

The X-Ray Crystal and Molecular Structure of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SBU}^n)_2\text{FeCl}_2$, a Model Compound of the Nitrogenase System

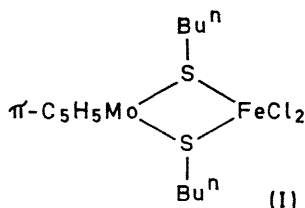
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Summary The crystal and molecular structure of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SBU}^n)_2\text{FeCl}_2$ has been determined and the molybdenum and iron atoms shown to be linked by a double sulphide bridge, Mo \cdots Fe 3.66 Å.

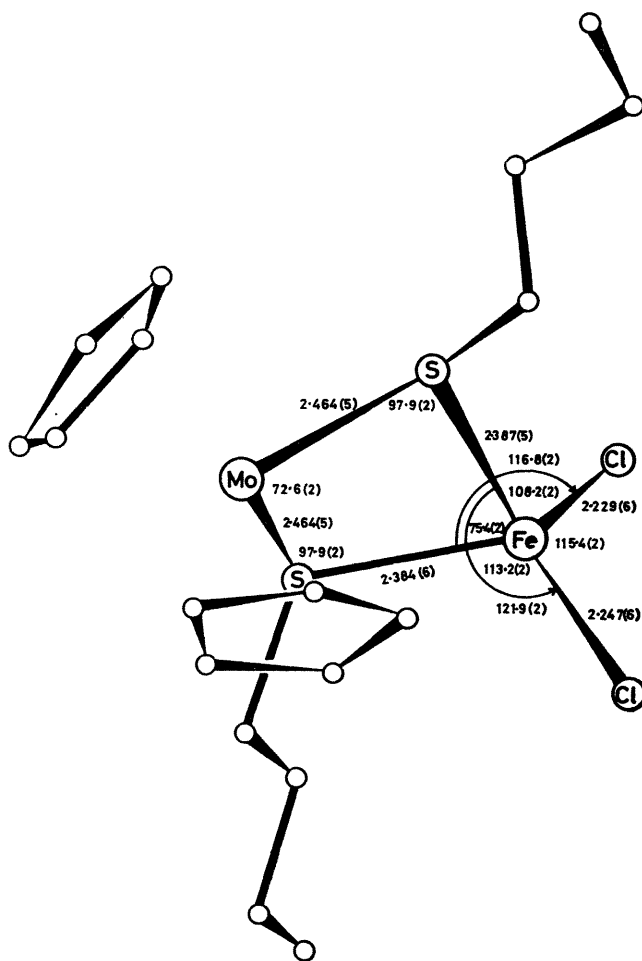
RECENT investigations suggest that sulphur-bridged molybdenum, iron systems are a significant feature of nitrogenase enzymes.¹ We report the crystal and molecular structure of the model compound (I), prepared by Dias and Green.²

Crystal data: $\text{C}_{18}\text{H}_{28}\text{Cl}_2\text{FeMoS}_2$ (I), $M = 531.24$, monoclinic, $a = 8.483$, $b = 19.686$, $c = 14.504$ Å, $\gamma = 116.7^\circ$. $D_m = 1.61$, $Z = 4$, $D_c = 1.623$ g cm⁻³, space group $P2_1/b$ (C_{2h}^5 , No. 14) Mo- K_α radiation, $\mu = 10.32$ cm⁻¹. 1885 independent reflections were measured with a Hilger and Watts linear diffractometer.



The crystal structure was determined by the heavy-atom method and refined by full-matrix least-squares, initially with isotropic and subsequently with anisotropic temperature factors on all atoms. After 6 cycles the R factor is 7%, hydrogen atoms have not yet been located, and the terminal atoms of the n -butyl groups show large thermal motions. Refinement is proceeding.

The molecule with important interatomic distances and interbond angles, is shown projected down c in the Figure. The cyclopentadienyl groups are in the staggered configuration, and the $(\pi\text{-C}_5\text{H}_5)_2\text{MoS}_2$ system is not significantly different from that found in bis- π -cyclopentadienyltoluenedithiolatomolybdenum(IV).³ The n -butyl groups, bonded to the bridging sulphur atoms are each on the same side of the MoS_2 plane; this plane is inclined at an angle of 148° to the FeS_2 plane. The metal atoms are bent away from the sulphur lone pair electrons towards the α carbon atoms of the n -butyl groups. This relieves the coulombic repulsion between the sulphur lone pairs and the electrons of the



FIGURE

Cl-Fe and $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}$ bonds. The tetrahedral environment of the iron atom permits this deformation without serious steric repulsions between the chlorine atom and the adjacent π -cyclopentadienyl group both on the opposite side of the sulphur bridge to the sulphur lone-pair electrons.

The Mo-Fe distance 3.66 Å, is somewhat shorter than the Cr-W distance⁴ 3.93 Å, in $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SPh})_2\text{Cr}(\text{CO})_4$ or the Mo-Rh distance⁵ 3.88 Å in $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SMe})_2\text{Rh}(\pi\text{-allyl})_2^+$ but longer⁴ than the supposed metal-metal bond 3.32 Å in $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{SMe})_2\text{Mo}(\text{CO})_4$ and very much longer than the Mo-Sn bond⁶ 2.66 Å, in $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{Cl})\text{SnCl}_3$. The relatively short Mo-Fe distance can be attributed to the shorter Fe-S bonds (2.38 Å *cf.* Cr-S 2.49 Å) and to the

deformation of the bridging system. Similar deformations are not observed in the $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SPh})_2\text{M}(\text{CO})_4$ (M = Cr, Mo, or W) compounds or in $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SMe})_2\text{Rh}(\pi\text{-allyl})_2^+$ -PF₆⁻ complexes,⁶ because such deformations would need too close an approach between either a carbonyl or a π -allyl group and a π -cyclopentadienyl ligand.

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¹ J. T. Spence, *Coordination Chem. Rev.*, 1969, **4**, 475; W. F. Hardy and G. W. Parshall, *Science*, in the press.

² A. R. Dias and M. L. H. Green, *Chem. Comm.*, 1969, 962.

³ J. R. Knox and C. K. Prout, *Acta Cryst.*, 1969, **B25**, 2013.

⁴ T. S. Cameron, M. L. H. Green, C. K. Prout, G. V. Rees, K. K. Joshi, G. R. Davies, B. T. Kilbourn, P. S. Braterman, and V. A. Wilson, *Chem. Comm.*, 1970, 14.

⁵ G. V. Rees and C. K. Prout, unpublished results.

⁶ T. S. Cameron and C. K. Prout, unpublished results.