

refined by a least-squares method, using 15 reflections ($21 \leq 2\theta \leq 32^\circ$). The intensities were measured using a θ - 2θ scan method and variable scan speed, up to a 2θ maximum of 55° . Three standard reflections were measured every 100 reflections. No significant fluctuation in standard reflections was observed. 2178 reflections were collected; 1503 were unique and had $I > 3\sigma(I)$. Lorentz and polarization corrections were applied.

The structure was solved by Patterson and Fourier techniques and refined by a full-matrix least-squares method, with anisotropic thermal parameters for all non-hydrogen atoms. The final R was 0.032 and shifts in atomic parameters were $\leq 0.08\sigma$. Fractional coordinates of the nine crystallographically independent atoms are listed in Table 1; bond lengths and angles within the molecule are given in Table 2.*

Discussion. Structural studies of eight-coordinate metal complexes with S bidentate ligands show (Bonamico, Dessy, Fares & Scaramuzza, 1975) that the inter-ligand repulsions are the main energy term determining the shape of the coordination polyhedra for chromophores [MS_8], whenever the normalized bite of the ligand (ratio of intraligand S—S distance to the mean metal—ligand distance) is about 1.10 (Blight & Kepert, 1972). However, for metals with the $d_{x^2-y^2}$ orbital filled or half-filled, and coordinated by ligands with high delocalization of the π -electron density (such as Mo^{IV} and V^{IV} dithiobenzoates) a further stabilization of the observed dodecahedra may be induced by the d - π bonding between the metal and the S atoms in the equatorial position (Piovesana & Sestili, 1974).

As a part of the chemical and physical study on eight-coordination in transition-metal ions by O. Piovesana, of Perugia University, we have undertaken

the structural study of the title compound and of the corresponding Ti^{IV} complex, in order to obtain further information on the behaviour of d^2 and d^0 metal ions with a ligand having a poor π -electron delocalization.

The structure of the title complex consists of discrete $Mo(CH_3CS_2)_4$ units, with the Mo^{4+} ion on the twofold axis [$2(f)$ position]. The two crystallographically independent $CH_3C(:S)S^-$ anions have their S atoms roughly arranged in a square, parallel to the b axis. In Fig. 1 the two pseudo-squares are marked by dotted lines. However, the coordination polyhedron can also

Table 2. Molecular geometry within the chemical unit, with estimated standard deviations in parentheses

The primed atoms refer to the following equivalent position:
 $1 - x, y, \frac{1}{2} - z.$

(a) Distances (Å)

Mo—S(1)	2.530 (2)	S(2)—C(1)	1.671 (8)
Mo—S(2)	2.501 (1)	S(3)—C(3)	1.689 (6)
Mo—S(3)	2.534 (1)	S(4)—C(3)	1.680 (6)
Mo—S(4)	2.499 (1)	C(1)—C(2)	1.497 (9)
S(1)—C(1)	1.678 (5)	C(3)—C(4)	1.492 (7)

(b) Angles ($^\circ$)

S(1')—Mo—S(1)	135.97 (5)	S(2)—Mo—S(3)	79.55 (4)
S(1')—Mo—S(2)	80.01 (5)	S(2)—Mo—S(4)	104.16 (4)
S(1')—Mo—S(3)	74.12 (5)	S(3)—Mo—S(4)	66.69 (5)
S(1')—Mo—S(4)	138.81 (5)	Mo—S(1)—C(1)	90.2 (3)
S(2')—Mo—S(2)	81.55 (4)	Mo—S(2)—C(1)	91.4 (2)
S(2')—Mo—S(3)	138.85 (6)	Mo—S(3)—C(3)	90.7 (2)
S(2')—Mo—S(4)	154.09 (6)	Mo—S(4)—C(3)	92.1 (2)
S(3')—Mo—S(3)	135.65 (5)	S(1)—C(1)—S(2)	111.5 (3)
S(3')—Mo—S(4)	79.94 (4)	S(1)—C(1)—C(2)	123.5 (6)
S(4')—Mo—S(4)	81.88 (4)	S(2)—C(1)—C(2)	125.0 (5)
S(1)—Mo—S(2)	66.78 (6)	S(3)—C(3)—S(4)	110.4 (2)
S(1)—Mo—S(3)	123.82 (4)	S(3)—C(3)—C(4)	124.3 (5)
S(1)—Mo—S(4)	79.27 (5)	S(4)—C(3)—C(4)	125.2 (5)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33615 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
Mo	5000 (0)	1842 (1)	2500 (0)
S(1)	7073 (2)	753 (2)	2080 (1)
S(2)	6779 (2)	-334 (2)	4013 (1)
S(3)	5936 (2)	2941 (1)	4707 (1)
S(4)	7099 (1)	4010 (2)	3287 (1)
C(1)	7732 (6)	-573 (6)	3263 (5)
C(2)	8975 (8)	-1834 (7)	3562 (6)
C(3)	7146 (5)	4282 (5)	4634 (4)
C(4)	8088 (7)	5546 (6)	5620 (5)

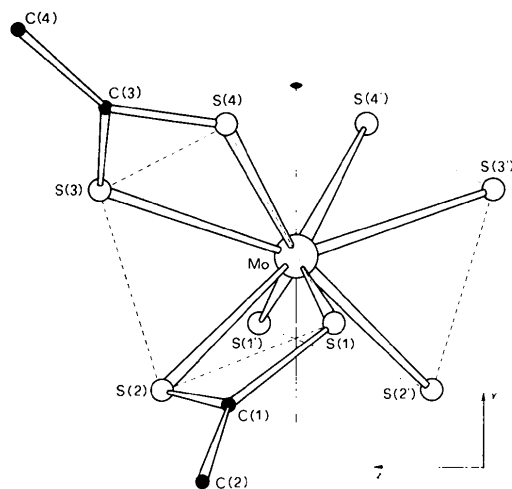


Fig. 1. View of the molecule along $a \sin \beta$. The primed atoms are the same as in Table 2.

be considered as a triangular dodecahedron, with its pseudo-4 axis parallel to the (101) plane, at ca 135° from the a axis. The packing of the two molecules in the cell is shown in Fig. 2. It may be noted that they are not simply related by a translation of $\frac{1}{2}c$, but also reversed with respect to the y direction. Although the molecules of the adjacent unit cells are not drawn, the complete intermolecular-distances calculation gave the following results: the shortest $S \cdots S$ distance is 3.70 \AA , shown in the diagram, the others being $\geq 4.1 \text{ \AA}$; the $S \cdots C$ distances are $\geq 3.8 \text{ \AA}$ and the $C \cdots C$ distances are $\geq 3.7 \text{ \AA}$.

The coordination polyhedron of the structure requires the following geometrical parameters for a correct description: (i) the angles θ_A and θ_B , according to the usual notation (Hoard & Silverton, 1963), (ii) the trapezoidal least-squares planes for the supposed dodecahedron and the dihedral angle between them, with the mean displacement d_T of the S atoms from these planes (Lippard & Russ, 1968), (iii) the least-squares planes of the 'squares' with the corresponding mean displacement d_S , (iv) the dihedral angles δ and δ' , the first calculated between the triangular faces whose intersections give the diagonals of the 'squares', the second between the lateral triangular faces of the supposed square antiprism (Muettterties & Guggenberger, 1974; Pinnavaia, Barnett, Podolsky & Tulinsky, 1975). Tables 3 and 4 list the results of these calculations. The angles θ_A and θ_B and the distances $Mo-S_A$, $Mo-S_B$ have usual values for a dodecahedron with the $R-C(:S)S^-$ groups along m edges, but the d_T displacements, together with δ and δ' average values, show a considerable distortion towards the square antiprism (isomer *ssss*); also the d_S displacements are relatively small.

A similar intermediate structure of tetrakis(*N,N*-diethyldithiocarbamato)molybdenum(IV), described as a distorted square antiprismatic *llss* isomer (van der Aalsvoort & Beurskens, 1974), seems to support the

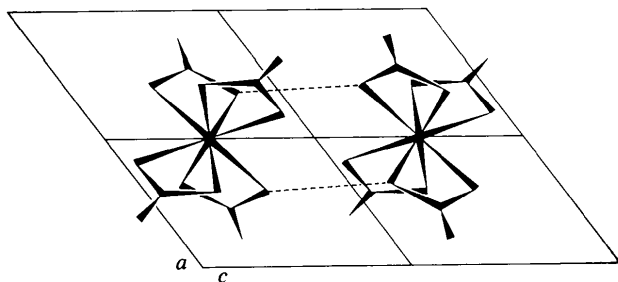


Fig. 2. The unit cell viewed along [010]. The dotted lines mark the shortest $S \cdots S$ contacts.

Table 3. Angles ($^\circ$) relevant for the choice of the coordination polyhedron: comparison of the experimental values with those from hard-sphere models (HSM), taken from Hoard & Silverton (1963) and Pinnavaia et al. (1975)

The angles θ_A and θ_B are computed respectively as $\frac{1}{2}[S(1')-Mo-S(3)]$ and $\frac{1}{2}[S(2')-Mo-S(4)]$. The intersections of the triangular faces giving the dihedral angles δ are the directions $S(2)-S(4)$ and $S(1)-S(3)$. The intersections giving the dihedral angles δ' are $S(4)-S(4')$, $S(2)-S(2')$, $S(1)-S(3)$ and $S(3)-S(4')$.

	Observed	HSM	
		Dodecahedron	Square antiprism
θ_A	37.1	36.9	59.25
θ_B	77.5	69.5	
δ	17.7	29.5	0.0
δ'	50.3	39.5	52.4

Table 4. Least-squares planes of the dodecahedron trapezoid and of the square antiprism base, with related distances d_T and d_S (\AA) for the atoms defining the planes

The primed atoms are the same as in Table 2.

Plane T : $S(1), S(2), Mo, S(3'), S(4')$
 $4.63x + 5.88y + 2.04z - 3.91 = 0$
 d_T : $S(1) 0.23, S(2) 0.15, Mo 0.00$

Dihedral angle between the two symmetry-related trapezoids: 86.0° .

Plane S : $S(1), S(2), S(3), S(4)$
 $6.30x + 2.73z - 5.20 = 0$
 d_S : $S(1) 0.17, S(2) -0.17, S(3) 0.17, S(4) -0.17$

tentative rationalization by Piovesana & Sestili (1974), but the virtually perfect dodecahedron of tetrakis(*N,N*-diethyldithiocarbamato)titanium(IV) (Colapietro, Vaciago, Bradley, Hursthouse & Rendall, 1972), a d^0 ion, has no consistent explanation. The crystallographic study of titanium dithioacetate would be helpful in clarifying this point.

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The Monopotassium Salt of 2*H*-1,2,6-Thiadiazine-3,5(4*H*,6*H*)-dione 1,1-Dioxide Monohydrate

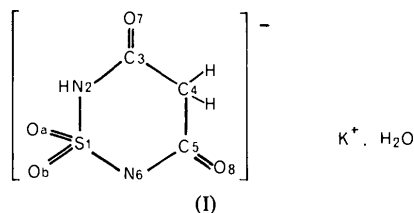
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Abstract. $C_3H_3N_2O_4SK \cdot H_2O$, monoclinic, *Cm*, $a = 9.3743$ (3), $b = 15.7092$ (6), $c = 5.3693$ (1) Å, $\beta = 104.47$ (2)°, $Z = 4$, $V = 765.61$ (3) Å³, $M_r = 220.2$, $D_x = 1.91$ g cm⁻³. The structure was solved by Patterson and Fourier syntheses and refined by least-squares methods to $R = 0.024$ for 1145 observed reflections. In the unit cell there are two K cations, eight and seven coordinating respectively. The thiadiazine ring has a flattened boat conformation.

Introduction. This compound, $K^+ \cdot C_3H_3N_2O_4S^- \cdot H_2O$ (I), is one of a series of *S*-dioxo analogues of uracil and barbituric acid (Ochoa & Stud, 1978). The structure has been determined to eliminate doubts about its conformation.



Intensity data were collected from a crystal of dimensions $0.21 \times 0.11 \times 0.29$ mm on a Philips PW 1100 four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The ω - 2θ scan technique was employed. Of the 1166 independent reflections, 1145 had $I > 2\sigma(I)$. Lorentz, polarization and absorption corrections were applied ($\mu = 9.38$ cm⁻¹). The statistical distribution of intensities tended to eliminate the centrosymmetric space group $C2/m$; the concentration of peaks only in the Harker sections $(0, v, 0)$ and $(\frac{1}{2}, v, 0)$ and the subsequent structure solution confirmed space group *Cm*. The structure was

solved by Patterson and Fourier syntheses and refined by full-matrix least-squares calculations. H atoms were found in a difference map and included in the final refinement. The weighting scheme was: $w = K/|f(F_o)|^2 f(S)$ with $f(F_o) = 0.53 - 0.03F_o$ for $F_o < 25$ and $f(F_o) = 0.83 - 0.03F_o$ otherwise and $f(S) = 12.01 - 52.61S + 61.72S^2$ for $S < 0.48$ and $f(S) = 10.58 - 34.30S + 29.67S^2$ otherwise, with $K = 0.586$ and $S = \sin \theta/\lambda$. Both R and R_w for the observed reflections were 0.024, where $R_w = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2}$. There were no peaks larger than 0.42 e Å⁻³ in the final difference map. Table 1 lists the fractional coordinates.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 2 contains the main molecular parameters. Distances and angles in the ring are consistent with values reported for other thiadiazine rings, e.g. Foces-Foces, Cano & García-Blanco (1975*a, b*); Smith-Verdier, Florencio & García-Blanco (1977); Cabezuelo, Cano, Foces-Foces & García-Blanco (1977); Foces-Foces, Smith-Verdier, Florencio-Sabaté & García-Blanco (1975). The packing and the numbering are illustrated in Fig. 1, which shows that the cations have two different geometrical environments, making use of atoms in symmetry-related molecules. The K(1) cation is surrounded by eight atoms which form a distorted *mm* (C_{2v}) hendeca-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33639 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.