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Preliminary communication

ORGANO-TRANSITION METAL OXIDES AND SULPHIDES: A TETRANUCLEAR η-CYCLOPENTADIENYLMOLYBDENUM OXIDE AND RELATED COMPOUNDS

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Summary

The compounds $[(\eta\text{-}C_5H_4R)_2M_2S_4]$ (I), and $\{[(\eta\text{-}C_5H_4R)_2M_2O_4]_2\}$ (II) (R = H or CH_3, M = Mo or W) are described and the crystal structures of I (R = CH_3) and II (R = CH_3, M = Mo) are reported.

In order to gain insight into the role of transition metals in the catalysis of reactions such as dehydrosulphurisation and the oxidation of olefins we have studied new types of organo-transition metal sulphides and oxides.

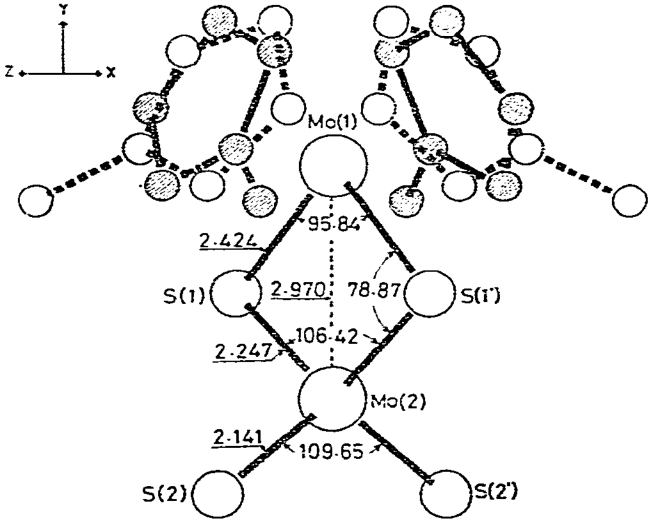

Fig. 1. View of the $[(\eta\text{-}C_5H_4CH_3)_2Mo_2S_4]$ molecule down a direction perpendicular to the two fold axes.

Treatment of aqueous solutions of [Mo(η-$C_5H_4R)_2Cl_2$] (III, R = H or CH_3) with sodium tetrathiomolybdate gives the compounds [(η-$C_5H_4R)_2Mo_2S_4$] (I). A crystal structure determination for I (R = Me) shows it to be binuclear (Fig. 1).

Crystal data. orthorhombic, *a* 10.949(4), *b* 9.524(3), *c* 14.271(6) Å, $Z = 4$, $D_c = 2.13$ g cm^{-3}; space group *Cmcm* (D_{2h}^{17}, No. 63). 1018 independent reflections were measured by four-circle diffractometry using Mo-K_α radiation (λ 0.71069 Å). The structure was solved by Patterson and Fourier methods and refined by full matrix least-squares. H-Atoms attached to the C_5 rings have been located from slant Fourier difference maps. The conventional *R* value is 0.035.

As shown on Fig. 1, the π-$C_5H_4CH_3$ rings are disordered. The length of the normal to the C_5 rings at the Mo atom is 2.027 Å and the angle between the normals is 128.2°. The Mo—Mo distance 2.970 Å and the obtuse S—Mo—S angles 95.84 and 106.42° suggest a slight Mo—Mo bonding interaction [1].

Treatment of aqueous solutions of III with sodium molybdate gives yellow-brown compounds [(η-$C_5H_4R)_4Mo_4O_8$] (II, R = CH_3 or H). The crystal structure of II (R = CH_3) has been determined and shows it to be tetranuclear.

Crystal data. monoclinic, *a* 15.38(1), *b* 9.049(5), *c* 17.72(1) Å, β 99.4(2)°, $Z = 4$, $D_c = 2.26$ g cm^{-3}; space group *C*2/*c* (C_{2h}^6, No 15); four-circle diffractometry data, Mo-K_α radiation, 1671 independent reflections. The structure was solved using methods previously described. The final *R* value is 0.071.

The unit cell contains four molecules with the structure shown in Fig. 2. This system with three dioxo bridges can be best described as a dimer of the binuclear group [(η-$C_5H_4CH_3)_2Mo_2O_4$], which is analogous to I. A crystallographic inversion centre relates both the parts of the molecule and is located in bridge II. Mo(2) has a trigonal bipyramidal geometry. The Mo(2)—O(1) distance 2.09 Å to the bridging oxygen in the equatorial plane is longer than that to the two bridging oxygens at the apices 1.85 and 1.98 Å. The equatorial plane also contains two terminal oxygen atoms. Mo(1) has a tetragonal geometry. This Mo_4O_4 is a planar system where the maximum deviation from the plane is 0.08 Å. Therefore the

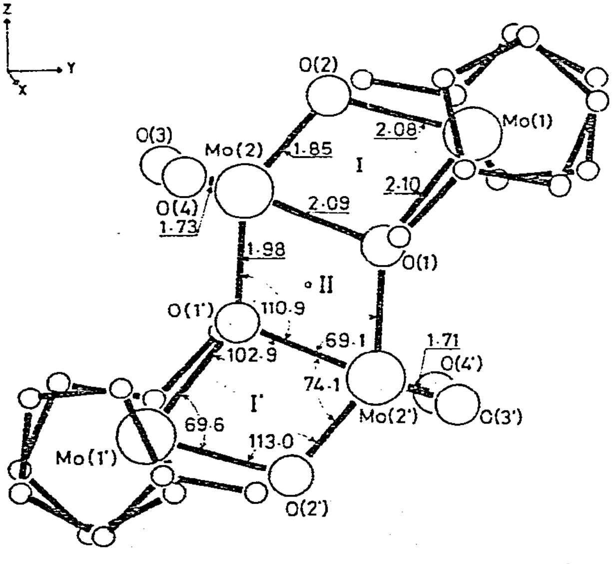

Fig. 2. The molecule [(η-$C_5H_4CH_3)_2Mo_2O_4]_2$ in projection onto the best plane of the Mo_4O_8 system.

structure and geometry of II indicate that Mo(1) and Mo(2) have the formal oxidation states +4 and +6. The Mo—Mo distances, 3.35 and 3.28 Å, and the very acute O—Mo—O angles 69.6, 69.1 and 74.1° are inconsistent with metal—metal bonding [1]. The bis(π-methylcyclopentadienyl) system has roughly the staggered conformation. The mean lengths of the normal to the C_5 rings at the Mo are 1.99 Å and the angle between the normals is 127.1°.

Tungsten analogues of II, namely $[(\eta\text{-}C_5H_4R)_4W_4O_8]$ (IV) are prepared from $[W(\eta\text{-}C_5H_4R)_2Cl_2]$ (R = H or CH_3) and sodium tungstate. The similarity of properties such as the IR spectra of the compounds II and IV strongly suggest they have the same basic structure. Compounds II and IV are slightly soluble in dimethylsulphoxide and they are stable in air.

We note that the differences between the layer structures of MoS_2 and MoO_3 arise in the greater degree of coordination of the bridging oxygen compared to the bridging sulphur atoms. Reflections of this difference are shown by greater degree of oligomerisation of compound II compared to I, indeed the tetranuclear Mo_4O_8 unit shows close analogy with the structure of a fragment of the MoO_3 lattice [2] as shown in Fig. 3.

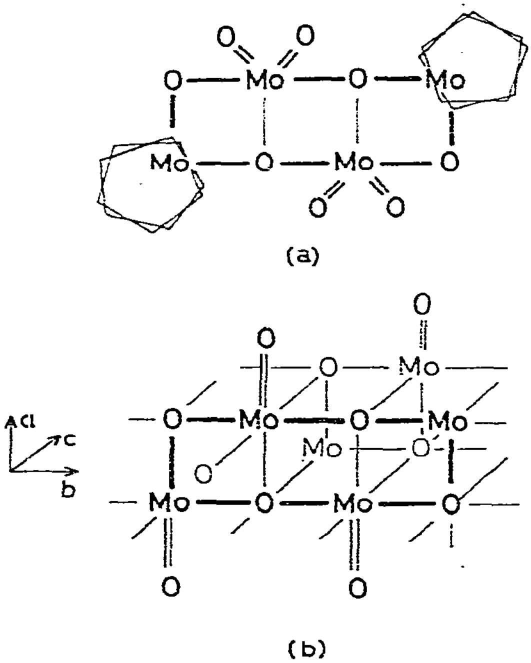

Fig. 3. (a) Structure of $(\eta\text{-}C_5H_4CH_3)_4Mo_4O_8$; (b) a fragment of the MoO_3 structure.

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