oxo group. The Tc2-O bond [1.646 (8) Å] is comparable to distances in similar compounds [range 1.634 (7) to 1.672 (8) Å] (DePamphilis, Jones, Davis & Davison, 1978; Bandoli, Nicolini, Mazzi, Spies & Munze, 1984; Bandoli, Mazzi, Wilcox, Jurisson & Deutsch, 1984; Franklin, Howard-Lock & Lock, 1982). The Tc-N [2.137 (7), 2.186 (8) Å] distances are comparable to those in similar compounds [range 2.055 (6) to 2.209 (6) Å] (Bandoli, Mazzi *et al.*, 1984; Kastner, Fackler, Clarke & Deutsch, 1984; Franklin *et al.*, 1982), but the Tc-S distances [2.266 (3), 2.238 (3) Å] are shorter than in similar complexes [range 2.283 (2) to 2.336 (6) Å] (DePamphilis *et al.*, 1978; Bandoli, Nicolini *et al.*, 1984; Franklin *et al.*, 1982) and much shorter than in Tc^{III} complexes [range 2.412 to 2.520 (3) Å] (Abrams, Davison, Faggiani, Jones & Lock, 1984; Baldas, Bonnyman, Pojer, Williams & MacKay, 1982). Distances within the organic moiety are normal and all angles lie within the ranges of related

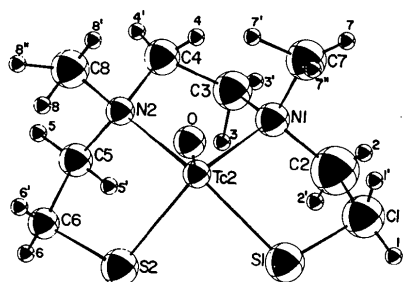


Fig. 1. The molecular cation showing the atom numbering. Hydrogen atoms are shown by affixes only, in smaller print.

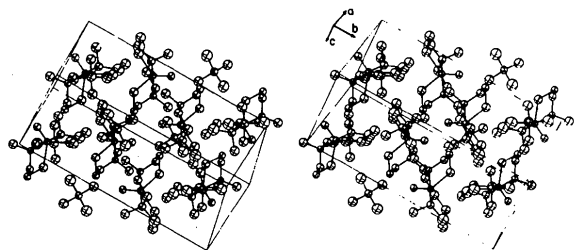


Fig. 2. The packing within the unit cell.

Table 1. Atomic positional parameters ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	U_{eq}
Tc1	3346 (1)	1384.8 (5)	3629.9 (7)	39.4
O1	4098 (11)	1836 (6)	4864 (7)	70
O2	1279 (11)	985 (5)	3685 (8)	68
O3	4840 (14)	623 (7)	3402 (9)	97
O4	3117 (13)	2079 (6)	2617 (8)	84
Tc2	567 (1)	8909.9 (5)	1641.4 (6)	30
O	1842 (9)	9663 (5)	1401 (6)	54
S1	2216 (4)	7806 (2)	1475 (2)	51
C1	3027 (16)	7530 (6)	2893 (9)	53
C2	1507 (17)	7960 (7)	3497 (8)	53
N1	774 (11)	8535 (5)	3325 (6)	34
C3	-1034 (15)	8518 (6)	2680 (8)	44
C4	-1930 (14)	9351 (8)	3248 (8)	52
N2	-1956 (10)	9408 (5)	2035 (7)	38
C5	-3566 (15)	9010 (7)	1414 (10)	57
C6	-3430 (10)	8929 (7)	188 (11)	58
S2	-1231 (4)	8483 (2)	105 (2)	52
C7	2126 (16)	9073 (7)	3970 (9)	58
C8	-2009 (15)	10270 (6)	1720 (10)	50

Table 2. Selected interatomic distances (Å) and angles (°)

Tc1-O1	1.702 (8)	C1-C2	1.48 (2)
Tc1-O4	1.70 (1)	C3-C4	1.50 (2)
Tc2-N1	2.137 (7)	C5-C6	1.53 (2)
S1-C1	1.80 (1)	N2-C8	1.51 (1)
N1-C3	1.49 (1)	Tc1-O3	1.68 (1)
N2-C5	1.47 (1)	Tc2-S1	2.266 (3)
N1-C7	1.50 (1)	Tc2-S2	2.238 (3)
Tc1-O2	1.693 (9)	C2-N1	1.53 (1)
Tc2-O	1.646 (8)	C4-N2	1.49 (1)
Tc2-N2	2.186 (8)	C6-S2	1.82 (1)
O1-Tc1-O2	108.1 (4)	C2-N1-Tc2	112.1 (6)
O2-Tc1-O3	110.7 (5)	Tc2-N1-C7	105.0 (6)
O-Tc2-S1	106.7 (3)	N1-C3-C4	109.3 (9)
O-Tc2-S2	112.5 (3)	C4-N2-C5	111.1 (9)
S1-Tc2-S2	85.9 (1)	Tc2-N2-C5	111.4 (7)
N2-Tc2-S2	83.1 (2)	C5-C6-S2	107.4 (8)
C1-C2-N1	112.8 (9)	O1-Tc1-O4	108.4 (5)
C2-N1-C7	107.3 (8)	O3-Tc1-O4	111.0 (5)
C7-N1-C3	112.4 (8)	O-Tc2-N2	106.4 (3)
C4-N2-Tc2	109.1 (6)	S1-Tc2-N2	146.9 (2)
Tc2-N2-C8	107.7 (6)	N1-Tc2-S2	130.6 (2)
N2-C5-C6	111 (1)	S1-C1-C2	105.8 (7)
O1-Tc1-O3	109.7 (5)	C2-N1-C3	110.3 (8)
O2-Tc1-O4	109.0 (4)	Tc2-N1-C3	109.7 (5)
O-Tc2-N1	116.9 (3)	C3-C4-N2	109.8 (9)
S1-Tc2-N1	83.6 (2)	C4-N2-C8	108.3 (8)
N1-Tc2-N2	80.1 (3)	C8-N2-C5	109.2 (8)
Tc2-S1-C2	103.2 (4)	C6-S2-Tc2	103.7 (4)

angles in similar compounds. The pertechnetate ion bond lengths and angles agree well with values found previously (Faggiani, Lock & Pocé, 1980).

The packing is shown in Fig. 2. The cations are arranged in double chains in the *a* direction, centred at $y = 0, 0.5$, with the oxo groups pointing towards the chain centres. Chains contact in the *b* direction through the bases of the molecular cations at $y = 0.25, 0.75$. In the *c* direction the chains are separated by per-

technetate ions. There is no evidence of any strong interactions and all intermolecular contacts are greater than the van der Waals distances.

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The Structure of Ammonium Decamolybdate $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$

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Abstract. $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$, $M_r = 1647.7$, triclinic, $P\bar{1}$, $a = 7.750$ (1), $b = 10.889$ (1), $c = 11.038$ (1) Å, $\alpha = 73.13$ (1), $\beta = 80.82$ (1), $\gamma = 81.71$ (1)°, $V = 875.25$ Å³, $Z = 1$, $D_x = 3.126$, $D_m = 3.12$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 3.51$ mm⁻¹, $F(000) = 780$, room temperature, final $R = 0.051$ for 3642 independent reflections. The title compound is formed by reaction between molybdenum trioxide and aqueous ammonia solution. The anionic asymmetric unit, Mo_5O_{17} , contains one MoO_4 tetrahedron connected to one of four MoO_6 octahedra by sharing of one common corner. The Mo_4O_{14} unit is built up of four edge-bridge condensed octahedra with seven terminal O atoms. Linkage of the asymmetric unit with its centrosymmetric counterpart gives rise to the $\text{Mo}_{10}\text{O}_{34}^{8-}$ anion. The overall structural framework is built up by a number of

close contacts of the cation N atoms with the anion terminal oxygens. The metal–oxygen bond lengths conform with those of similar compounds.

Introduction. Molybdenum chemistry research has been given considerable attention because of the widespread versatility and the varied industrial applications of Mo compounds (Mitchell, 1973; Stiefel, 1977; Braithwaite, 1978). Ammonium molybdates are compounds of great interest for applications demanding high-purity molybdenum trioxide. Several structures have been determined for compounds formed in the ternary system $\text{NH}_3\text{–MoO}_3\text{–H}_2\text{O}$ (Böschén, Buss & Krebs, 1974; Evans, Gatehouse & Leverett, 1975; Armour, Drew & Mitchell, 1975; Vivier, Bernard & Djomaa, 1977; Garin & Blanc, 1985). The anion