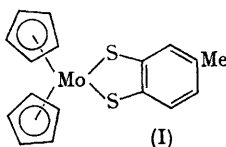


The Molecular Structure of Bis- π -cyclopentadienyl(toluene-3,4-dithiolato)molybdenum

By J. R. KNOX* and C. K. PROUT

(Chemical Crystallography Laboratory, South Parks Road, Oxford)

IN bis- π -cyclopentadienyl(toluene-3,4-dithiolato)molybdenum (I)¹ the bonding might be expected to resemble that in the dihydride (π -C₅H₅)₂MoH₂² where the lone-pair appears to lie between the ψ_y and ψ_{-y} orbitals.³ A similar arrangement in (I) should destabilise the metal-sulphur bonding but there is no chemical evidence for this. The crystal structure of (I) has been determined to discover if the lone-pair has a stereochemical influence and to measure the molybdenum-sulphur bond.



(π -C₅H₅)₂MoS₂C₆H₃CH₃, $M = 380.4$, Monoclinic prismatic, $a = 14.969 \pm 0.003$, $b = 17.691 \pm 0.003$, $c = 12.628 \pm 0.003$ Å, and $\beta = 115.5 \pm 0.2^\circ$; $D_m = 1.685$ g.cm.⁻³, $D_c = 1.705$ g.cm.⁻³, $Z = 8$, Cu- K_α radiation, $\mu = 98$ cm.⁻¹ space group $P2_1/n$ (C_{2h}^2 No. 14). 3550 independent reflections estimated visually. No absorption correction.

The structure was solved by three-dimensional Patterson and Fourier methods and refined by the least-squares method with isotropic temperature factors ($R = 0.103$) for 3550 non-zero reflections. One of the two similar molecules in the asymmetric unit contains a disordered toluenedithiol ring. The results given below are for the ordered molecule which we do not expect to change significantly in the further refinement we propose to carry out.

The molecule has planar cyclopentadienyl rings staggered with respect to each other. The angle between plane normals is 133° and the bond lengths and angles are equivalent within experimental error. The rings lie on either side of the S-Mo-S plane. This arrangement differs from that of the molecule (π -C₅H₅)₂MoH₂² which has eclipsed rings and an angle between ring normals of 145° , because the larger sulphur atoms push the cyclopentadienyl rings backwards. This compels the rings to take up the staggered configuration to avoid close contacts between the hydrogens of the >CH groups at the rear of the molecule. The

overcrowding is shown by the very close intramolecular approaches (3.05 Å to both rings) of the sulphur atoms to the cyclopentadienyl carbon atoms.

The Figure shows (a) the angles that the cyclopentadienyl ring normals make with N_z , the

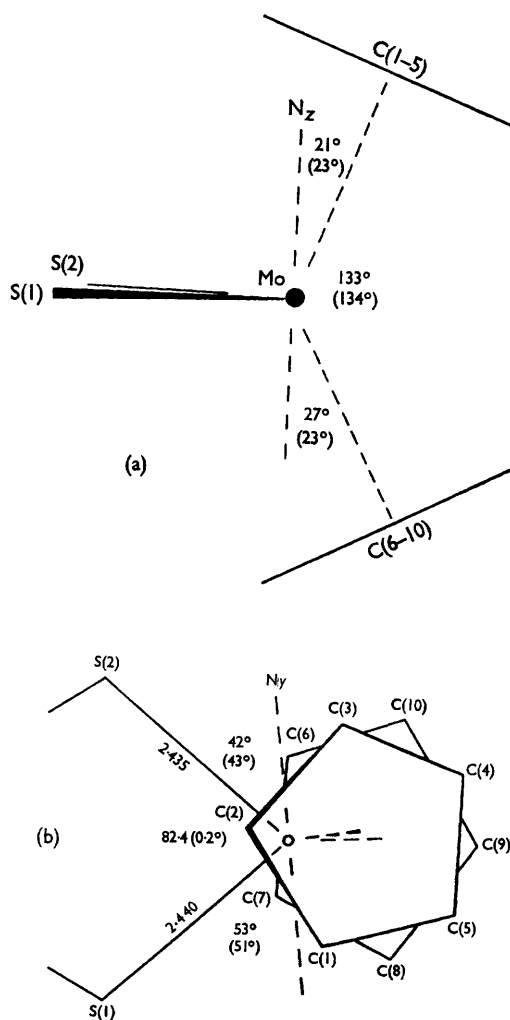


FIGURE. The bis- π -cyclopentadienyl(toluene-3,4-dithiolato)molybdenum molecule. [The benzene ring of the toluenedithiol molecule has been omitted.]

normal to the S-Mo-S plane, and (b) the angles that the Mo-S bonds make with N_y , the normal to the plane defined by the cyclopentadienyl ring normals meeting at the molybdenum atom. The angles in parentheses are with respect to (a) the vector from the molybdenum atom to the centroids of the cyclopentadienyl rings and (b) the normal to the plane defined by these vectors. The standard deviations of the angles given are about 1° and N_y and N_z are orthogonal within experimental error. The co-ordination polyhedron has symmetry C_s when defined using the molybdenum atom to ring centroid vectors and C_1 using the ring normals. However, in both cases the symmetry approximates to C_{2v} although the deviations are greater than experimental error.

It appears that each sulphur atom either lies

between the ψ_0 and ψ_y orbitals of the Ballhausen scheme³ or more likely requires a rehybridised system⁴ which has an angle between ψ_y and ψ_{-y} considerably less than 150° , and the ψ_0 orbital no longer directed towards the chelate ring. The lone-pair of electrons has no obvious stereochemical influence and there is no crystallographic evidence to suggest these electrons are involved in Mo-S π -bonding. The Mo-S distances 2.435 and 2.440 (± 0.006) Å are very close to the value of 2.45 Å obtained from Slater's⁵ radii.

This work was supported by a grant from the National Institute of General Medical Sciences, U.S. Public Health Service.

(Received, October 23rd, 1967; Com. 1134.)

¹ M. L. H. Green and W. E. Lindsell, *J. Chem. Soc.*, 1967, 1455.

² M. Gerloch and R. Mason, *J. Chem. Soc.*, 1965, 296.

³ C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, 1961, 15, 1333.

⁴ N. W. Alcock, *J. Chem. Soc.*, in the press.

⁵ J. C. Slater, *J. Chem. Phys.*, 1964, 41, 3199.