

A Monomeric Molybdenum Thiolato-complex with a Chelated η^6 -Arene Ligand. The Preparation and Structure of $[\text{Mo}\{\{\eta^6\text{-Ph}\}\text{PhC}_6\text{H}_3\text{S-2,6}\}\{\text{SC}_6\text{H}_3\text{Ph}_2\text{-2,6}\}(\text{CO})]$

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Sodium 2,6-diphenylbenzenethiolate reacts with $[\text{MoBr}_2(\text{CO})_4]$ to give the chelated η^6 -arene complex $[\text{Mo}\{\{\eta^6\text{-Ph}\}\text{PhC}_6\text{H}_3\text{S-2,6}\}\{\text{SC}_6\text{H}_3\text{Ph}_2\text{-2,6}\}(\text{CO})]$ (1) in good yield, the X-ray crystal structure of which reveals a distorted 'piano-stool' geometry.

The establishment by EXAFS spectroscopy of a predominantly sulphur co-ordination sphere about molybdenum in molybdoenzymes^{1,2} has stimulated considerable recent interest in molybdenum-sulphur chemistry. However the molybdenum-sulphur species reported to date have only been capable of binding a relatively limited range of ligands. In particular there have, with the exception of cyclopentadienyl

complexes, been few reports of monomeric π -bonded organometallic species with anionic sulphur co-ligands. The complex $[\text{Mo}_2(\eta^2\text{-SMe})_4(\eta^6\text{-PhMe})_2]^{2+}$ contains a quadruply bridging thiolate system³ which dominates the chemistry. We have been employing bulky thiolate ligands to generate coordinatively unsaturated, reactive, metal-sulphur systems such as $[\text{MLL}'(\text{SAr})_3]^{n-}$ ($M = \text{Mo}$ or W , $n = 1$, $M = \text{Re}$, $n = 0$; $L = \text{MeCN}$, $L' = \text{CO}$, RNC , or PhN_2 ; $L = \text{CO}$, $L' = \text{CO}$).⁴ Here we report the preparation and structure of a monomeric 16-electron thiolato-complex of molybdenum containing a chelated η^6 -arene ligand which can be reversibly displaced by CO.

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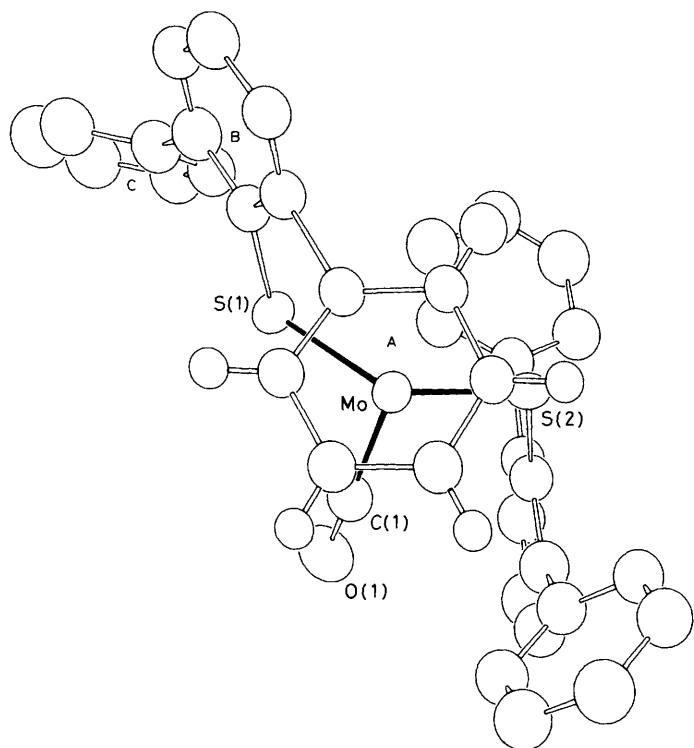


Figure 1. An ORTEP view of $[\text{Mo}\{\eta^6\text{-Ph}\}\text{PhC}_6\text{H}_3\text{S-2,6}\}\{\text{SC}_6\text{H}_3\text{Ph}_2\text{-2,6}\}(\text{CO})]$ (**1**) viewed normally to the η^6 -arene group, showing labelling of phenyl groups, and including hydrogen atoms for the η^6 -arene group only.

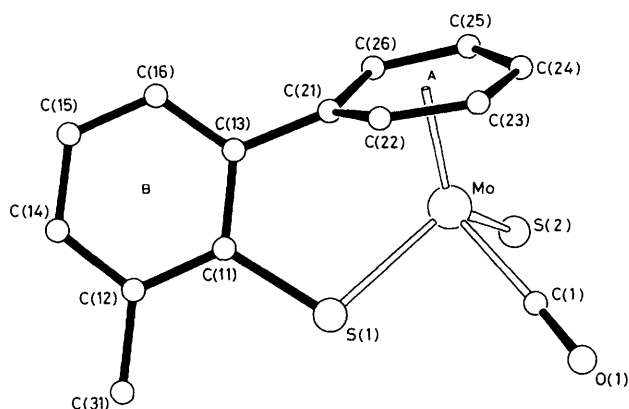


Figure 2. An ORTEP view of $[\text{Mo}\{\eta^6\text{-Ph}\}\text{PhC}_6\text{H}_3\text{S-2,6}\}\{\text{SC}_6\text{H}_3\text{Ph}_2\text{-2,6}\}(\text{CO})]$ (**1**) showing a partial atom labelling scheme. Selected bond lengths in Å and bond angles in degrees. Mo–S(1), 2.358(3); Mo–S(2), 2.329(4); Mo–C(1), 1.978(16); C(1)–O(1), 1.133(19); Mo–C(21), 2.267(12); Mo–C(22), 2.385(13); Mo–C(23), 2.361(12); Mo–C(24), 2.329(11); Mo–C(25), 2.390(11); Mo–C(26), 2.358(13); $\angle\text{S(1)–Mo–S(2)}$, 113.1(1); C(1)–Mo–S(1), 85.4(4); C(1)–Mo–S(2), 89.1(4); Mo–S(1)–C(11), 105.8(4); C(11)–C(13)–C(21), 117.9(11).

The new thiol 2,6-diphenylthiophenol (Hdpt) was prepared in about 20% yield from commercially available 2,6-diphenylphenol using the Newman–Kwart rearrangement.⁵ The molybdenum(II) carbonyl $[\text{MoBr}_2(\text{CO})_4]$ was treated with Na(dpt) (2 equiv.) in 1,2-dimethoxyethane. Evaporation of the solvent and warming to ca. 50 °C in hexane gave a bright green product, recrystallised as needles from CH_2Cl_2 –hexane

in 60–70% yield. Elemental analysis suggested the formulation $[\text{Mo}(\text{CO})(\text{dpt})_2]$ (**1**).

The i.r. spectrum of (**1**) shows a single strong band assigned to $\nu(\text{C–O})$ at 1915 cm^{-1} . Its ^1H n.m.r. spectrum in CD_2Cl_2 confirmed its diamagnetism in solution and the appearance of a series of doublets and triplets in the δ 3–6 region integrating as 5 protons implies the presence of an η^6 -arene ligand [δ 6.97 (d, *ortho*-H), 5.65 (t, *meta*-H), 5.07 (t, *meta*-H), 4.44 (d, *ortho*-H), and 3.14 (t, *para*-H)]. An upfield shift of η^6 -arene proton resonances is a common feature of such complexes. The presence of 5 such protons for (**1**) suggests that one of the *ortho*-phenyl substituents is η^6 -bonded.

This was verified by an X-ray crystal structure determination for (**1**), suitable monoclinic crystals being obtained from dichloromethane–hexane. *Crystal data*: space group $P2_1/c$, $a = 19.939(3)$, $b = 10.548(3)$, $c = 20.863(5)$ Å, $\beta = 106.88(1)^\circ$, $U = 2935$ Å³, $Z = 4$. 4220 Reflections were collected on a Nicolet R3m instrument with Mo- K_α radiation and the 1612 with $I > 3\sigma(I)$ used in structure solution to give $R = 0.056$ and $R_w = 0.052$. Patterson synthesis yielded the Mo atom position; all other atoms were located *via* standard Fourier techniques. Hydrogen atoms were included as fixed contributors in calculated positions in the final cycle of refinement. The structure is shown in Figures 1 and 2.‡

The overall geometry is a distorted variant of the ‘piano-stool’ structure commonly found for mono- η^6 -arene complexes. Steric interactions between the two thiolato-ligands cause an opening of the S(1)–Mo–S(2) angle to 113.1° compared to 85.4 and 89.1° for the S(1)–Mo–C(1) and S(2)–Mo–C(1) angles respectively. There is a slight inequivalence in the Mo–S distances [Mo–S(1), 2.358(3); Mo–S(2) 2.329(4) Å] but both lie within the range found for other molybdenum thiolato-complexes.

The plane of the non-co-ordinated *ortho*-phenyl ring c lies at 50.0° to the thiophenyl ring b. Co-ordination of the other *ortho*-phenyl ring a causes an increase of this interplanar angle to 70.8°. This rotation of ring a relative to ring b accompanies a displacement of the molybdenum atom from the plane of the chelate ring atoms C(21), C(13), C(11), and S(1), so that it achieves a position on the normal through the centroid of ring a. The co-ordination through the chelate ring system also causes a marked distortion from planarity within the η^6 -arene ring a. C(21) lies 0.14 Å from the best plane through the remaining five carbon atoms. A similar but smaller distortion was observed in the structure of $[\text{Cr}(\text{CO})_2\{\eta^6\text{-PhCH}_2\text{-CH}_2\text{P}(\text{O}^i\text{Ph})_2\}]$.⁶ The additional atom in the chelate ring of $[\text{Cr}(\text{CO})_2\{\eta^6\text{-PhCH}_2\text{C}(\text{Ph})\text{NPh}\}]$ ⁷ introduces more flexibility and permits the η^6 -arene ligand to be nearly planar. With the exception of Mo–C(21) the Mo–C distances are similar to those found in a range of molybdenum mono- η^6 -arene derivatives.⁸ Despite the distortion from planarity the C–C distances within ring a lie in the range 1.382(7)–1.429(17) Å.

As with other η^6 -arene complexes the π -bonded phenyl group is readily displaced by a variety of two-electron-donor ligands. Thus the ^1H n.m.r. resonances of the η^6 -arene group of complex (**1**) are lost on the introduction of CO but reappear on gentle warming of the CD_2Cl_2 solution. The *ortho*-phenyl group therefore functions as a convenient protecting group which can subsequently be readily displaced by small molecules to give access to further thiolato-derivatives. Preliminary experiments suggest that a related series of η^6 -arene

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

complexes is available using *o*-phenyl substituted phenylphosphines and phenols.

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References

- 1 S. P. Kramer, K. O. Hodgson, W. O. Gillum, and L. E. Mortenson, *J. Am. Chem. Soc.*, 1978, **100**, 3398.
 - 2 J. Bordas, R. C. Bray, C. D. Garner, S. Gutteridge, and S. A. Hasnain, *Biochem. J.*, 1980, **191**, 499.
 - 3 W. E. Silverthorn, C. Coldwell, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1978, 1009.
 - 4 J. R. Dilworth, J. Hutchinson, and J. A. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1983, 1034, and unpublished results.
 - 5 M. S. Newman and H. A. Karnes, *J. Org. Chem.*, 1966, **31**, 3980.
 - 6 A. N. Nesmeyanov, V. V. Krivykh, G. A. Panosyan, P. V. Petrovskii, and M. I. Rybinskaya, *J. Organomet. Chem.*, 1969, **164**, 167.
 - 7 A. Solladie-Cavallo, J. Suffert, and A. de Cain, *J. Organomet. Chem.*, 1982, **236**, 1982.
 - 8 C. Coldwell and K. Prout, *Acta Crystallogr., Sect. B*, 1982, **38**, 759.
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