Synthesis and X-Ray Crystallographic Characterization of $[Et_4N]_2[W_2(CO)_8H_2]$ including the Direct Location and the Refinement of the Two Bridging Hydride Ligands

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Summary The new complex $[Et_4N]_2[W_2(CO)_8H_2]$ has been synthesized and its structure determined by an X-ray structural analysis; all atoms have been located (including hydrogens), the two W–H–W linkages being equivalent and symmetrical, with d(W–H) = 1·85(7) Å; $\angle$(W–H–W′) = 110(6)°, and $\angle$(H–W–H′) = 70(6)°.

IT has previously been shown[1] that the reaction of $W(CO)_6$ with BH_4^- (2:1 mole ratio) for short periods produces the ion $[W_2(CO)_{10}H^-]$. We now report that the reaction of $[Et_4N][BH_4]$ and $W(CO)_6$ in tetrahydrofuran (THF) under reflux for extended periods (2—4 days) yields $[Et_4N]_2[W_2(CO)_8H_2]$, which may be obtained as red crystals from THF–MeCN. The i.r. spectrum shows ν(C≡O)(MeCN) at 1976m, 1884vs, 1829s, and 1800s. This new complex may also be prepared by the reaction of $[Et_4N][BH_4]$ with either $[W_2(CO)_{10}H^-]$ or $[W(CO)_4(B_3H_8)^-]$.

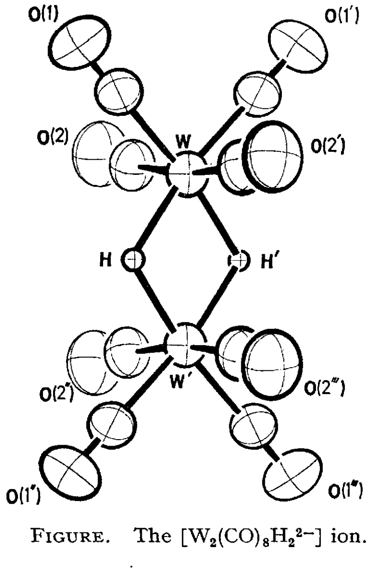

FIGURE. The $[W_2(CO)_8H_2^{2-}]$ ion.

The stoicheiometry and molecular geometry of $[Et_4N]_2[W_2(CO)_8H_2]$, have been demonstrated unambiguously *via* a three-dimensional X-ray structural analysis.

Crystal data: $C_{24}H_{42}N_2O_8W_2$, $M = 854{\cdot}31$, monoclinic, space group $C2/m$, $a = 15{\cdot}8625(40)$, $b = 12{\cdot}1292(20)$, $c = 8{\cdot}1449(17)$ Å, $\beta = 105{\cdot}28(2)°$, $U = 1511{\cdot}7$ Å^3, $D_m = 1{\cdot}86(1)$, $D_c = 1{\cdot}877$ for $Z = 2$.

Diffraction data (Mo-K_α radiation) to $2\theta = 45°$ were collected with a Picker FACS-1 diffractometer and were corrected for absorption ($\mu = 79{\cdot}75$ cm^{-1}). Following least-squares refinement (anisotropic for W,O,N,C; isotropic for H), the R-factor is 3·4% for the 1051 independent reflections. No data were rejected on the basis of being 'not significantly above background'; this is important since the co-ordinates of the tungsten atoms are $\pm(0,$ *ca.* $1/8, 0)$, and all data with $h \neq 4n$ are very weak.

The geometry of the $[W_2(CO)_8H_2{}^{2-}]$ ion is shown in the Figure. This anion has precise C_{2h} symmetry, and approximate D_{2h} symmetry. The two independent tungsten–carbonyl bond lengths are: W–C(1) = 1·956(8) and W–C(2) = 1·998(8) Å; angles within these terminal carbonyl ligands are W–C(1)–O(1) = 178·1(6) and W–C(2)–O(2) = 174·5(8)°. The angles W′–W–C(1) and W′–W–C(2) are 136·1(2) and 93·9(2)°, respectively. The tungsten–tungsten distance of 3·017(1) Å is about 0·2 Å shorter than the W–W single-bond distance of *ca.* 3·18 Å. This value comes from a study of $W_2(CO)_8H_2(SiEt_2)_2$[2] and is consistent with the value of 3·22 Å for Mo–Mo in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$[3], since Mo and W atoms have essentially the same size as a result of the lanthanide contraction.

The most significant result of this structural analysis is the location and successful refinement of the two (symmetry-related) μ_2-bridging hydride ligands. The four **W–H** distances are each 1·846(67) Å, angles being H–W–H′ = H–W′-H′ = 70(6) and W–H–W′ = W–H′–W′ = 110(6)°. The bridging hydride ligands are almost *trans* to the ligands C(1)–O(1) and C(1′)–O(1′), with H′–W–C(1) = H–W–C(1′) = H–W′–C(1‴) = H′–W′–C(1″) = 171(4)°.

Bridging hydride ligands have been directly located in few transition metal complexes.[4] [First-row metals: Mn–H = 1·86(6) in $Mn_2(CO)_8(H)(PPh_2)$,[5a] Mn–H = 1·65(10) (av) in $Mn_3(CO)_{10}(H)(BH_3)_2$,[5b] and Mn–H = 1·72(3) Å in $Mn_3(CO)_{12}H_3$;[5c] second-row metal: Rh–H = 1·85(5) Å in $[(\pi\text{-}C_5Me_5)RhCl]_2$ HCl.[5d]]

The present structural analysis represents the first example of the direct location of a hydride ligand in the presence of two third-row transition metal atoms.

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[1] R. G. Hayter, *J. Amer. Chem. Soc.*, 1966, **88**, 4376.

[2] M. J. Bennett and K. A. Simpson, *J. Amer. Chem. Soc.*, 1971, **93**, 7156.

[3] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

[4] B. A. Frenz and J. A. Ibers in 'Transition Metal Hydrides,' ed E. L. Muetterties, Marcel Dekkar, *New York*, 1971, *pp.* **33—74**, especially Table 3-3, p. 42.

[5] (a) R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1967, **89**, 4323; (b) H. D. Kaesz, W. Fellman, G. R. Wilkes, and L. F. Dahl, *ibid.*, 1965, **87**, 2753; (c) S. W. Kirtley, J. P. Olsen, and R. Bau, *ibid.*, 1973, **95**, 4532; (d) M. R. Churchill and S. W.-Y. Ni, *ibid.*, p. 2150.