Crystal and Molecular Structure of Dicaesium μ-(Ethylenediaminetetra-acetato)-di-μ-sulphido-bis[oxomolybdate(V)] Dihydrate

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The crystal and molecular structure of the title compound was determined by Patterson and Fourier methods from *X*-ray diffraction data collected by counter methods. Crystals are orthorhombic, space group *Pnam*, with $Z = 4$ in a unit cell of dimensions: $a = 12{\cdot}385(3)$, $b = 7{\cdot}108(3)$, $c = 24{\cdot}537(3)$ Å. Full-matrix least-squares refinement of 2196 reflections gave R 0·059. The hexadentate ethylenediaminetetra-acetate (edta) ligand co-ordinates to each molybdenum atom through two carboxylato-oxygens and a nitrogen while two bridging sulphur atoms and a terminal oxygen complete the co-ordination sphere around each molybdenum. The short Mo–Mo bond [2·799(1) Å] suggests that the co-ordination geometry around each metal atom may be described as a distorted capped octahedron sharing a common edge determined by the two sulphur atoms. The molecule possesses a mirror plane, passing through the two sulphur atoms, which necessitates disorder in the ethylenic carbon atoms of the bridging edta ligand.

THE sulphur atom is an important ligand in certain biological systems, *e.g.* in some molybdenum-containing enzymes the molybdenum atom is believed to be bound, at least in part, to the sulphur atom of a cysteine residue.[1] The role of sulphido-ions is exemplified in the non-heme iron proteins, the ferredoxins, where it is known that sulphido-bridges play a vital role in their function.[2] Thus, complexes of biologically important transition-metals containing sulphido-bridges or thiol ligands are of considerable interest as possible model compounds for such enzymes, particularly for water-soluble complexes containing simple σ-donor ligands such as α-amino-acids.

Recently, several sulphido-bridged complexes of Mo^V have been isolated [3,4] and the crystal structure analysis for two of these have been reported.[5,6]

As part of our study of the chemical and structural aspects of sulphido-bridged complexes of molybdenum, we now report the structure of the title compound, $Cs_2[Mo_2S_2O_2(edta)],2H_2O$.

EXPERIMENTAL

The complex was prepared by slowly bubbling H_2S through an aqueous solution of $Cs_4[(MoO_3)_2(edta)]$, which was prepared in an analogous manner to the sodium salt.[7] Filtration and evaporation of the resulting red solution on a hot-plate yielded a red-orange crystalline material {Found: C, 13·5; H, 1·85; N, 3·2; S, 7·2. $Cs_2[Mo_2S_2O_2(edta)],2H_2O$ requires C, 13·65; H, 1·8; N, 3·2; S, 7·3%}. Red-orange prismatic crystals suitable for *X*-ray structural analysis were obtained by slow evaporation of a water solution of the complex.

Crystal Data.—$C_{10}H_{16}Cs_2Mo_2N_2O_{12}S_2$, $M = 879{\cdot}22$, Orthorhombic, $a = 12{\cdot}385(3)$, $b = 7{\cdot}108(3)$, $c = 24{\cdot}537(3)$ Å, $U = 2166{\cdot}7$ Å^3, $D_m = 2{\cdot}70$ (by flotation), $Z = 4$, $D_c = 2{\cdot}70$, Mo-K_α (graphite monochrometer) radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 47·3 cm^{-1}. Space group *Pnam* (D_{4h}^{17}, No. 53) or $Pna2_1$ (C_{2v}^{9}, No. 33) from systematic absences: $0kl$ for $k + l$ odd and $h0l$ for h odd; shown to be the former.

A crystal of dimensions $0{\cdot}1 \times 0{\cdot}1 \times 0{\cdot}3$ mm was selected and mounted perpendicular to the prismatic axis. Preliminary unit-cell and space-group data were obtained from precession and Weissenberg photographs. Unit-cell dimensions were obtained from back-reflection Weissenberg and inclined beam oscillation photographs with Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å).[8]

By use of equi-inclination Weissenberg geometry, intensity data were collected for the levels 0—10*kl* on a Stoe semi-automatic diffractometer by the stationary-background—$\omega/2\theta$ scan—stationary-background counting sequence. Data were collected to $\sin\theta$ 0·82. Crystal alignment was checked before and after data collection for each level, and crystal stability was monitored by measurement of 2 standard reflections for each level after every 20 reflections. No significant variations from the mean (*i.e.* <2·5%) were observed in the intensities of the standards throughout the data collection.

The intensity of the *hkl* reflection was calculated as: $I(hkl) = \left(C - \dfrac{B \times T}{T_1}\right)$ where C is the total count, B is the total background count, T is the scan time, and T_1 is the sum of the background times. Data were assigned standard deviations according to $\sigma(I) = [C - B(T/T_1)^2 + B^2(T/T_1)^2]^{\frac{1}{2}}$. Intensities were corrected for absorption (transmission factors ranged from 0·283 to 0·639), Lorentz and polarization effects. The F_o values were brought to an approximate scale through a modification of Wilson's procedure.

A statistical analysis of normalized $|E|$ values [9] suggested that the correct space group is the centrosymmetric one, *Pnam* (Table 1), and this was confirmed by the subsequent successful refinement.

In addition to the Setting and Data processing programs supplied by Stoe Co., the main programs used in this work were local modifications of the Busing–Levy ORFLS least-squares program, the Zalkin FORDAP Fourier program, and Johnson's ORTEP plotting program. Various other local programs were also used. All computing was performed on the Technion's IBM 370/165 computer.

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[1] R. C. Bray and J. C. Swann, *Structure and Bonding*, 1972, **11**, 107.

[2] J. C. Tsibris and R. W. Woody, *Co-ordination Chem. Rev.*, 1970, **5**, 417; L. C. Sieker, E. Adman, and L. H. Jensen, *Nature*, 1972, **235**, 40.

[3] B. Spivack and Z. Dori, *Chem. Comm.*, 1970, 1716.

[4] A. Kay and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1970, 2421.

[5] B. Spivack, A. P. Gaughan, and Z. Dori, *J. Amer. Chem. Soc.*, 1971, **93**, 5265.

[6] M. G. B. Drew and A. Kay, *J. Chem. Soc.* (*A*), 1971, 1851.

[7] R. L. Pecsok and D. T. Sawyer, *J. Amer. Chem. Soc.*, 1956, **78**, 5696.

[8] F. H. Herbstein, *Acta Cryst.*, 1963, **16**, 255.

[9] P. T. Beurskens and J. H. Noordik, *Acta Cryst.*, 1971, **A27**, 187.

Solution and Refinement of Structure.—The positions of the caesium and molybdenum atoms were determined from a three-dimensional Patterson function. After three cycles of refinement (*vide infra*) of the positional parameters of the two atoms and their isotopic temperature factors, the R was 0·27 and R' 0·33 $\{R' = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o{}^2]^{\frac{1}{2}}\}$. A difference-Fourier map based on the phases of the heavy atoms revealed the positional parameters of all other atoms except for the water molecule and the ethylenic carbon atoms, which must be disordered if our choice of the centric space group is correct. The sulphur atoms were found to lie on the mirror plane at $Z = 1/4$ and each was assigned an occupancy factor of 0·5 in the least-squares refinement.

TABLE 1

Statistical distribution of $|E|$ values and comparison with theoretical values for determining space group

	Obs.	Centrosymmetric	Non-centrosymmetric
Mean $\|E\|$	0·7878	0·798	0·886
Mean $\|E\|^2$	1·0000	1·000	1·000
Mean $\|E^2 - 1\|$	0·9873	0·968	0·736
$\|E\| > 3$	0·44%	0·27%	0·01%
$\|E\| > 2$	4·53%	4·55%	1·83%
$\|E\| > 1$	30·16%	31·73%	36·79%

The trial structure was refined by a least-squares procedure, the function minimized being $\Sigma\omega(|F_o| - |F_c|)^2$; the weights were arbitarily assigned as $\omega = 1/7$ for $|F_o| < 49$ and $\omega = (1/F_o)^{\frac{1}{2}}$ for $|F_o| > 49$. Refinement of the structure was based only on those reflections for which $F_o{}^2 > 3\sigma(F_o)^2$. In these calculations, neutral atomic scattering factors were taken from ref. 10. The anomalous dispersion effects were included in the calculation with the values of $\Delta f'$ and $\Delta f''$ for Cs, Mo, and S taken from ref. 11. This refinement of positional and isotropic thermal parameters converged to discrepancy factors R 0·132 and R' 0·157. A difference-Fourier map based upon this refinement clearly revealed two orientations for the ethylenic group and the position of the water molecule. Three cycles of full-matrix least-squares refinement of the complete structure, in which the ethylenic carbon atoms were assigned occupancy factors of 0·5, including scale factors, positional and isotropic thermal parameters converged to R 0·089 and R' 0·102. An additional three cycles of anisotropic refinement converged to the final discrepancy indices of R 0·059 and R' 0·070. Refinement of the structure in the noncentrosymmetric space group $Pna2_1$ led to higher discrepancy factors, and the bond angles and the bond distances showed unrealistic deviations from accepted values.

The parameters obtained from this refinement are considered as the final parameters of this structure determination. The largest parameter shifts were $<0·1\sigma$. The estimated standard deviation of an observation of unit weight is 0·82 electrons and the final difference Fourier map shows peak heights *ca.* 10% of those found for a carbon atom in this structure. The parameters obtained from the final refinement are presented in Table 2 along with their estimated standard deviations. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20667 (3 pp., 1 microfiche).*

TABLE 2

Final positional and thermal parameters ($\times 10^4$) [a]

Atom	X	Y	Z	β_{11} [b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs	1615(1)	1307(1)	313(0)	45(1)	146(1)	11(0)	−11(1)	−2(0)	−3(0)
Mo	2065(1)	3246(1)	1930(0)	14(1)	65(1)	11(0)	−6(1)	−2(0)	−6(0)
S(1)	3411(3)	2248(4)	2500	21(3)	68(4)	14(1)	10(2)	0	0
S(2)	1023(3)	5056(4)	2500	6(3)	90(5)	13(1)	7(2)	0	0
O(1)	1394(7)	4748(9)	1265(3)	72(8)	118(12)	13(1)	0(7)	11(2)	2(3)
O(2)	3112(6)	2649(12)	1277(3)	41(6)	260(2)	10(1)	2(8)	3(2)	−24(4)
O(3)	1404(9)	7074(14)	671(4)	76(10)	295(24)	27(2)	−12(1)	−10(3)	48(6)
O(4)	4213(9)	3598(17)	638(3)	61(9)	535(37)	14(1)	95(13)	17(3)	19(6)
O(5)	1341(7)	1295(9)	1805(3)	42(7)	103(11)	21(2)	−20(6)	−6(2)	−13(3)
H_2O	4238(8)	−662(13)	489(4)	481(8)	255(20)	22(2)	−29(10)	59(3)	21(5)
N	3164(8)	6064(11)	1793(3)	51(8)	139(14)	8(1)	−44(8)	3(2)	−4(3)
C(1)	2497(10)	7357(13)	1482(5)	35(10)	86(14)	27(2)	−1(9)	11(4)	6(5)
C(2)	1704(9)	6332(13)	1108(5)	15(9)	143(8)	20(2)	14(8)	0(30)	14(5)
C(3)	4060(11)	5464(16)	1456(44)	55(12)	212(23)	15(2)	−27(12)	8(3)	19(5)
C(4)	3813(11)	3815(18)	1094(4)	41(11)	286(29)	11(2)	58(1)	2(3)	6(5)
C(5)	3897(14)	6764(23)	2259(6)	−31(14)	125(29)	128(2)	−2(14)	−1(4)	5(6)
C(5) * [c]	3275(15)	7521(20)	2241(6)	26(15)	52(22)	8(2)	−6(14)	−0(4)	−4(6)

[a] Estimated standard deviations in the least significant figure in this and following Tables are given in parentheses. [b] The form of the anisotropic thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}kl + 2\beta_{23}kl)]$. [c] Carbon atom of the second conformer.

DISCUSSION

Description of the Structure.—A drawing of the $[Mo_2S_2O_2(edta)]^{2-}$ anion showing the atom numbering is presented in Figure 1, and the important bond lengths and bond angles are listed in Table 3. The sexadentate edta ligand co-ordinates to each molybdenum atom through two carboxylato-oxygens and one nitrogen (Figure 1). Two sulphur atoms and a terminal oxygen atom complete the co-ordination sphere around each molybdenum. By taking the Mo–Mo bond into consideration, the co-ordination geometry around each metal atom can be described as a distorted capped octahedron (*vide infra*), in which the two octahedra share a common edge determined by the two sulphur atoms.

The six atoms O(1), O(2), S(1), S(2), O(1′), and O(2′) (primed atoms are related by a mirror plane) define a plane (Table 4) from which the molybdenum atoms are displaced by 0·37 Å towards the molybdenyl oxygens.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[10] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[11] 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, Table 3.3.2.

Similar behaviour occurs in the complexes $[Mo_2S_2O_2(histidine)_2]$ and $[Mo_2O_4(cysteine)_2]^{2-}$, where the molybdenum displacement was found to be 0·32 and 0·38 Å respectively.[5,12] It is reasonable to suggest that this tetragonal distortion is due to the multiple bonding between the molybdenum and the molybdenyl oxygen atom, resulting in a short Mo–O distance of 1·682(1) Å. This short bond length is by no means unusual; in fact, in all complexes of Mo^V and Mo^{VI} containing molybdenyl oxygens, the Mo–O bond length was found to lie between 1·67 and 1·74 Å. The out-of-plane displacement of the molybdenum and the large *trans*-effect imposed by the oxygen atom are undoubtedly responsible for the long Mo–N distance of 2·448(1) Å. This lengthening of the bond *trans* to a molybdenyl oxygen has been observed previously.[12,13] The Mo–O(1) and Mo–O(2) distances of 2·120(6) and 2·102(7) Å are within the expected values for σ bonded oxygens to Mo^V,[14] and the difference between the two bond lengths is not chemically significant.

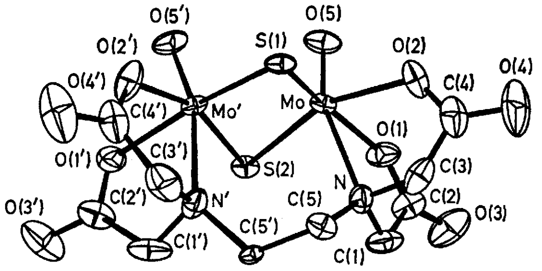

FIGURE 1 The anion $[Mo_2S_2O_2(edta)]^{2-}$

TABLE 3

Significant intramolecular distances (Å) and angles (°)

(*a*) Distances			
Mo–Mo′	2·799(1)	C(2)–C(1)	1·53(2)
Mo–S(1)	2·289(1)	C(1)–N	1·45(1)
Mo–S(2)	2·298(1)	O(2)–C(4)	1·29(2)
S(1)–S(2)	3·568(4)	O(4)–C(4)	1·23(1)
Mo–O(5)	1·683(6)	C(4)–C(3)	1·50(2)
Mo–O(1)	2·120(6)	C(3)–N	1·45(1)
Mo–O(2)	2·102(7)	N–C(5)	1·53(2)
Mo–N	2·448(8)	N–C(5)*	1·52(2)
O(1)–C(2)	1·25(2)	C(5)–C(5)*′	1·54
O(3)–C(2)	1·25(2)		
(*b*) Angles			
S(1)–Mo–S(2)	102·1(1)	O(1)–Mo–O(2)	75·9(5)
Mo–S(1)–Mo′	75·4(1)	O(2)–Mo–N	73·6(4)
Mo–S(2)–Mo′	75·0(1)	O(2)–Mo–O(5)	91·5(5)
S(1)–Mo–N	86·1(2)	O(5)–Mo–N	161·6(6)
S(1)–Mo–O(5)	104·3(2)	Mo–O(1)–C(2)	124·7(8)
C(1)–N–C(5)*	89·8(8)	O(1)–C(2)–O(3)	123·6(1·0)
C(3)–N–C(5)	94·6(9)	O(1)–C(2)–C(1)	116·2(1·0)
C(3)–N–C(5)*	123·4(9)	O(3)–C(2)–C(1)	120·2(1·0)
N–C(5)–C(5)*′	115·1(1·1)	C(2)–C(1)–N	112·4(8)
N–C(5)*–C(5′)	112·4(1·0)	C(1)–N–Mo	105·7(6)
S(1)–Mo–O(1)	139·6(2)	Mo–O(2)–C(4)	123·7(7)
S(1)–Mo–O(2)	87·4(2)	O(2)–C(4)–O(4)	120·4(1·2)
S(2)–Mo–N	86·4(2)	O(2)–C(4)–C(3)	115·6(9)
S(2)–Mo–O(5)	105·7(2)	O(4)–C(4)–C(3)	124·0(9)
S(2)–Mo–O(1)	82·0(2)	C(4)–C(3)–N	114·6(1·0)
S(2)–Mo–O(2)	157·3(2)	C(3)–N–Mo	105·2(6)
O(1)–Mo–N	72·6(4)	C(3)–N–C(1)	108·9(8)
O(1)–Mo–O(5)	93·7(4)	C(1)–N–C(5)	121·2(8)

TABLE 4

Equations of least-squares planes[a] for several bridged molybdenum structures, with distances (Å) of atoms from the planes in square brackets

(*a*) $Cs_2[Mo_2S_2O_2(edta)],2H_2O$

Plane (1):

S(1), S(2), O(1), O(1′), O(2), O(2′)	$0{\cdot}5607X + 0{\cdot}8282Y + 0{\cdot}0Z - 3{\cdot}7149 = 0$

[S(1) −0·02, S(2) −0·03, O(1) 0·05, O(1′) 0·05, O(2) 0·01, O(2′) 0·01, Mo −0·37, Mo′ −0·37]

Plane (2):

Mo, O(2), C(4), C(3), N	$0{\cdot}6525X - 0{\cdot}3870Y + 0{\cdot}6514Z - 3{\cdot}8613 = 0$

[Mo 0·0, O(2) −0·04, C(4) −0·08, C(3) 0·24, N −0·10]

Plane (3):

Mo, O(1), C(2), C(1), N	$-0{\cdot}6144X + 0{\cdot}4522Y + 0{\cdot}6455Z - 2{\cdot}5327 = 0$

[Mo 0·0, O(1) −0·06, C(1) 0·28, C(4) −0·04, N −0·15]

Plane (4):

Mo, Mo′, O(5), O(5′), N, N′	$0{\cdot}8282X - 0{\cdot}5604Y + 0{\cdot}0Z - 0{\cdot}8303 = 0$

[Mo −0·01, Mo′ −0·01, O(5) 0·03, O(5′) 0·03, N −0·0, N′ 0·0]

(*b*) $Mo_2S_2O_2(histidine)_2$ [b]

Plane:

S(1), S(2), N(1), N(2), N(1′), N(2′)	$0{\cdot}5207X + 0{\cdot}5078Y + 0{\cdot}6863Z - 1{\cdot}4734 = 0$

[S(1) 0·04, S(2) 0·03, N(1) −0·12, N(2) 0·04, N(1) −0·09, N(2′) 0·01, Mo(1) 0·32, Mo(2) 0·24]

(*c*) $Na_2[Mo_2O_4(cysteine)_2]$ [c]

Plane :

S(1), S(2), N(1), N(2), O(1), O(2)	$-0{\cdot}0496X - 0{\cdot}9982Y + 0{\cdot}0327Z + 13{\cdot}3159 = 0$

[S(1) 0·03, S(2) 0·03, N(1) 0·03, N(2) 0·04, O(1) −0·07, O(2) −0·10, Mo(1) −0·42, Mo(2) −0·41]

[a] Given in directional cosines. [b] Unpublished results. [c] Parameters taken from ref. 12.

The two crystallographic independent glycinato-rings [ring (I): Mo, O(2), C(4), C(3), N; ring (II): Mo, O(1), C(2), C(1), N] are not planar (Table 4), and the sums of their internal angles are 532·7 and 531·6°, which, according to the criteria established by Hoard,[15] indicates that some strain exists in the two rings. Chemically equivalent bond distances and bond angles in the crystallographically independent glycinato-rings are nearly the same and similar to those found in other complexes containing the edta ligand (Table 3).

The presence of the crystallographic mirror plane in the molecule requires the ethylenic carbon atoms to be disordered. The appearance of two distinct peaks on the difference-Fourier map and the reasonable temperature factors obtained for these carbon atoms, when

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[12] J. R. Knox and C. K. Prout, *Acta Cryst.*, 1969, **B25**, 1857.

[13] A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Amer. Chem. Soc.*, 1964, **86**, 3024.

[14] F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, 1965, **4**, 1377.

[15] J. J. Park, M. D. Glick, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1969, **91**, 301, and references therein.

assigned a multiplicity of 0·5, suggests that the disorder is two-fold, resulting in equal amounts of two conformers which are related to one another by flipping of the two carbon atoms. This flipping, which involves rotation about the C–N and the Mo–N bonds, necessitates movement of the glycinato-rings. However, the crystal structure analysis clearly indicates that the molecule is rigid and without any disorder except for the ethylenic carbon atoms. This rigid configuration imposes considerable amount of strain on the ethylenic bridge which manifests itself in the angles subtended by the two nitrogen atoms. Thus, for one of the conformations, the angles C(1)–N–C(5) and C(3)–N–C(5) are 121·2(8) and 94·6(9)° respectively, while for the other conformer, the respective angles at 89·8(8) and 123·4(9)°.

The rigidity of the complex appears to be maintained in solution as is evident from its complicated n.m.r. spectra which suggests that the two conformers are not interconverted at room temperature.[3] In contrast, the analogous oxo-bridged complex $[Mo_2O_4(edta)]^{2-}$, whose solid-state structure has been shown to be similar to that of $[Mo_2S_2O_2(edta)]^{2-}$, exhibits an n.m.r. spectra consisting of an AB quartet and a singlet at a higher field,[16] suggesting that rapid interconversion of the two conformers occurs in solution. The different behaviour exhibited by these two complexes is undoubtedly related to the larger dimensions of the Mo_2S_2 bridge and particularly the longer Mo–Mo distance.

TABLE 5

Structural parameters of several oxo- and sulphido-bridged complexes of molybdenum

	Mo–Mo	Mo–S	Mo–O [a]	Mo–N	Mo–X–Mo	X–Mo–X	Dih. Ang.	Mo–Mo–O	Mo–Mo–Y *	Mo displacement
$Cs_2[Mo_2S_2O_2(edta)]$,-$2H_2O$	2·779	2·289	1·682(t) 2·120(c) 2·102(c)	2·448	X = S 75·0	X = S 102·1	152·3	100·5	Y = N 97·9	0·37
$Mo_2S_2O_2$-(histidine)$_2$ [b]	2·82	2·32	1·72(t) 2·23(c)	2·24	X = S 74·8	X = S 103·5	153·0	99·9	Y = O 98·0	0·32
$Mo_2S_2O_2$-(cyst-Me-ester)$_2$ [c]	2·804	2·31(b) 2·37(c)	1·65	2·23	X = S 75·0	X = S 102·2				
Mo_2O_4(cyst-Et-ester)$_2$ [d]	2·562	2·38(c)	1·67(t) 1·93 (b)	2·23	X = O 83·0	X = O 93·0				
$Na_2[Mo_2O_4$-(cysteine)$_2]$ [e]	2·569	2·490(c)	1·71(t) 1·93(b) 2·30(c)	2·33	Y = O 83·0	X = O 93·0	151·0	99·7	Y = O 96·2	0·38
$[(\pi\text{-}C_5H_5)Mo_2O_2]S_2$	2·894	2·32	1·68(t)		X = S 77·3	X = S 103·0				
MoS_2 [g]		2·35								

[a] b, c and t Refer to bridging, complexed, and terminal atoms respectively. [b] Ref. 5. [c] A five-co-ordinate sulphido-bridged complex of Mo^V; M. G. B. Drew and A. Kay, *J. Chem. Soc. (A)*, 1971, 1851. [d] A five-co-ordinate oxo-bridged complex of Mo^V; footnote (*c*), p. 1846. [e] Ref. 12. [f] This structure has *trans*-molybdenyl oxygen atoms; D. L. Stevenson and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 3720. [g] R. G. Dickinson and L. Pauling, *J. Amer. Chem. Soc.*, 1923, **45**, 1466.

* Y is the atom *trans* to the molybdenyl oxygen.

The dimensions of the Mo_2S_2 bridge are similar to those found in other sulphur bridged molybdenum complexes (Table 5). The six atoms Mo, Mo′, O(5), O(5′), N, and N′ lie on a plane which is perpendicular to the S(1) ··· S(2) vector and having an arrangement as depicted in Figure 2 (the atoms O, S, and O′ are projected on this plane). The O(5) ··· O(5′) non-bonded distance [3·411(7) Å] is considerably larger than the sum of the van der Waal's radii[17] (2·80 Å) for two oxygen atoms. This coupled with the Mo–Mo distance of 2·799(1) Å results in an obtuse Mo–Mo–O bond angle of 100·5° which can be thought to arise from non-bonded repulsions between the Mo–Mo and the Mo–O bonds as predicted by the Nyholm–Gillespie model.[18] Similarly, the obtuse Mo–Mo–N bond angle of 97·9°, leads to an N–N distance of 3·47(3) Å, which is intermediate between values for those complexes having the edta ligand bound to one metal atom (*i.e.* N–N *ca.* 2·88 Å) and the maximum distance of 3·87 Å found in $[(MoO_3)_2(edta)]^{4-}$.[15] In the related complexes $[Mo_2S_2O_2(histidine)_2]$ and $[MoO_4$-$(cysteine)_2]^{2-}$, the Mo–Mo–Y angles (where Y is *trans* to the molybdenyl oxygen) are also larger than 90° (Table 5).

The strong Mo–Mo bond, which results in the diamagnetism of the complex, coupled with the displacement of the molybdenum atom towards the molybdenyl oxygen (*vide supra*) is undoubtedly responsible for the dihedral angle of 152·3(2) Å, between the planes Mo, S(1), S(2) and Mo′, S(1), S(2). Thus it is reasonable to

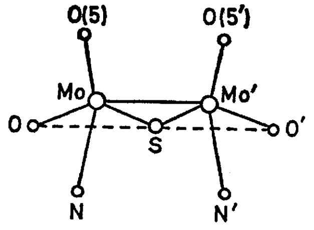

FIGURE 2

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[16] L. V. Haynes and D. T. Sawyer, *Inorg. Chem.*, 1967, **6**, 2146.

[17] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, p. 260.

[18] R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, 1957, **11**, 339; R. J. Gillespie, *Angew. Chem. Internat. Edn.*, 1967, **6**, 819.

consider each molybdenum atom as being seven-coordinate with a distorted capped octahedral geometry.

Unit cell.—A stereoscopic drawing of the unit cell is presented in Figure 3. Each caesium atom is surrounded by six oxygen atoms in a distorted octahedral geometry at distances ranging from 3·07 to 3·36 Å. The mean Cs–O distance of 3·17 Å is 0·10 Å larger than that predicated by Pauling.[19] Hydrogen bonding in the crystal is confined to only two weak interactions between the water molecule and the uncomplexed carboxylato-oxygens O(3) and O(4) of different molecules. The bond distances found are 2·91 and 3·05 Å with a bond angle of 109·5° between O(3) · · · O(H_2O) · · · O(4).

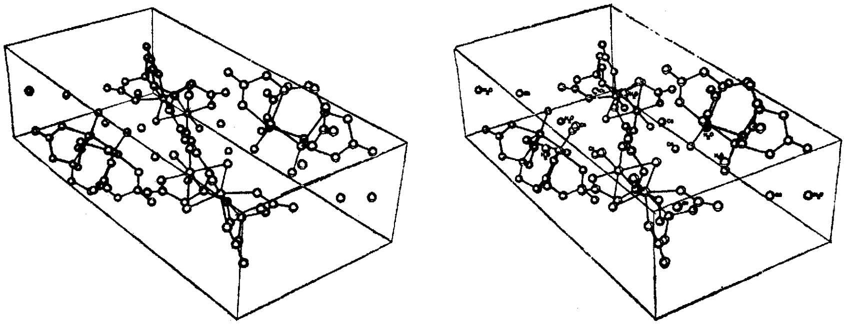

FIGURE 3 Stereoscopic drawing of the unit cell

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[19] Ref. 7, p. 257.