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Structure of Tetrabutylammonium μ-Oxo-μ-sulfido-bis[(1,2-dithiosquarato-*S*,*S'*)oxomolybdate(V)]

BY DIRK ALTMEPPEN AND RAINER MATTES

Anorganisch-Chemisches Institut der Universität, Gievenbecker Weg 9, 4400 *Münster, Federal Republic of Germany*

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Abstract. $C_{40}H_{72}Mo_2N_2O_7S_5$, $[N(C_4H_9)_4]_2[Mo_2O_3S(C_4O_2S_2)_2]$, triclinic, $P\bar{1}$, $a = 13{\cdot}75$ (3), $b = 18{\cdot}44$ (4), $c = 10{\cdot}55$ (2) Å, $\alpha = 80{\cdot}5$ (1), $\beta = 83{\cdot}4$ (2), $\gamma = 83{\cdot}0$ (2)°, $V = 2606{\cdot}4$ Å^3, $Z = 2$, D_m (flotation) = 1·29 (2), $D_x = 1{\cdot}31$ Mg m^{-3}, $F(000) = 1084$. The μ-O-μ-S bridged dimeric complex anion is chelated *trans* to the bridge bonds through S to two 1,2-dithiosquarato dianions. The Mo—Mo distance of 2·700 (1) Å is intermediate between those in the related di-μ-sulfido- and di-μ-oxo-molybdenum(V) dimers. The anion adopts the *syn* configuration.

Introduction. There has been considerable activity in the area of Mo coordination chemistry since it was suggested that Mo has a functional role in various enzymes (Stiefel, 1976; Wentworth, 1976). In particular, the chemistry and structure of complexes with S donor ligands have been studied. Among these ligands we have so far investigated the behavior of the 1,2-dithiooxalate dianion (Mennemann & Mattes, 1979). A very similar ligand is the dianion of 1,2-dithiosquaric acid (dts) (3,4-dimercapto-3-cyclobutene-1,2-dione) (Coucouvanis & Hollander, 1974). Its interesting ligand properties have already been shown (Coucouvanis, Holah & Hollander, 1975; Hollander & Coucouvanis, 1977). The aim of the present work was to study the structure of the complex formed by the reaction of K_2dts with dimeric Mo^V species in aqueous solution, especially with respect to the coordination of Mo, and to study the change in the molecular geometry of the ligand compared to its free state. Suitable crystals of the title compound could be prepared by adding $[N(C_4H_9)_4]$Br in excess to an aqueous solution of $MoCl_5$ and K_2dts in the molar ratio 1:5. A yellow-greenish specimen 0·1 × 0·1 × 0·06 mm was used in the data collection performed on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Using the ω–2θ scan technique and variable scan speeds (2–29·3° min^{-1}), 6423 reflections were collected to $\theta_{max} = 23{\cdot}5°$. Backgrounds were measured at each end of the scan for a total time equal to the scan time. No absorption correction was applied ($\mu = 0{\cdot}67$ mm^{-1}). The structure determination was based on 5064 reflections with $I > 3{\cdot}92\sigma(I)$. The structure was solved using the Syntex *XTL* program system by a combination of Patterson and Fourier methods and refined by full-matrix least-squares calculations.

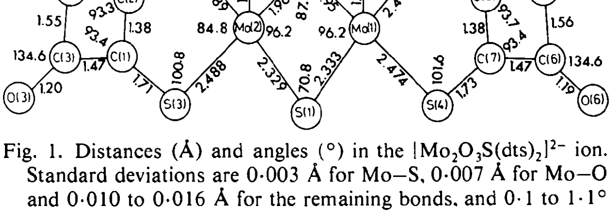

Fig. 1. Distances (Å) and angles (°) in the $[Mo_2O_3S(dts)_2]^{2-}$ ion. Standard deviations are 0·003 Å for Mo—S, 0·007 Å for Mo—O and 0·010 to 0·016 Å for the remaining bonds, and 0·1 to 1·1° for the bond angles.

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Table 1. *Final fractional coordinates* [$\times 10^4$ *for* Mo, S, O, N *and carbon atoms* C(1) *to* C(8); $\times 10^3$ *for the remaining carbon atoms*] *and isotropic temperature factors* (Å^2)

E.s.d.'s are given in parentheses.

	x	y	z	B	Site-occupation factor
Mo(1)	9808 (1)	8221 (0)	2330 (1)	5·3 (0)	1
Mo(2)	1392 (1)	7199 (1)	2387 (1)	5·0 (0)	1
S(1)	713 (2)	7808 (2)	4098 (3)	5·5 (1)	1
S(2)	8284 (2)	8096 (1)	1342 (2)	5·1 (1)	1
S(3)	2243 (2)	6396 (2)	4149 (2)	4·4 (1)	1
S(4)	8665 (2)	8737 (2)	4024 (3)	5·9 (1)	1
S(5)	1527 (2)	6053 (2)	1391 (3)	5·3 (1)	1
O(1)	256 (5)	8974 (4)	1443 (7)	7·7 (4)	1
O(2)	2283 (5)	7668 (4)	1540 (7)	6·8 (4)	1
O(3)	3892 (6)	4636 (4)	4354 (7)	6·1 (4)	1
O(4)	3303 (7)	4371 (4)	1543 (8)	7·0 (4)	1
O(5)	5712 (6)	8939 (5)	1612 (8)	7·9 (5)	1
O(6)	6053 (7)	9562 (5)	4242 (8)	8·1 (5)	1
O(7)	209 (4)	7361 (3)	1459 (6)	5·5 (3)	1
N(1)	7368 (6)	5656 (4)	1988 (6)	3·6 (3)	1
N(2)	2559 (5)	87 (4)	2214 (7)	4·2 (4)	1
C(1)	2688 (7)	5649 (5)	3411 (8)	3·9 (4)	1
C(2)	2410 (7)	5516 (5)	2256 (9)	4·6 (5)	1
C(3)	3365 (8)	4970 (6)	3574 (10)	5·0 (5)	1
C(4)	3063 (8)	4824 (6)	2271 (10)	4·9 (5)	1
C(5)	6377 (8)	8919 (6)	2262 (11)	6·7 (6)	1
C(6)	6555 (9)	9225 (7)	3501 (11)	6·3 (6)	1
C(7)	7569 (7)	8876 (5)	3325 (9)	5·2 (5)	1
C(8)	7411 (7)	8608 (5)	2229 (9)	4·9 (5)	1
C(9)	816 (1)	555 (1)	91 (1)	5·6 (2)	1
C(10)	860 (1)	626 (1)	25 (1)	6·3 (2)	1
C(11)	64 (1)	394 (1)	83 (1)	7·4 (3)	1
C(12)	18 (1)	321 (1)	155 (1)	9·2 (3)	1
C(13)	709 (1)	491 (1)	264 (1)	6·2 (2)	1
C(14)	653 (1)	452 (1)	177 (1)	8·2 (3)	1
C(15)	638 (1)	372 (1)	253 (1)	10·0 (4)	1
C(16)	726 (2)	321 (1)	243 (2)	10·2 (6)	0·66
C(16A)	614 (4)	324 (3)	153 (6)	13·1 (2)	0·33
C(17)	648 (1)	618 (1)	139 (1)	6·5 (2)	1
C(18)	553 (1)	626 (1)	237 (1)	9·1 (3)	1
C(19)	476 (1)	686 (1)	166 (2)	11·7 (5)	1
C(20)	441 (2)	659 (1)	59 (2)	16·3 (7)	1
C(21)	770 (1)	607 (1)	300 (1)	7·2 (3)	1
C(22)	860 (1)	567 (1)	362 (1)	8·4 (3)	1
C(23)	862 (2)	626 (1)	480 (2)	8·8 (5)	0·66
C(23A)	921 (3)	610 (2)	424 (4)	7·8 (9)	0·33
C(24)	60 (2)	411 (1)	455 (2)	15·0 (6)	1
C(25)	245 (1)	967 (1)	107 (2)	4·9 (4)	0·50
C(25A)	330 (2)	−2 (1)	97 (2)	7·5 (5)	0·50
C(26)	329 (1)	941 (1)	28 (1)	8·6 (3)	1
C(27)	683 (1)	87 (1)	83 (2)	7·5 (4)	0·66
C(27A)	605 (2)	75 (2)	74 (3)	5·6 (6)	0·33
C(28)	605 (1)	118 (1)	162 (2)	13·3 (5)	1
C(29)	331 (1)	963 (1)	316 (2)	5·3 (4)	0·50
C(29A)	243 (2)	939 (1)	319 (2)	7·6 (6)	0·50
C(30)	325 (1)	892 (1)	360 (2)	12·2 (5)	1
C(31)	352 (2)	840 (1)	467 (2)	16·6 (7)	1
C(32)	436 (2)	797 (1)	472 (2)	19·0 (9)	1
C(33)	294 (1)	83 (1)	167 (2)	4·9 (4)	0·50
C(33A)	294 (2)	68 (1)	288 (2)	7·6 (6)	0·50
C(34)	300 (2)	128 (1)	268 (2)	5·1 (5)	0·50
C(34A)	286 (2)	145 (2)	214 (3)	9·1 (9)	0·50
C(35)	325 (2)	207 (1)	206 (2)	6·9 (5)	0·50
C(35A)	331 (3)	185 (2)	304 (4)	12·5 (10)	0·50
C(36)	336 (2)	258 (1)	282 (2)	14·9 (6)	1
C(37)	155 (1)	17 (1)	297 (2)	5·3 (4)	0·50
C(37A)	152 (2)	40 (1)	171 (2)	6·7 (5)	0·50
C(38)	79 (1)	64 (1)	247 (1)	9·2 (3)	1
C(39)	982 (2)	66 (2)	307 (3)	9·0 (7)	0·50
C(39A)	972 (2)	89 (2)	205 (3)	10·1 (8)	0·50
C(40)	900 (3)	135 (2)	245 (4)	10·9 (10)	0·50
C(40A)	889 (3)	101 (2)	301 (4)	10·5 (9)	0·50

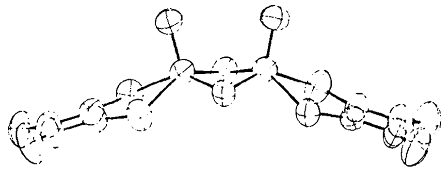

Fig. 2. Side view of the $[Mo_2O_3S(dts)_2]^{2-}$ ion.

The final R and R' [$= (\sum w\Delta^2/\sum wF_o^2)^{1/2}$] values are 0·062 and 0·097, respectively. H atoms were not included because of the size of the parameter matrix and partial disorder within the cations (see below). Only the atoms of the complex anion were refined anisotropically. Atomic coordinates are listed in Table 1. Bond distances and bond angles within the complex ion are given in Fig. 1. Fig. 2 contains a perspective view of the anion.*

Discussion. The X-ray structural determination establishes the stoichiometry of the anion of the title compound to be $[Mo_2O_2(\mu\text{-}OS)(dts)_2]^{2-}$. The geometry about each of the Mo atoms in the binuclear ion is best described as a distorted square pyramid. Equivalent bond distances and angles in both halves of the dimer are very similar in magnitude. Two S atoms from the dts ligand (S_L), the bridging S atom (S_b) and the bridging O atom (O_b) form the basal plane; the axial sites are occupied by O atoms. The molecule adopts the *syn* configuration and each Mo atom is displaced 0·68 Å from the basal plane towards the axial atom.

An unusual feature of the structure is the kind of bridge between the Mo atoms. The mixed O–S bridge has been found so far in only two further compounds: $Mo_2O_3S[S_2CN(n\text{-}C_3H_7)_2]_2$ (Dirand-Colin, Ricard & Weiss, 1976), and $Cs_2[Mo_4O_6S_2(C_2O_4)_5].H_2O$ (Mennemann & Mattes, 1979). The Mo···Mo distances in these compounds and in the present study [2·700 (1) Å] are intermediate between those found in the (μ-OO) and (μ-SS) dimers, 2·51–2·56 Å and 2·80–2·86 Å respectively (Newton, McDonald, Yamanouchi & Enemark, 1979). The same is valid for the S_b—Mo—O_b angles. The presence of some strain in the mixed bridge is documented by the Mo—S_b—Mo bond angle of 70·8 (1)° which is 4–6° smaller than in (μ-SS) dimers, and by the Mo—O_b—Mo angle of 87·3 (2)° which is larger by the same amount than in (μ-OO) dimers. The Mo—O_b and Mo—O_t distances are in the range observed for other compounds with Mo_2O_4, Mo_2O_3S or $Mo_2O_2S_2$ cores. The Mo—S_b distances, 2·329 (3) and 2·333 (3) Å, are at the higher end of the range observed

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35238 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in these compounds. The dihedral angle between the planes O(7)—Mo(1)—S(1) and O(7)—Mo(2)—S(1) is 145°, a value which is usual for five-coordinated Mo^V dimers. The Mo—S_L bond lengths vary between 2·474 (3) and 2·495 (3) Å (mean 2·486 Å). Only at Mo(1) is there a significant difference between the bond lengths *cis* and *trans* to the μ-S bond, 2·474 (3) and 2·495 (2) Å respectively. This shows the greater *trans* effect of a μ-MoS bond relative to a μ-MoO bond, as already mentioned by Mennemann & Mattes (1979). The mean Mo—S_L bond length is significantly longer (0·04 to 0·08 Å) than in other Mo^V complexes with uni- and bidentate S donor ligands (Newton, McDonald, Yamanouchi & Enemark, 1979; Dance, Wedd & Boyd, 1978). dts is obviously a rather poor ligand towards Mo^V.

The six π electrons in the free ligand are at least partially delocalized (D. Altmeppen & R. Mattes, in preparation). The delocalization is removed to a great extent in the complex. This is reflected by the decrease from 1·43 (1) to 1·38 (1) Å of the C—C bond between the two C—S bonds; d(CO) and d(CS) in the complex may be compared with the structure of the free ligand as well. But, unfortunately, it has not so far been possible for us to determine the structure of $K_2dts.H_2O$ completely. A comparison of these parameters with those of the 1,2-dithiooxalate ion (Mattes & Meschede, 1976) or the *S*-methyl-1,2-dithiooxalate ion (Mattes, Meschede & Niemer, 1977) seems to be adequate. Here d(CS) and d(CO) vary between 1·69–1·70 Å and 1·21–1·22 Å respectively. In the present complex d(CS) (mean 1·718 Å) has slightly increased and d(CO) (mean 1·200 Å) has slightly decreased. This trend in molecular geometry of the ligand is also indicated by the increase of the C—O stretching vibrations from 1620 and 1700 cm^{-1} in the free ligand to 1700 and 1730 cm^{-1} in the complex.

One of the two symmetrically independent $[N(C_4H_9)_4]^+$ ions is strongly disordered. Already in the first coordination sphere around the N atom eight C atoms were found at the corners of a distorted cube [C(25), C(25*A*), C(29), C(29*A*), C(33), C(33*A*), C(37) and C(37*A*)]. They could be refined well with site-occupation factors of 0·5. Their *B* values range from 4·9 (4) to 7·6 (6) $Å^2$. Further splitting was necessary at the periphery of both cations. In total, 43 C atoms for both cations have been included in the refinement, with site-occupation factors ranging from 0·33 to 0·67 and isotropic temperature factors ranging from 5·1 to 16·6 $Å^2$.

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{2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}-nitritonitronickel(II) Hemihydrate

By Michael G. B. Drew and Stephen Hollis†

Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, England

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Abstract. $C_{15}H_{26}N_6NiO_4.\frac{1}{2}H_2O$, M_r = 421·9, monoclinic, a = 11·450 (8), b = 11·677 (8), c = 14·490 (9) Å, β = 91·1 (1)°, U = 1937·0 $Å^3$, Z = 4, D_m = 1·45, D_c = 1·45 Mg m^{-3}, F(000) = 892, Mo $K\alpha$ radiation, λ = 0·7107 Å, μ = 1·041 mm^{-1}; space group $P2_1/a$ from the systematic absences $h0l$, $h = 2n + 1$, $0k0$, $k = 2n + 1$. The Ni atom in the complex occupies an approximately octahedral environment with the four

† Deceased.

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