

of 76° and to the mean plane, C(1)–C(17), at an angle of 79° . Views of the molecules, as projected parallel to their respective least-squares planes through atoms C(1)–C(17), are given in Fig. 4.

The length of the nucleus of the steroid molecule, calculated as the distance between atoms C(3) and C(16) is 9.13 \AA in molecule 1 and 9.16 \AA in molecule 2.

Molecular packing

The hydroxyl oxygen atom, 1O(3), of molecule 1 is hydrogen-bonded to the ketone oxygen atom 2O(20) of another molecule, not related to the former by symmetry, as well as to the hydroxyl oxygen atom 2O(3) of a third molecule related to the second by the *a*-screw axis, but not related to the first one by symmetry. These hydrogen bonds are indicated by dotted lines in the axial projections given in Fig. 5(a) and (b). The distance between the hydrogen-bonded atoms 1O(3) and 2O(20) is 2.81 \AA , and the hydrogen-bond distance between 1O(3) of one molecule and 2O(3) of another molecule is 2.76 \AA .

Table 5 lists the forty-one intermolecular contacts shorter than 4.0 \AA (ignoring hydrogen atoms). The two bromine atoms not related by crystal symmetry are in

van der Waals contact, being separated by a distance of 3.81 \AA . Apart from this contact, the bromine atoms do not have intermolecular contacts shorter than 4.0 \AA . Of the forty-one contacts less than 4.0 \AA , the side chain atoms carry eighteen contacts, and, therefore, play a major part in the molecular packing.

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The Crystal and Molecular Structure of Bis- π -cyclopentadienyl(2-aminoethanethiolato)molybdenum Iodide

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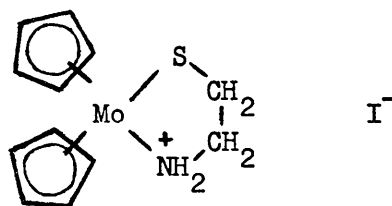
(Received 3 December 1968)

$(\pi\text{-C}_5\text{H}_5)_2\text{MoS}(\text{CH}_2)_2\text{NH}_2^+\text{I}^-$ crystallizes in space group *Pbcn* with $a=11.86 \pm 0.01$, $b=14.97 \pm 0.01$, $c=15.46 \pm 0.01 \text{ \AA}$ and $Z=8$. Full-matrix least-squares refinement with anisotropic temperature factors for molybdenum and iodide gave an *R* index of 0.087 for 1746 absorption-corrected photographic data. The Mo–S and Mo–NH₂ bonds are 2.438 ± 0.005 and $2.211 \pm 0.015 \text{ \AA}$ respectively, and lie in a plane between staggered cyclopentadienyl rings. The angle between ring normals is 130.9° . There are intermolecular hydrogen bonds from the amino group to the sulphur atom (3.3 \AA) and to the iodide ion (3.6 \AA).

Introduction

In $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ (Gerloch & Mason, 1965) and $(\pi\text{-C}_5\text{H}_5)_2\text{MoS}_2\text{C}_6\text{H}_3\text{CH}_3$ (Knox & Prout, 1967) the cyclopentadienyl rings have the non-parallel arrangement predicted by Ballhausen & Dahl (1961). The rings are eclipsed in the former compound and are staggered in the latter. To see what effect ligand atoms of different size have on ring configuration and molec-

ular geometry, we have determined the structure of bis- π -cyclopentadienyl(2-aminoethanethiolato)molybdenum iodide:



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Experimental

Red air-stable crystals were prepared by M.L.H. Green and M.G. Harriss (Harriss, 1967) of the Inor-

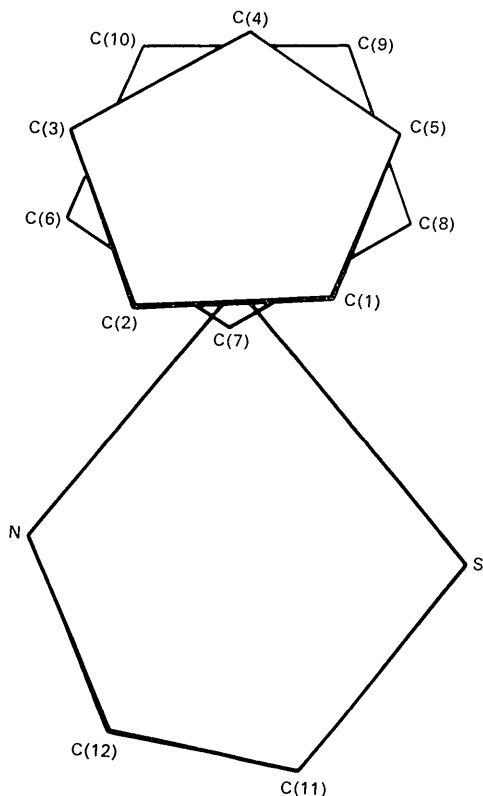


Fig. 1. View of the structure normal to the N-Mo-S plane.

ganic Chemistry Laboratory, Oxford. Cell dimensions were calibrated with aluminum powder lines superposed on Weissenberg photographs. The crystal data are:

$\text{MoC}_{12}\text{H}_{16}\text{NSI}$, $M = 429.2$, $F(000) = 1648$. Orthorhombic, $a = 11.86 \pm 0.01$, $b = 14.97 \pm 0.01$, and $c = 15.46 \pm 0.01$ Å. $D_m = 2.051$ g.cm $^{-3}$ by flotation, $Z = 8$, $D_c = 2.077$ g.cm $^{-3}$. Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 264$ cm $^{-1}$. Systematic extinctions: $k = 2n + 1$ for $0kl$, $l = 2n + 1$ for $h0l$ and $h + k = 2n + 1$ for $hk0$. Space group $Pbcn$ (D_{2h}^{14} , no. 60).

From a crystal $0.50 \times 0.05 \times 0.15$ mm mounted along the rod axis a , 1709 observable $0kl$ to $9kl$ reflexions were obtained by the equi-inclination Weissenberg method. Another crystal $0.26 \times 0.12 \times 0.20$ mm gave 109 $hk0$ reflexions. A general absorption correction was applied to the visually estimated data from each axis, and the merging R index $\Sigma |F_1^2 - F_2^2| / \Sigma (F_1^2 + F_2^2)$ was 0.077. 1746 non-zero reflexions resulted.

Solution and refinement of the structure

The Patterson function gave positions for the molybdenum atom and for two iodide ions in special positions 4(c). A structure factor calculation produced an R index $\Sigma |F_o - F_c| / \Sigma |F_o| = 0.25$. Light atoms were located with a minimum function and Fourier syntheses; no attempt was made to locate hydrogen atoms.

In the full-matrix least-squares refinement the quantity minimized was $\Sigma w(F_o - F_c)^2$ where

$$w = \{1 + [(|F_o| - a)/b]^2\}^{-1}$$

and $a = b = 50$ electrons. Scattering curves (*International Tables for X-ray Crystallography*, 1962) for neutral Mo

Table 1. Fractional atomic coordinates ($\times 10^4$) and temperature factors ($\times 10^4$) with standard deviations in parentheses

	x	y	z	$U(\text{Å}^2)$
Mo	2100 (1.2)	1337 (0.7)	5446 (0.7)	*
I(1)	0000	1170 (1.1)	2500	*
I(2)	5000	365 (1.7)	2500	*
S	3295 (5)	2464 (3)	4770 (3)	423 (11)
N	886 (13)	2030 (8)	4594 (8)	313 (28)
C(1)	2208 (20)	2425 (13)	6557 (13)	469 (46)
C(2)	1093 (21)	2285 (15)	6412 (14)	566 (55)
C(3)	918 (22)	1357 (15)	6613 (15)	573 (53)
C(4)	1994 (19)	1012 (13)	6851 (12)	428 (42)
C(5)	2777 (24)	1648 (16)	6789 (16)	616 (59)
C(6)	1516 (18)	141 (12)	4637 (12)	420 (42)
C(7)	2458 (18)	498 (12)	4235 (12)	400 (43)
C(8)	3437 (21)	389 (14)	4763 (14)	521 (54)
C(9)	3050 (19)	67 (14)	519 (14)	517 (48)
C(10)	1901 (20)	198 (14)	415 (14)	501 (48)
C(11)	2384 (21)	2929 (15)	3934 (15)	579 (57)
C(12)	1200 (21)	2963 (14)	4292 (14)	530 (51)

* Coefficients have the form: $\exp[-2\pi^2(U_{11}h^2a^*2 + U_{22}k^2b^*2 + U_{33}l^2c^*2 + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Mo	305 (9)	246 (5)	159 (5)	-56 (9)	-2 (10)	-21 (11)
I(2)	471 (12)	420 (8)	221 (6)	0	-109 (14)	0
I(2)	550 (15)	929 (15)	367 (8)	0	-203 (18)	0

Table 2. Observed and calculated structure amplitudes (electrons)

Columns are headed by h, k and contain l, |F_o| and F_c.

Table with columns for h, k, l, |F_o|, and F_c. The data is organized in a grid-like format with multiple columns for each h and k value, showing the corresponding l values and the observed/observed+calculated amplitudes.

Table 2 (cont.)

Table with multiple columns of numerical data, likely representing bond lengths or angles for various atoms in a complex molecule. The table is organized in a grid-like structure with columns and rows of numbers.

Table 3. Distances (Å, σ × 10³) and angles (deg, σ × 10)

The molybdenum-chelate ring

	With S(CH ₂) ₂ NH ₂	With SCH ₂ CH(NH ₂)CO ₂ *
Mo-N	2:211 (15)	2:230 (16)
Mo-S	2:438 (6)	2:490 (6)
S—C	1:823 (25)	1:865 (24)
C—C	1:511 (35)	1:496 (32)
C—N	1:519 (29)	1:503 (26)
N—Mo—S	78.4 (4)	80.3 (5)
Mo—S—C	102.9 (8)	98.2 (8)
Mo—N—C	117.0 (12)	107.0 (12)
S—C—C	107.7 (17)	110.8 (16)
N—C—C	108.1 (19)	108.2 (17)
NC-CS (dihedral)	55.1	57.2
Distance of C(NH ₂) and C(S) from N—Mo—S plane	0.47, -0.28	0.91, 0.29

Bonded distances and angles involving cyclopentadienyl rings

Mo—C(1)	2:369 (23)	Mo—C(6)	2:291 (21)
Mo—C(2)	2:380 (25)	Mo—C(7)	2:295 (21)
Mo—C(3)	2:284 (26)	Mo—C(8)	2:376 (26)
Mo—C(4)	2:229 (22)	Mo—C(9)	2:388 (23)
Mo—C(5)	2:273 (28)	Mo—C(10)	2:312 (23)
C(1)—C(2)	1:357 (34)	C(6)—C(7)	1:386 (30)
C(2)—C(3)	1:439 (36)	C(7)—C(8)	1:428 (33)
C(3)—C(4)	1:426 (34)	C(8)—C(9)	1:429 (34)
C(4)—C(5)	1:333 (36)	C(9)—C(10)	1:387 (33)
C(5)—C(1)	1:392 (37)	C(10)—C(6)	1:383 (31)
C(1)—C(2)—C(3)	104.7 (22)	C(6)—C(7)—C(8)	110.8 (19)
C(2)—C(3)—C(4)	106.1 (21)	C(7)—C(8)—C(9)	105.2 (20)
C(3)—C(4)—C(5)	110.2 (22)	C(8)—C(9)—C(10)	106.7 (21)
C(4)—C(5)—C(1)	106.1 (23)	C(9)—C(10)—C(6)	112.0 (21)
C(5)—C(1)—C(2)	112.7 (23)	C(10)—C(6)—C(7)	105.4 (19)

Non-bonded distances

S—C(1)	3.05	N—C(2)	2.85
S—C(8)	3.11	N—C(6)	2.93
S—C(7)	3.21	N—C(7)	3.01
C(1)—C(8)	4.37	C(2)—C(6)	4.25
C(5)—C(8)	3.74	C(3)—C(6)	3.62
C(5)—C(9)	3.25	C(3)—C(10)	3.19
C(4)—C(9)	2.90	C(4)—C(10)	2.87
N—S(x - ½, ½ - y, 1 - z)	3.32	N—I(1)	3.64

* Average values from two halves of the binuclear chelate: Na₂Mo₂O₄(cysteine)₂. 5H₂O.

and I were corrected for the real part of the dispersion effect ($\Delta f' = -0.5$ and -1.2 e). Unobserved reflexions were omitted from the refinement. After four cycles with isotropic temperature factors parameter shifts were less than their standard deviations; the R index was 0.130. The molybdenum atom and iodide ions were assigned anisotropic temperature factors, and after three cycles no shift was greater than 0.3σ . The final atomic coordinates and temperature factors (Table 1) gave an R index of 0.087 for the 1746 observed reflexions (Table 2). A final difference map did not show any unexplained features.

Discussion

The dimensions of the chelate ring are compared in Table 3 with those in $\text{Na}_2\text{Mo}_2\text{O}_4[\text{SCH}_2\text{CH}(\text{NH}_2)\text{CO}_2]_2$ (Knox & Prout, 1968, 1969). The Mo-N bonds are equal, but the Mo-S bonds differ significantly. Cyclopentadienyl ligands apparently exert less of a *trans*-lengthening effect than bridging oxo ligands. Differences exist in the Mo-S-C angles and in the Mo-N-C angles because of carboxyl group coordination in the cysteine compound. The distances in the C(1-5) ring vary by 0.11 Å. The inferred pattern of electron delocalization is unlike that discussed by Bennett, Churchill, Gerloch & Mason (1964).

The orientation with respect to the metal atom of the flat, 7 Å effective (van der Waals) diameter, cyclopentadienyl rings is strongly influenced by the inter- and intramolecular repulsive forces in the crystal. The normal to the C(1-5) ring is inclined 63.1° ($\sigma \approx 1.5^\circ$) to the N-Mo-S plane, and the C(6-10) normal is inclined 67.8° . This difference arises because the C(6-10) ring makes closest contacts with NH_2 and S groups not at the frontal C(7) atom but at C(6) and C(8), allowing the ring normal to move forward by 4.7° . The staggered configuration of the rings (Fig. 1) and the small angle between normals (130.9°) are results of intramolecular repulsions between the aminoethanethiol ligand and the rings, which make the nearest C...C distances only 2.90 and 2.87 Å for C(4)-C(9) and C(4)-C(10). If the rings were eclipsed the separation would be 2.70 Å, compared with 3.07 Å in the less crowded ($\pi\text{-C}_5\text{H}_5$) $_2\text{MoH}_2$ structure (Gerloch & Mason, 1965) where an eclipsed configuration is permitted by a larger inter-ring angle (146°).

The plane of the ring normals is perpendicular (88.8°) to the N-Mo-S plane, but there is rotation of the ($\pi\text{-C}_5\text{H}_5$) $_2\text{Mo}$ group about the normal to the N-Mo-S plane at the molybdenum atom; the Mo-N and Mo-S bonds are unequally inclined to the plane of the ring normals by 41.8° and 36.5° . Ring-to-ligand contacts show that the sulphur radius is at least 0.2 Å larger than the amino group radius directed towards the rings, and the separation between rings is 0.12 Å greater on the sulphur side of the molecule than on the NH_2 side. Longer Mo-C distances might be expected on the sulphur side, as further decrease of the inter-ring

angle is hindered by C...C repulsions. However, for the C(1-5) ring Mo-C(1)=Mo-C(2) and Mo-C(3)=Mo-C(5); the only way for C(1) to move away from the sulphur atom is by rotation of the ring about its normal, and not by expansion of Mo-C(1-5) distances on the sulphur side, because the C(1)-C(5) side of the ring is subject to a 3.38 Å intermolecular repulsion

Table 4. *Least-squares planes*

Distances (Å) of atoms from planes.
(Parentheses denote atoms not in calculation.)

	1	2
Mo	(-1.976)	(2.002)
C(1)	0.021	
C(2)	-0.013	
C(3)	0.000	
C(4)	0.012	
C(5)	-0.021	
C(6)		0.001
C(7)		-0.003
C(8)		0.003
C(9)		-0.002
C(10)		0.000

Equations of planes: $lxa + myb + nzc = p$.

Plane	l	m	n	p
1	-0.1735	0.2309	0.9574	10.064
2	-0.1802	0.8800	0.4394	3.009
N-Mo-S	-0.2156	0.6390	0.7384	6.957
C ₅ H ₅ normals	0.9809	0.1274	0.1471	3.937

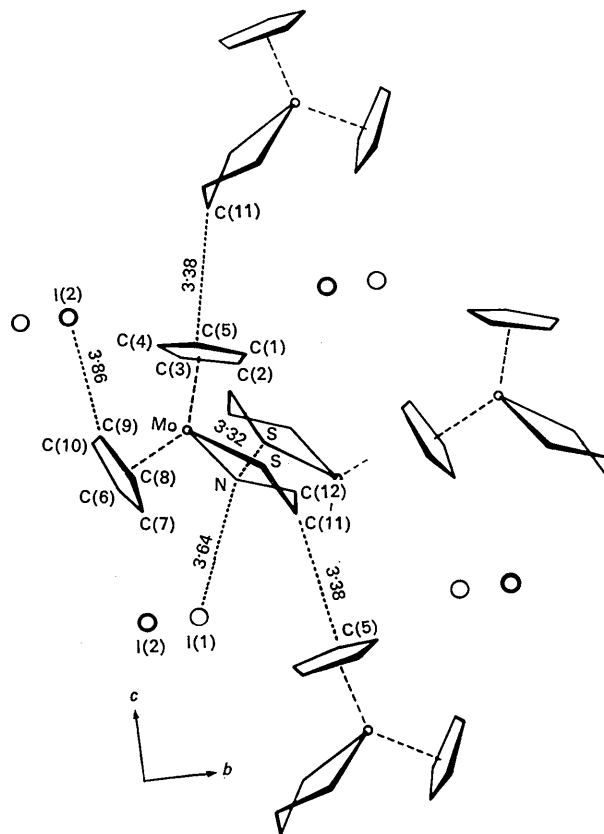


Fig. 2. Projection of the structure down a .

from C(11), directed perpendicular to the ring at C(5) (Fig. 2). The C(6–10) ring is unable to rotate because of a 3.86 Å in-plane repulsion between C(9) and I(2); the sulphur atom is then accommodated by an expansion of Mo–C(6–10) distances on the sulphur side: Mo–C(8) > Mo–C(6) and Mo–C(9) > Mo–C(10) (see Table 3).

The molecule cannot yield to these crystal repulsions, for it is held at the amino group by intermolecular hydrogen bonds to sulphur (3.32 Å) and to I(1) (3.64 Å). Ligand atoms C(11) and C(12) are forced nearer to the C(1–5) side of the N–Mo–S plane by a third repulsion from C(5) of another molecule acting against the chelate ring at C(11); this initiates and re-enforces the repulsions just described.

The minimum and maximum root-mean-square vibration amplitudes of the molybdenum atom are 0.125 and 0.175 Å. Maximum vibration of the I(1) ion (0.22 Å) is generally perpendicular to the N–H...I hydrogen bond. The displacement of I(2) is greater (0.30 Å) with alignment nearly normal to the C(9)...I(2) repulsion.

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Stereochemistry of Thioxanthenes and Related Folded Molecules.

I. Crystal Structure and Conformation of *cis*-9-Methylthioxanthene 10-Oxide*

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cis-9-Methylthioxanthene 10-oxide crystallizes in the space group *Pnma* with four molecules per unit cell of dimensions: $a = 8.609$, $b = 11.012$ and $c = 11.977$ Å. The two halves of the molecule are related by a mirror plane. The crystal structure was solved by means of the heavy atom method and refined by full-matrix least-squares on 867 observed reflections to a reliability index of 4.6%. Although the structure was also refined successfully ($R = 4.2\%$) in the wrong space group, $P2_12_12_1$, the molecular dimensions were chemically implausible. Both the 9-methyl and 10-oxygen substituents are 'boat-equatorial'. The best planes of the benzene rings make a dihedral angle of 127°. The *meso* atoms, C(9) and S, are significantly displaced from the benzene plane. The two S–C bond distances are equal (required by symmetry), 1.782 ± 0.002 Å, and the S–O bond distance is 1.492 ± 0.003 Å. The C(9)–CH₃ bond distance is 1.518 ± 0.006 Å, while the carbon–carbon bond involving C(9) and the benzenoid ring is 1.521 ± 0.003 Å. The intramolecular distance between the sulfoxide oxygen atom and the *peri* proton is 2.55 Å. The closest approach distance between the methyl proton and the *peri* proton is 2.35 Å. A comparison of the conformation of *cis*-9-methylthioxanthene 10-oxide with those of related folded structures indicates that the central boat ring is quite 'rigid'.

Introduction

Each of the two configurational isomers of 9-methylthioxanthene 10-oxide (*cis* and *trans*) could exist in two

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conformations, I to IV (Fig. 1). Spectroscopic investigations have failed to provide configurational and conformational assignments unambiguously to these various isomers (Ternay, 1968). This X-ray analysis on *cis*-9-methylthioxanthene 10-oxide (I) was carried out to determine whether the substituents on the 9 and 10 positions were 'boat-equatorial' (*e'*) (I) or 'boat-axial' (*a'*) (II).§ Moreover, this information would facilitate future interpretation of spectral data on these isomers and related compounds. An added reason for carrying out the present investigation was to determine accurate-

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