

Fig. 1. An example of the deviation of the measured redox potential of dithionite-sulfite solutions from the theoretical one (broken line), calculated using the corresponding standard potential in Table 1. $[S_2O_4^{2-}] = 0.01$ M; $[HSO_3^-] + [SO_3^{2-}] = 0.01$ M. Temperature = 60°C .

volving also the H_2/H^+ potential. This is, however, improbable as the redox potential was dependent on the sulfite concentration also in the alkaline region.

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The Crystal Structure of an Eight-Coordinated Tellurium(IV) Complex

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During the study of compounds of divalent selenium and tellurium with bidentate dithio- and related ligands, it was found that the ligand 4-morpholinecarbodithioate (previously termed, morpholyl dithiocarbamate) upon reaction with Te(IV) gave a remarkably stable complex.¹ Unlike the corresponding diethyldithiocarbamate complex, it was only very slowly converted to the Te(II) dithiocarbamate and the corresponding disulphide, when heated in solution.^{2,3}

Crystals of tetrakis (4-morpholinecarbodithioato)tellurium(IV) including three benzene molecules of crystallization, $[Te(OC_4H_8NCS_2)_4] \cdot 3C_6H_6$, were prepared by adding an aqueous solution of sodium 4-morpholinecarbodithioate to a solution of tellurium dioxide dissolved in dilute hydrochloric acid, in the molar ratio 4:1. The resulting precipitate was then recrystallized from a mixture of benzene and ethanol. The following unit cell data were found: $a = 15.445$ (4) Å, $b = 13.565$ (4) Å, $c = 26.591$ (10) Å, $\beta = 122.23$ (4) $^\circ$ and $Z = 4$. The observed and calculated densities are 1.45 and 1.43 g/cm³, respectively, and the space group is $P2_1/c$.

Based on 2721 reflections above background obtained with a Siemens paper-tape controlled AED-1 diffractometer, the structure was solved by Patterson and Fourier syntheses and refined by a full-matrix least-squares program to an R -value of 0.094.

The dodecahedral D_{2d} coordination found around the central tellurium atom is shown on Fig. 1, while some bond lengths and angles are listed in Table 1. The dodecahedral TeS_8 group has a structure similar to that found for the corresponding group in tetrakis(diethyldithiocarbamate)tellurium(IV).^{3,4} Thus the lone pair of electrons in the valency shell of the central tellurium atom is essentially stereochemically inert. Each ligand spans an edge m between one corner of type A and one of

Table 1. Some bond lengths and angles with standard deviations in brackets.

Te-S1	2.824 (6) Å	\angle S1-Te-S2	64.4 (2)°
Te-S2	2.694 (8)	\angle S3-Te-S4	65.3 (2)
Te-S3	2.684 (5)	\angle S5-Te-S6	64.6 (2)
Te-S4	2.752 (7)	\angle S7-Te-S8	65.2 (2)
Te-S5	2.672 (6)	\angle S1-Te-S6	75.8 (2)
Te-S6	2.824 (8)	\angle S4-Te-S7	73.8 (2)
Te-S7	2.744 (6)		
Te-S8	2.702 (5)		

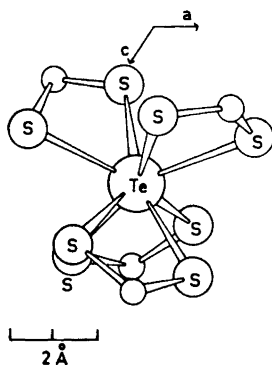


Fig. 1. The tetrakis (4-morpholinecarbodithioato) tellurium(IV) molecule seen along *b*. Unlabelled spheres represent carbon atoms. The nitrogen atoms and the ethyl groups are omitted.

type B in the dodecahedron.⁵ The corresponding bond length ratio $\text{Te-S}_A/\text{Te-S}_B$ is 1.04, with the Te-S_A and Te-S_B bond lengths ranging from 2.74 to 2.82 Å and from 2.67 to 2.70 Å, respectively. The average bite, *b*, as defined by Blight and Kepert,⁶ is 1.07, and the angles θ_A and θ_B are 37.4 and 77.8° respectively, as compared to 35.2 and 73.5° given for Hoard and Silvertons "most favourable" dodecahedron.⁵ The corresponding average values for tetrakis(diethyldithiocarbamato)tellurium(IV) are 35.1 and 79.9°, respectively.

The two interlocking TeS_4 trapezoids are both nearly planar, and their interplanar angle is 89.8°. As in the analogous diethyldithiocarbamate of tetravalent tel-

lurium, the average Te-S bond length found in the present investigation, is 2.74 Å. This may be compared to 2.59 Å, the sum of the octahedral radius of tellurium and the covalent radius of sulphur. The large bond lengths may be due to increasing use of high energy *d* orbitals, the antibonding nature of the lone pair, and steric crowding.^{3,4} However, in light of nuclear quadrupole measurements on octahedral tellurium(IV) complexes and MO calculations on IF_7 , BrF_5 , AsF_5 , and PF_5 ,⁷⁻⁹ it is possible that the *d*-orbitals on the tellurium atom are only slightly involved in the bonding.^{10,11}

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