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The Mo=S Bond Distance in Di-μ-sulfido-bis[sulfido(N,N-diethyldithiocarbamato)molybdenum(V)]

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There are relatively few structural studies of molybdenum compounds in which the molybdenum atom is ligated exclusively by sulfur atoms.[1,2] Such compounds are of particular interest in view of recent X-ray absorption data[3] which provide convincing evidence for sulfur ligation of molybdenum in the enzyme nitrogenase and which conclusively rule out the presence of Mo=O groups in that enzyme.

Recently we reported the structures[4] of the syn and anti isomers of $[Mo_2S_4(dme)_2]^{2-}$, binuclear anions[5] in which each Mo(V) contains a terminal sulfido ligand. The range of Mo–S_t distances is 2.085 (3)–2.129 (2) Å. These distances are substantially larger than the average Mo–S_t distance of 1.937 (6) Å found previously[6] for the closely related compound *syn*-$Mo_2S_4(S_2CN(n\text{-}C_4H_9)_2)_2$. Two different organometallic compounds with terminal sulfido ligands η-$(C_5H_4CH_3)_2Mo_2S_4$[7] and η-$(C_5H_5)_2Mo_2S_4$[8] have Mo–S_t distances of 2.141 Å. In order to determine whether very short Mo–S_t distances are a general feature of dithiocarbamate complexes of the $[Mo_2S_4]^{2+}$ moiety we have determined the structure of *syn*-di-μ-sulfido-bis[sulfido(N,N-diethyldithiocarbamato)molybdenum(V)], $Mo_2S_4(S_2CN(C_2H_5)_2)_2$.

Experimental Section

Red crystals of $[Mo_2S_4(S_2CN(C_2H_5)_2)_2]$ were obtained from dichloromethane solution by slow evaporation in air at ambient temperatures. The IR spectra of the original red-brown powder supplied by Dr. W. E. Newton[19] and of the recrystallized material in KBr pellets are identical. No strong bands are seen in the 1000–900 cm^{-1} region of ν(Mo=O).[9,10] A medium-intensity band occurs at 540 cm^{-1} and a weak band assigned to the molybdenum–bridging sulfur stretching frequency[9,10] is observed at 450 cm^{-1}.

X-ray diffraction data were collected with a computer-controlled Syntex $P2_1$ four-circle diffractometer [Mo Kα (λ 0.71073 Å)]. Initially, 25 reflections with $5 \leq 2\theta \leq 25°$ were used to calculate cell constants. Axial photographs and systematic absences in the 2170 data indicated the orthorhombic space group $P2_12_12_1$ with $Z = 4$. Final cell parameters are a = 10.528 (2) Å, b = 13.795 (5) Å, and c = 14.728 (2) Å, corresponding to a cell volume of 2139 (1) Å^3. The agreement between the calculated density, 1.915 (1) g cm^{-3}, and the observed value of 1.904 (7) g cm^{-3} corresponds to the formula $Mo_2S_8N_2C_{10}H_{20}$ (mol wt 616.7) per asymmetric unit.

Data were corrected for absorption (μ = 18.91 cm^{-1}) by an empirical method.[11] Three check reflections collected after every 97 data points showed linear intensity decay of 18, 15, and 16%. An average linear decay correction factor was calculated and applied to each individual F_o and $\sigma(F_o)$. The largest decay correction factor was 1.21.

Details concerning computer programs used can be found in a previous report.[12] Scattering factor tables for neutral atoms[13] and spherically bonded hydrogen[14a] were generated from the coefficients of analytical approximations; the real and imaginary parts of the anomalous dispersion correction were included only for Mo and S.[14b] The structure was solved by direct methods which revealed the coordinates of two Mo and six S atoms. All remaining nonhydrogen atoms were located by subsequent structure factor calculations and difference electron density maps. Only the ethyl carbons C9 and C10 were not refined anisotropically; these atoms have large isotropic thermal parameters of 11.8 (8) and 17.0 (13) Å^2 due to disorder (vide infra). Fifteen hydrogen positions were calculated for C3 through C8 and included as fixed contributions in the final refinement. The final discrepancy values are $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.040$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2} = 0.044$. Refinement was based on F_o with $\sum w(|F_o| - |F_c|)^2$ being minimized. The weights were taken with $w = 4F_o^2/\sigma^2(F_o^2)$ and a value of 0.03 assigned to p in the expression for $\sigma(F^2)$.[15] The 1665 data having $F_o^2 \geq 3\sigma(F_o^2)$ were used in refinement. A structure factor calculation for all 2170 data with $2\theta \leq 50°$ gave R = 0.060 and R_w = 0.046. The final electron density difference map had an estimated standard deviation of 0.10 e/Å^3 and revealed seven peaks ranging from 0.66 to 0.90 e/Å^3 near the C9–C10 ethyl group and within 1.0 Å of each Mo atom. All other peaks in this map were less than 0.52 e/Å^3. The absolute configuration of the data crystal could not be assigned because the R_w values for the two enantiomers (0.0435 and 0.0443) are indistinguishable by the R-factor ratio test.[16] The final positional parameters appear in Table I. Thermal parameters (Table II), parameters for H atoms (Table III), and tables of observed and calculated structure factors (Table IV) are available as supplementary material.

Table I. Final Positional Parameters for $[Mo_2S_4(S_2CN(C_2H_5)_2)_2]$.[a]

Atom	x	y	z
Mo1	.27874(9)	.48329(7)	.71753(6)
Mo2	.48870(9)	.51034(7)	.83303(6)
ST1	.2546(4)	.6159(2)	.6505(3)
ST2	.5432(4)	.6541(2)	.8110(3)
SB1	.2771(3)	.5071(3)	.8734(2)
SB2	.4835(3)	.4311(2)	.6947(2)
SL1	.0666(3)	.4170(2)	.7473(2)
SL2	.2304(3)	.3602(2)	.6027(2)
SL3	.5239(3)	.4816(3)	.9959(2)
SL4	.6826(4)	.4146(3)	.8534(2)
N1	.0019(9)	.2792(7)	.6269(6)
N2	.748(1)	.3951(8)	1.0288(7)
C1	.084(1)	.3437(8)	.6534(8)
C2	.665(1)	.4261(9)	.9699(8)
C3	-.116(1)	.2605(9)	.6811(9)
C4	-.228(1)	.297(1)	.633(1)
C5	.023(1)	.2194(10)	.5441(8)
C6	.088(2)	.124(1)	.567(1)
C7	.723(2)	.408(1)	1.1266(10)
C8	.649(2)	.326(2)	1.167(1)
C9	.893(3)	.361(2)	1.003(2)
C10	.891(4)	.288(2)	1.028(2)

[a] x, y, z are in fractional coordinates. The standard deviation of the least significant figure is given in parentheses.

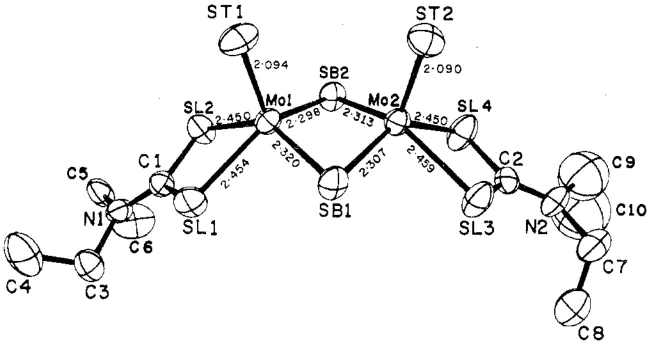

Figure 1. Perspective view of $[Mo_2S_4(S_2CN(C_2H_5)_2)_2]$ with hydrogens omitted for clarity. Probability ellipsoids of 50% are shown. The estimated standard deviations of Mo–S bonds are in the range 0.003–0.004 Å. Other distances and angles follow: Mo···Mo = 2.814 (1) Å; SB1–Mo1–SB2 = 101.3 (1), SB1–Mo2–SB2 = 101.3 (1), Mo1–SB1–Mo2 = 74.94 (9), Mo1–SB2–Mo2 = 75.22 (9)°; within the ligand C1–SL1 = 1.72 (1), C1–SL2 = 1.73 (1), C2–SL3 = 1.71 (1), C2–SL4 = 1.73 (1), C1 – N1 = 1.30 (1), C2–N2 = 1.30 (2) Å.

Results and Discussion

We have illustrated the important features of the molybdenum coordination geometry in Figure 1. Each molybdenum

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atom is bound to two bridging sulfur atoms (SB), two sulfur donor atoms from the diethyldithiocarbamate ligands (SL), and one terminal sulfur atom (ST).

Of particular interest are the Mo1–ST1 and Mo2–ST2 bond lengths which average 2.092 Å. This is well within the range that we have reported[4] for *syn*- and *anti*-$[Mo_2S_4(dme)_2]^{2-}$. The dimer exhibits the usual sharing of an edge by two square-pyramidal five-coordinate Mo(V) centers with the apex atoms, ST1 and ST2, in the syn conformation.[4] Each molybdenum atom is displaced from the basal plane of its square pyramid toward ST1 or ST2 by 0.73 and 0.72 Å, respectively. The dihedral angle between planes formed by SB1–Mo1–SB2 and SB1–Mo2–SB2 is 147.9 (2)°. The average Mo–SL distance is 2.453 (4) Å.

Except for the disordered C9–C10 ethyl group, the diethyldithiocarbamate ligands present no unusual geometries. There are five residual electron density peaks within 1 Å of C9, but no combination of these positions yields a more reasonable geometry for the disordered ethyl group, which lies in an open pocket between molecules.

The primary interest in this investigation are the Mo–ST bond distances. We concur with Spivack, Dori, and Stiefel[6] that such distances are substantially shorter than Mo–S single bonds of ~2.45 Å which have been observed for dithiocarbamate,[6] 1,2-dimercaptoethane,[4] and cysteine[17,18] ligands. Thus, terminal sulfido groups can be written as Mo=S, analogous to the well-known molybdenyl group, Mo=O. However, our five determinations of Mo=S distances in three different complexes[4] containing $[Mo_2S_4]^{2+}$ moieties give Mo=S distances in the range 2.085–2.129 Å, with an average distance of 2.10 (2) Å. These Mo=S distances are more than 0.1 Å longer than those given in the preliminary report[6] of the structure of $Mo_2S_4(S_2CN(n\text{-}C_4H_9)_2)_2$.

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Supplementary Material Available: Table II, atomic thermal parameters; Table III, hydrogen parameters; Table IV, listings of the structure factor amplitudes ×10 (9 pages). Ordering information is given on any current masthead page.

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Structure of Diethylammonium Ethoxybis(diethylmonothiocarbamato)dioxouranate(VI), $(C_2H_5)_2NH_2^+[UO_2((C_2H_5)_2NCOS)_2OC_2H_5]^-$[1]

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While a rather large number of metal dithiocarbamate complexes[3,4] have been extensively investigated, relatively little attention has been given to the analogous monothiocarbamate species. This is particularly unfortunate in light of recent reports[5–9] which indicate that the chemistry of this class of compounds will be as interesting and novel as that of the corresponding dithiocarbamates. The tris(dialkylmonothiocarbamato)iron(III) chelates,[5] $Fe(R_2mtc)_3$, for example, have been shown to exhibit anomalous magnetic behavior arising from $^2T(\text{low spin}, S = {}^1/_2) \rightleftarrows {}^6A(\text{high spin}, S = {}^5/_2)$ spin-state interconversion processes. As a result, these compounds with their FeS_3O_3 metal centers are electronically and structurally similar to their iron(III) dithiocarbamate analogues containing the FeS_6 core.

In the uranyl monothiocarbamate alkoxide series[6] of complexes, however, one sees several features that are markedly different from those displayed by the corresponding dithiocarbamates. The reaction of dialkylammonium monothiocarbamates with uranyl salts affords a new synthetic route for the preparation of uranyl alkoxides; also, these compounds represent the first examples of a mixed alkoxide–bidentate chelate system (where the donor atoms are sulfur and oxygen) of an actinide ion. Since these compounds also contain three different types of uranium–oxygen bonds in the same molecule, their structural and bonding parameters are of considerable interest. The present paper represents the first structural investigation of this class of uranyl compounds and is part of an ongoing research program centered around the chemistry of the lanthanide and actinide–sulfur bond.

Experimental Section

The title compound was prepared according to a method described elsewhere[6] which essentially consisted of bubbling carbonyl sulfide (Matheson, 97.5% purity) through a solution of diethylamine in ethanol at 0 °C for 5–10 min followed by the addition of a saturated ethanolic solution of $UO_2Cl_2 \cdot 3H_2O$ (Alfa Products) with stirring. The bright yellow complex that precipitated from solution was filtered on a Büchner funnel and air-dried. The yield was 60% or better. Anal. Calcd for $(C_2H_5)_2NH_2^+[UO_2((C_2H_5)_2NCOS)_2OC_2H_5]^-$: C, 29.46; H, 5.67; N, 6.44; S, 9.81. Found: C, 29.47; H, 5.64; N, 6.42; S, 9.38.

A crystal suitable for data collection was inserted into a 0.2-mm quartz capillary and sealed. It was later ascertained that the crystals are stable in air and the precaution of sealing them in capillaries was not necessary. The crystal had the shape of a hexagonal prism with dimensions approximately 0.2 mm in cross section and 0.25 mm long. It was examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1)$ 0.709 30 Å). ω scans of several low-angle reflections showed peaks with half-widths of 0.09–0.12°. The space group is $P2_1/n$. The setting angles of 12 manually centered reflections ($39° < 2\theta < 45°$) were used to determine by least squares the following cell parameters: $a = 9.518$ (4) Å, $b = 12.457$ (5) Å, $c = 22.490$ (10) Å, $\beta = 93.77$

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