Crystallographic Studies on Molybdenum–Azulene Complexes

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OUR earlier investigation of azulenedi-iron pentacarbonyl, $C_{10}H_8Fe_2(CO)_5$, showed that the metal–azulene bonding in this complex could be described in terms of separate π-cyclopentadienyl–iron and π-allyl–iron linkages.[1] We have now extended our crystallographic studies of transition-metal azulene derivatives to cover the following molybdenum complexes:

Azulenedimolybdenum hexacarbonyl,[2] (I) $C_{10}H_8Mo_2(CO)_6$, space group $A\bar{1}$ (no. 2),† $a = 6·98$, $b = 16·25$, $c = 14·94$ Å, $\alpha = 105·0°$, $\beta = 100·7°$, $\gamma = 103·4°$, $Z = 4$.

Guaiazulenedimolybdenum hexacarbonyl[2] (II), $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$, space group $P2_1/n$ (no. 14), $a = 11·82$, $b = 16·39$, $c = 10·95$ Å, $\beta = 99·3°$, $Z = 4$.

Single-crystal X-ray crystallographic analyses of both complexes have been undertaken using complete three-dimensional data collected with a Buerger Automated Diffractometer. The present discrepancy indices are: $R = 13·0\%$ with 3200 reflections for (I), and $R = 10·2\%$ with 1890 reflections for (II). In each of these complexes the two $Mo(CO)_3$ groups are in an overall *cis*-configuration (*i.e.*, on the same side of the ligand) and are linked *via* a metal–metal bond [Mo–Mo = 3·25Å in (I), 3·27Å in (II)]. The azulene complex (I) is disordered, the two orientations being related by an approximate two-fold rotation axis through the centre of the Mo–Mo bond, such that the five- and seven-membered rings of the azulene ligand interchange positions, as do the two $Mo(CO)_3$ groups. However, to a first approximation, only atoms C-4, C-8, C-9, and C-10 fail to overlap with other atoms of the molecule in the alternative orientation (see Figure 1). Nevertheless, this pattern of disorder precludes an accurate determination of ligand geometry and prompted our study of the guaiazulene complex (II) which has an ordered crystal structure. Important stereochemical features of the two molecules are identical within experimental error; values below refer to the more accurate results obtained for the guaiazulene derivative.

The two $Mo(CO)_3$ groups have essentially identical stereochemistries [thus accounting for the excellent overlap of alternative $Mo(CO)_3$ groups in (I)]: OC–Mo–CO(*cis-*) = 80°, OC–Mo–CO(*trans-*) = 92°, Mo–Mo–CO(*trans-*) = 158°. One $Mo(CO)_3$ group is bonded symmetrically to all carbon atoms in the five-membered ring of the azulene ligand [Mo-1–C = 2·37 Å (av.)] [Mo-1–C = 2·37 Å (av.)] forming the anticipated π-cyclopentadienyl–molybdenum linkage. The second $Mo(CO)_3$ group is bonded to the five non-fused carbon atoms of the seven-membered ring (Mo-2–C-4 = 2·49, Mo-2–C-5 = 2·37, Mo-2–C-6 = 2·27, Mo-2–C-7 = 2·36, Mo-2–C-8 = 2·42 Å). The remaining two carbon atoms of the seven-membered ring already participate in the π-cyclopentadienyl–metal bonding and are sufficiently distant from Mo-2 (Mo-2 . . .C-9 = 2·82, Mo-2 . . . C-10 = 2·85 Å) to preclude any significant interaction with this atom. The molecule thus contains a *non-cyclic* π-pentadienyl–metal linkage; this is the first crystallographic analysis to be reported for such a system. The azulene skeleton of the molecule is maintained, but is distorted from planarity, the five atoms constituting the π-pentadienyl ligand being

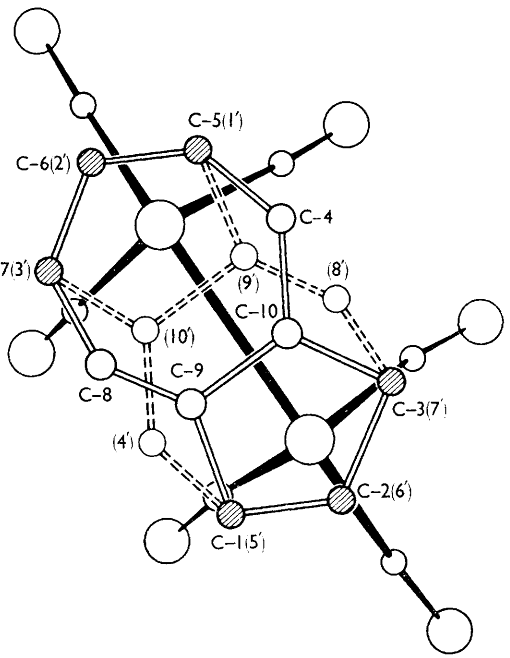

FIGURE 1. *Azulenedimolybdenum hexacarbonyl, viewed down "a" axis.*

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† Professor I. C. Paul has informed us that he has studied a monoclinic modification of this molecule. We have checked that our triclinic cell and its primitive equivalent are "reduced cells" and are therefore crystallographically distinct from the monoclinic form.

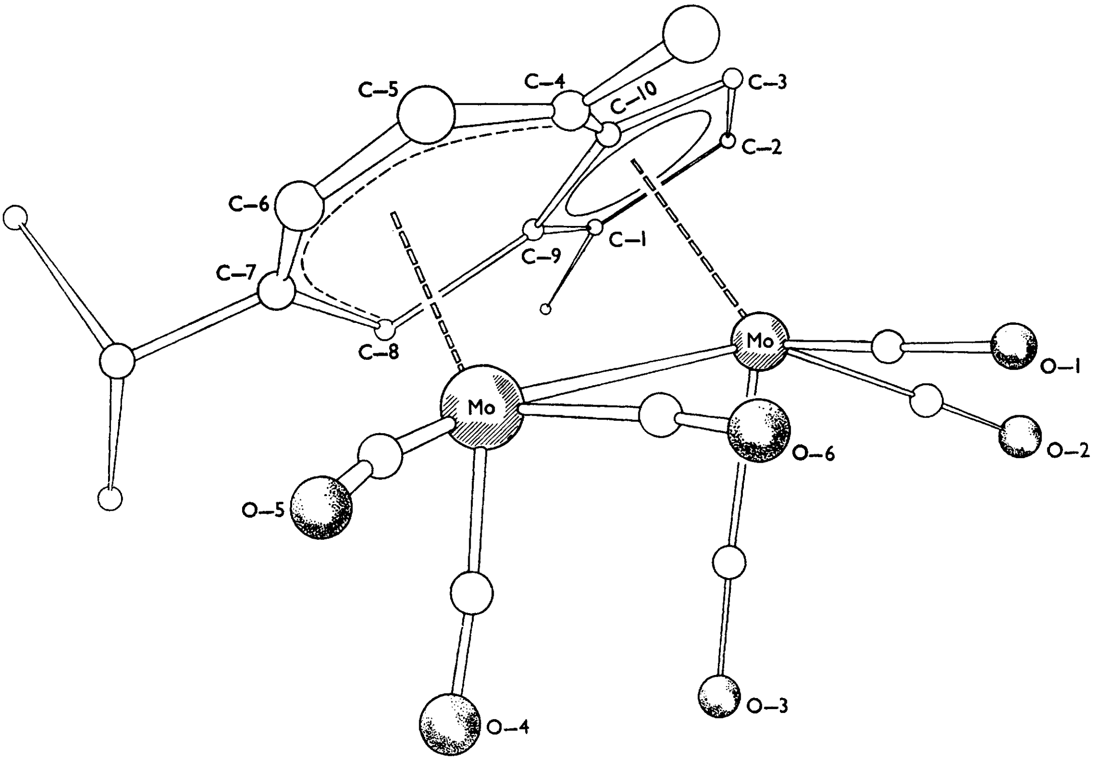

FIGURE 2. *Guaiazulenedimolybdenum hexacarbonyl, viewed down "b" axis.*

bent *away* from the molybdenum atoms by 18° relative to the least-square plane through the π-cyclopentadienyl ring. This results from a combination of (i) stereochemical requirements for simultaneous metal–π-cyclopentadienyl, metal-π-pentadienyl, and metal–metal bonding, and (ii) van der Waals repulsive forces between carbonyl groups O-1 . . . . O-6 = 3·04, O-3 . . . O-4 = 2·98 Å).

Studies are continuing on other transition-metal azulene complexes.

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[2] R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1960, 4290.