Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

For standard deviations, see Table 2.

Bond (X–H···Y)	X···Y	X–H	H···Y	X–H···Y
O(1)–H1(01)···N(21)*	3·154	0·84	2·48	139
O(1)–H1(01)···N(22)*	2·968	0·84	2·21	150
O(1)–H2(01)···N(14)	3·040	0·71	2·36	162
O(2)–H1(02)···N(13)	3·190	1·06	2·14	168
O(2)–H2(02)···N(13^{i})	2·971	0·95	2·07	160
O(3)–H1(03)···O(1)	2·838	0·88	1·98	166
O(3)–H2(03)···O(2)	2·978	0·89	2·11	167

* Asymmetrically bifurcated.

comparison of all intramolecular distances less than 3·5 Å on both sides of this line, gave a linear array with slope $m = 1·30$ (6) and zero intercept at $y_o = 0·15$ (6). The values of slope and intercept could not be interpreted as significant for the existence of any bias because the data are not independent, but the linearity of the plot, and consequently the high value of the correlation coefficient of the fit ($r = 0·98$), support the above-mentioned symmetry of the molecule. A similar comparison applied to the free DMP molecule also gives a linear array, $m = 2·49$ (8), $y_o = 0·25$ (8), and a correlation coefficient for the fit of $r = 0·99$, which also confirms the existence of a twofold axis in this molecule. A comparison of both DMP molecules gives a straight line with $m = 4·1$ (1), $y_o = -0·6$ (1) and $r = 0·98$, indicating their geometrical identity. The interatomic distances less than 3·5 Å obtained by averaging both DMP molecules in the present compound have also been compared with the corresponding distances in the DMP molecule of the $Zn(CN)_2$DMP adduct (Monge, Martinez-Ripoll & Garcia-Blanco, 1977). A linear array was obtained with $m = 1·58$ (2), $y_o = 0·06$ (2) and $r = 1·00$. The high value of the correlation coefficient indicates the DMP molecules were identical in both adducts. The value of the zero intercept, within its standard deviation, shows no bias in either experiment. The value of the slope indicates that the calculated standard deviations for the interatomic distances of both compounds are underestimated by a factor of 1·58.

Most of the calculations were carried out using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of the Centro de Proceso de Datos del Ministerio de Educación y Ciencia, Madrid, for the facilities provided on the 1108 Univac computer.

References

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* **A27**, 157–165.

Cano, M., Santos, A. & Ballester, L. (1977). *Inorg. Chim. Acta*, **21**, 41–46.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Main, P., Woolfson, M. M., Declercq, J. P. & Germain, G. (1974). *MULTAN. A Computer Program for the Automatic Solution of Crystal Structures*, Univ. of York, England.

Martínez-Ripoll, M. & Cano, F. H. (1975). *PESOS* program. Instituto Rocasolano, CSIC, Serrano 119, Madrid-6, Spain.

Monge, A., Martínez-Ripoll, M. & García-Blanco, S. (1977). *Acta Cryst.* **B33**, 2329–2331.

Rich, A. & Davidson, N. (1968). *Structural Chemistry and Molecular Biology*, p. 456. San Francisco: Freeman.

Schwarzenbach, D. (1972). *ORABS* program, Zürich.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1978). **B34**, 2850–2853

Caesium Di-μ-sulphido-bis[aquaoxalatooxomolybdate(V)] Dihydrate

By W. S. McDonald

Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT, England

(*Received* 3 *April* 1978; *accepted* 12 *May* 1978)

Abstract. $C_4H_8Cs_2Mo_2O_{14}S_2$, $M_r = 801·9$, monoclinic, $P2_1/n$, $a = 12·427$ (3), $b = 16·197$ (2), $c = 9·590$ (3) Å, $\beta = 109·77$ (2)°, $Z = 4$, $D_x = 2·933$ g cm^{-3}, $V = 1816$ (1) Å^3, μ(Mo $K\alpha$) = 55·5 cm^{-1}. The binuclear complex anion approximates C_2 symmetry, with the aqua- and μ-sulphido ligands all *cis* to the oxo ligand. There is no detectable *trans* influence of the oxo ligand, the Mo—O(oxalate) bond lengths *trans* to oxo being 2·155 (5) and 2·164 (6) Å while those *trans* to S are 2·159 (5) and 2·166 (5) Å.

Introduction. Armstrong, Shibahara & Sykes (1978) describe the preparation of this compound, and they provided a sample of good crystalline quality for use in this work. Features of particular interest are the di-μ-sulphido Mo^V dimer with its Mo—Mo interaction, and the *trans* influence of the multiply-bonded oxo ligand.

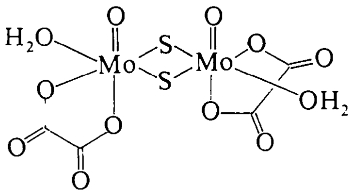
Measurements were made on a Syntex $P2_1$ diffractometer using monochromatized Mo $K\alpha$ radiation (λ = 0·71069 Å). Cell dimensions and their e.s.d.'s were obtained by least-squares treatment of the setting angles of 15 reflexions having $35 < 2\theta < 40°$. The structure analysis used the 1552 independent reflexions in the range $5 < 2\theta < 40°$ and with $I \geq 3\sigma(I)$ [$\sigma(I)$ based on counting statistics]; 155 reflexions with $I < 3\sigma(I)$ were excluded. Lorentz, polarization and absorption corrections were applied and the structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971). Least-squares refinement of coordinates and anisotropic temperature factors for all non-hydrogen atoms converged at R = 2·78% and R' = 3·55%. A difference map now showed, as its most prominent feature, a peak of height 2·3 e Å^{-3} situated 1·15 Å from Cs(1). The next four highest peaks, in the range 0·5–0·6 e Å^{-3}, were in expected positions for the four hydrogen atoms of the water molecules coordinated to Mo. Among the lower peaks were some in expected positions for hydrogen atoms of the other two water molecules, but they were not so clearly identifiable as to justify their inclusion. The first four hydrogen atoms were included as fixed contributions with U_{iso} = 0·05 Å^2, and the refinement of the non-hydrogen atoms reconverged to R = 2·66% and R' = 3·49%. The refinement used weights $w^{-1} = \sigma^2(F)$ calculated from counting statistics, and gave a fairly uniform distribution of $\langle w\Delta^2 \rangle$ as a function of F_o and $\sin\theta/\lambda$, although the final value of $[\sum w\Delta^2/(n-m)]^{1/2} = 3{\cdot}42$. Atomic scattering factors were calculated using the analytical approximation and coefficients given in *International Tables for X-ray Crystallography* (1974).

The atomic coordinates and their e.s.d.'s (by inversion of the 9 × 9 block-diagonal least-squares matrix) are given in Table 1.*

Table 1. *Atomic coordinates and e.s.d.'s*

	x	y	z
Mo(1)	0·1157 (1)	0·3541 (1)	0·3268 (1)
Mo(2)	0·1517 (1)	0·3617 (1)	0·0519 (1)
Cs(1)	0·2877 (1)	0·0979 (1)	0·2499 (1)
Cs(2)	0·8236 (1)	0·4914 (1)	0·2902 (1)
S(1)	−0·0101 (2)	0·3174 (1)	0·0967 (2)
S(2)	0·2891 (2)	0·3617 (1)	0·2866 (2)
O(1)	0·0879 (5)	0·4551 (3)	0·3495 (6)
O(2)	0·1206 (5)	0·4623 (3)	0·0101 (6)
O(3)	−0·0276 (4)	0·3270 (3)	0·4103 (6)
O(4)	0·2927 (5)	0·3771 (3)	−0·0351 (6)
O(5)	0·1438 (5)	0·2248 (3)	0·3797 (6)
O(6)	0·2119 (5)	0·3471 (3)	0·5607 (6)
O(7)	0·2228 (6)	0·1305 (3)	0·5548 (7)
O(8)	0·2976 (5)	0·2651 (4)	0·7516 (6)
O(9)	0·1917 (5)	0·2343 (3)	0·0216 (6)
O(10)	0·0630 (5)	0·3317 (3)	−0·1786 (6)
O(11)	0·1486 (6)	0·1233 (3)	−0·1251 (7)
O(12)	0·0194 (5)	0·2316 (3)	−0·3504 (6)
W(1)	0·4851 (5)	0·4549 (4)	0·1206 (8)
W(2)	0·0149 (10)	0·0608 (9)	0·1423 (18)
C(1)	0·2012 (7)	0·2015 (6)	0·5121 (10)
C(2)	0·2423 (6)	0·2768 (5)	0·6177 (9)
C(3)	0·1405 (8)	0·1979 (6)	−0·1024 (9)
C(4)	0·0658 (7)	0·2565 (5)	−0·2241 (9)
H(31)	−0·0910	0·2941	0·3451
H(32)	−0·0173	0·2991	0·4909
H(41)	0·3042	0·3448	−0·1004
H(42)	0·3650	0·4001	0·0113

Discussion. The structure and atom numbering of the $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$ (I) anion are shown in Fig. 1, and the bond lengths and angles are listed in Table 2. The anion has non-crystallographic C_2 symmetry with the sulphido and aqua ligands all *cis* to the strongly bonded oxo ligand.



(I)

Mo—Mo distances of 2·80–2·85 Å in octahedral di-μ-sulphido Mo^V dimers have been found (Spivack & Dori, 1975) and the present value of 2·822 (1) Å lies within that range. The folding of the Mo_2S_2 ring is evident in Fig. 1 – the dihedral angle about the S(1)···S(2) line is 24·4°. This folding may be

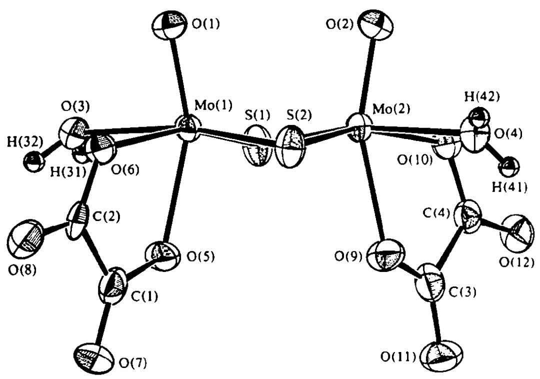


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$ ion showing the atom numbering.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33627 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with their e.s.d.'s*

(*a*) The complex anion

Mo(1)–S(1)	2·310 (2)	Mo(2)–S(2)	2·320 (2)
Mo(1)–S(2)	2·318 (2)	Mo(2)–S(1)	2·308 (2)
Mo(1)–O(1)	1·702 (6)	Mo(2)–O(2)	1·692 (6)
Mo(1)–O(3)	2·229 (6)	Mo(2)–O(4)	2·196 (7)
Mo(1)–O(5)	2·155 (5)	Mo(2)–O(9)	2·164 (6)
Mo(1)–O(6)	2·159 (5)	Mo(2)–O(10)	2·166 (5)
Mo(1)–Mo(2)	2·822 (1)	S(1)···S(2)	3·617 (3)
C(1)–O(5)	1·285 (10)	C(3)–O(9)	1·286 (10)
C(1)–O(7)	1·220 (11)	C(3)–O(11)	1·238 (12)
C(1)–C(2)	1·557 (12)	C(3)–C(4)	1·546 (12)
C(2)–O(6)	1·264 (10)	C(4)–O(10)	1·299 (11)
C(2)–O(8)	1·250 (9)	C(4)–O(12)	1·221 (10)
O(1)···O(2)	3·416 (9)	O(5)···O(9)	3·681 (9)
O(1)–Mo(1)–S(1)	105·6 (1)	O(2)–Mo(2)–S(2)	105·3 (1)
O(1)–Mo(1)–S(2)	102·1 (2)	O(2)–Mo(2)–S(1)	101·5 (2)
O(1)–Mo(1)–O(3)	85·6 (2)	O(2)–Mo(2)–O(4)	87·0 (3)
O(1)–Mo(1)–O(6)	89·0 (2)	O(2)–Mo(2)–O(10)	88·7 (2)
O(5)–Mo(1)–S(1)	88·8 (1)	O(9)–Mo(2)–S(2)	90·2 (1)
O(5)–Mo(1)–S(2)	90·3 (2)	O(9)–Mo(2)–S(1)	89·0 (2)
O(5)–Mo(1)–O(3)	79·0 (2)	O(9)–Mo(2)–O(4)	79·0 (2)
O(5)–Mo(1)–O(6)	73·5 (2)	O(9)–Mo(2)–O(10)	73·1 (2)
S(1)–Mo(1)–S(2)	102·8 (1)	S(2)–Mo(2)–S(1)	102·8 (1)
S(1)–Mo(1)–O(3)	85·9 (1)	S(2)–Mo(2)–O(4)	87·1 (1)
S(2)–Mo(1)–O(6)	87·5 (1)	S(1)–Mo(2)–O(10)	86·9 (1)
O(3)–Mo(1)–O(6)	81·1 (2)	O(4)–Mo(2)–O(10)	80·4 (2)
Mo(1)–S(1)–Mo(2)	75·4 (1)	Mo(2)–S(2)–Mo(1)	75·0 (1)

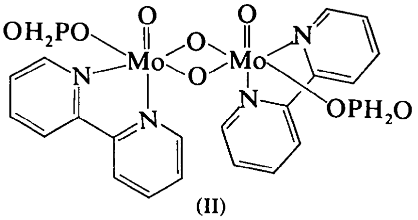
(*b*) Caesium coordination

Cs(1)–O(5)	3·237 (6)	Cs(2)–O(1)	3·193 (6)
Cs(1)–O(7)	3·328 (7)	Cs(2)–O(1′)	3·365 (5)
Cs(1)–O(9)	3·056 (5)	Cs(2)–O(2)	3·269 (7)
Cs(1)–O(11)	3·448 (6)	Cs(2)–O(3)	3·226 (5)
Cs(1)–O(1′)	3·105 (6)	Cs(2)–O(4)	3·196 (5)
Cs(1)–O(2′)	3·105 (6)	Cs(2)–O(6)	3·083 (6)
Cs(1)–O(10′)	3·448 (6)	Cs(2)–O(7)	2·942 (6)
Cs(1)–*W*(2)	3·247 (12)	Cs(2)–O(10)	3·515 (6)
Cs(1)–S(1)	3·687 (2)	Cs(2)–O(11)	3·168 (7)

(*c*) Hydrogen bonding

O(3)···O(8′)	2·648 (7)	O(3)–H(31)	0·98
O(3)···O(12′)	2·661 (8)	O(3)–H(32)	0·87
O(4)···O(8′)	2·749 (9)	O(4)–H(41)	0·86
O(4)···*W*(1)	2·668 (8)	O(4)–H(42)	0·93
W(1)···O(11)	2·886 (8)	*W*(1)···*W*(1′)	2·86 (2)
H(31)···O(8′)	1·67	H(42)···*W*(1)	1·75
H(32)···O(12′)	1·80	*W*(1)···*W*(2)	2·85 (2)
H(41)···O(8′)	1·90		

necessary to allow sufficiently close contact of the Mo atoms, although the narrowing of the angles at the S atoms to 75° also serves this purpose. Also associated with the Mo–Mo interaction is the widening of the inter-ligand bond angles around the Mo–Mo bond; these O–Mo–S and S–Mo–S angles are 102–105° (Table 2) whereas the remaining inter-ligand angles are 90° or less. These distortions suggest capped octahedral seven-coordination, with a bent Mo–Mo bond in the seventh coordination site. Surprisingly, there is no significant difference between the Mo to oxalate bond lengths *trans* to oxo and *trans* to sulphido ligands. The structure of the di-μ-oxo analogue of this anion was determined as its Ba salt by Cotton & Morehouse (1965), and they also found no difference between the Mo to oxalate oxygen bond lengths *trans* to terminal or bridging oxo ligands. In most other structures of this type, however, a considerable lengthening of the bond *trans* to the multiply-bonded terminal oxo ligand has been observed (Spivack & Dori, 1975). In the similar bipyridyl complex (II) (Gatehouse & Nunn, 1976) the Mo–N bond length *trans* to terminal oxo is 2·32 (1) Å while that *trans* to bridging oxo is 2·25 (1) Å. Possibly the absence of a *trans* influence on the bond lengths in the oxalate complexes indicates that the oxalate ligand has a low '*trans* susceptibility' compared with the bipyridyl and other ligands, but without bond-length data on a greater variety of complexes this point cannot be tested.



(II)

The coordination of the Cs atoms is quite irregular, each making the nine contacts listed in Table 2. The hydrogens of the coordinated water molecules participate in clearly identifiable hydrogen bonds with H···O distances of 1·67–1·90 Å. There is also a probable hydrogen bond between the water molecule *W*(1) and the oxalate oxygen O(11), but the *W*(1)···*W*(1′) distance of 2·86 (2) Å is across a centre of symmetry, and must therefore involve disorder of the hydrogen atom. The water molecule *W*(2) shows only one hydrogen-bonding contact (to the other water molecule) and is also bonded to Cs(1), whereas *W*(1) forms four tetrahedrally directed hydrogen bonds. The lower coordination of *W*(2) is reflected in its high temperature factor [$U_{\rm iso} = 0{\cdot}18$ Å^2, that for *W*(1) is $U_{\rm iso} = 0{\cdot}05$ Å^2] which may reflect some disorder of its position. During the refinement of the structure, attempts to refine a fractional occupancy and a more normal temperature factor for *W*(2) led to a return to an occupancy close to 1·0 and the original high temperature factor. The high peak close to Cs(1) in the final difference map may also result from a very small amount of disorder of Cs(1) associated with the disorder of *W*(2) bonded to it.

The author is grateful to Dr A. G. Sykes for supplying the crystals and for discussion of the structural problems involved, and to the Science Research Council for an equipment grant.

References

Armstrong, F. A., Shibahara, T. & Sykes, A. G. (1978). *Inorg. Chem.* **17**, 189–191.

Cotton, F. A. & Morehouse, S. M. (1965). *Inorg. Chem.* **4**, 1377–1381.
Gatehouse, B. H. & Nunn, E. K. (1976). *Acta Cryst.* B**32**, 2627–2630.
Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Spivack, B. & Dori, Z. (1975). *Coord. Chem. Rev.* **17**, 99–136.

Acta Cryst. (1978). B**34**, 2853–2856

The Structure of Diiodo{*S*,*S*′-dimethyl-2,6-bis[1-(2-thiophenylimino)-ethyl]pyridine}cadmium(II)

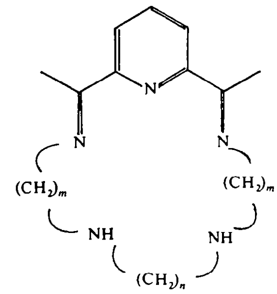
By Michael G. B. Drew and Stephen Hollis

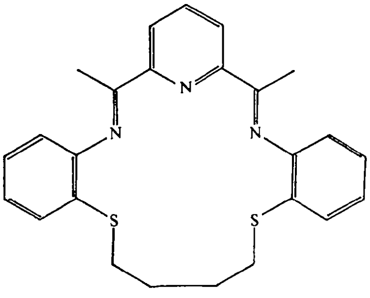
Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, England

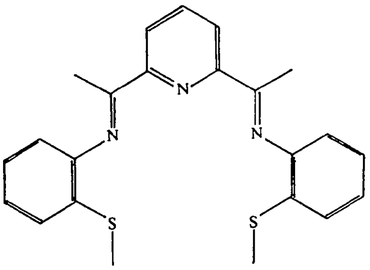
(*Received* 10 *April* 1978; *accepted* 15 *May* 1978)

Abstract. $C_{23}H_{23}N_3S_2CdI_2$, M_r = 771·8, orthorhombic, $Pbn2_1$, $Z = 4$, a = 13·366 (9), b = 19·266 (8), c = 10·230 (11) Å, d_c = 1·95, d_m = 1·89 (5) g cm^{-3}, U = 2634·3 Å^3, $F(000)$ = 1380, μ(Mo $K\alpha$) = 34·3 cm^{-1}. 1148 independent above-background reflections were measured on a diffractometer and refined by a full-matrix least-squares method to R = 0·068. In the complex, the potentially quinquedentate ligand is only terdentate bonding to the Cd through three N atoms [2·40 (4), 2·33 (3), 2·41 (3) Å] with the two S atoms twisted out of the ligand plane well away from the metal. The coordination sphere is completed by two I atoms [2·713 (4), 2·726 (4) Å]. The geometry of the coordination sphere is close to a trigonal bipyramid with both I atoms in equatorial sites.

Introduction. Seven-coordinate (pentagonal bipyramidal) structures of the type $ML_2(L\text{-}L\text{-}L\text{-}L\text{-}L)$, L and $L\text{-}L\text{-}L\text{-}L\text{-}L$ being monodentate and pentadentate ligands respectively, have become well established (Drew, 1977). In the majority of examples the pentadentate ligand is closely planar. Indeed with ligands 2,2,2-N_5 and 2,3,2-N_5 [shown as (I)] the deviations of contributing atoms from the ML_5 girdle are less than 0·25 Å (Drew, Othman, McFall, McIlroy & Nelson, 1977*a*). We have been investigating structures of complexes which contain analogous but more flexible ligands to determine whether they too have seven-coordinate structures. We have previously shown (Drew & Hollis, 1978*a*) that the complex $Zn(2,4,2\text{-}N_3S_2)I_2$, [2,4,2-$N_3S_2$ shown as (II)] has a five-coordinate structure with a ZnN_3I_2 coordination sphere. We have suggested that this is due to the steric requirements of the butane linkage between S atoms. As a further example of this class of compounds we have chosen Cd(2,0,2-$N_3S_2Me_2$)I_2 [2,0,2-$N_3S_2Me_2$ shown as (III)] and report here its crystal and molecular structure.


(I) $n = 2, m =$ (2,2,2-N_5)
$n = 3, m = 2$ (2,3,2-N_5)
$n = 2, m = 3$ (3,2,3-N_5)


(II) (2,4,2-N_3S_2)


(III) (2,0,2-$N_3S_2Me_2$)