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Preliminary communication

THE FLEXIBLE GEOMETRY OF THE $[HW_2(CO)_{10}]^-$ ANION

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Summary

It is found that the $[HW_2(CO)_{10}]^-$ anion exists in both linear and bent forms: in $[Et_4N]^+$ $[HW_2(CO)_{10}]^-$ the anion adopts a linear D_{4h} structure with eclipsed equatorial carbonyl groups, but in $[(Ph_3P)_2N]^+$ $[HW_2(CO)_{10}]^-$ the anion has a bent backbone and staggered equatorial carbonyl groups.

Ever since the $[HCr_2(CO)_{10}]^-$ anion was shown to have D_{4h} symmetry [1], it has been generally assumed that the analogous $[HW_2(CO)_{10}]^-$ anion would have the same structure, i.e., with a linear M—H—M backbone and eclipsed equatorial carbonyl groups. The close similarities between the infrared spectra [2] of the $[HM_2(CO)_{10}]^-$ species (M = Cr, Mo, W) certainly gave little hint that they would be anything but isostructural, at least in solution.

In this communication we wish to report that the solid state structure of the $[HW_2(CO)_{10}]^-$ anion can adopt both linear/eclipsed and bent/staggered forms, depending on the cation used.

$[(Ph_3P)_2N]^+$ $[HW_2(CO)_{10}]^-$ was prepared by using $(Ph_3P)_2N^+$ Cl^- in place of Et_4N^+ Cl^- in the published synthesis of $[Et_4N]^+$ $[HW_2(CO)_{10}]^-$ [2]. Crystals of $[(Ph_3P)_2N]^+$ $[HW_2(CO)_{10}]^-$ are triclinic (space group $P\bar{1}$), with $a = 11.433(3)$, $b = 14.244(3)$, $c = 16.791(3)$ Å, $\alpha = 58.20(1)$, $\beta = 96.55(1)$, $\gamma = 99.84(1)°$, $V = 2288.9$ Å^3, $Z = 2$. The structure was solved by heavy-atom methods and refined to a final R factor of 5.0 % for 3282 non-zero reflections**. The structure of the $[HW_2(CO)_{10}]^-$ anion in $[(Ph_3P)_2N]^+$ $[HW_2(CO)_{10}]^-$ (Fig.1) closely resembles that of the neutral isoelectronic $HW_2(CO)_9(NO)$ [3], with a bent backbone and staggered equatorial carbonyl groups. The angle of bending, defined as the angle between the two equatorial

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[**] Data were collected with Mo-K_α radiation on a fully-automated Nonius CAD-3 diffractometer. The major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. R.E. Marsh and his co-workers at the California Institute of Technology.

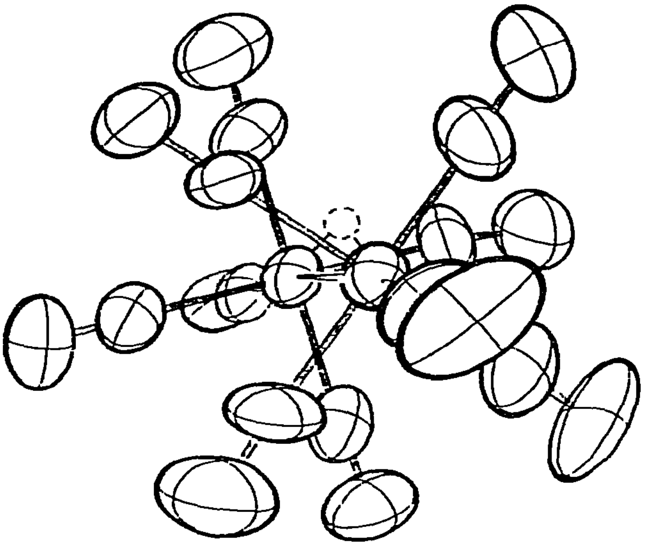

Fig. 1. Geometry of the $[HW_2(CO)_{10}]^-$ anion in $[(Ph_3P)_2N]^+$ $[HW_2(CO)_{10}]^-$. Note the slight bending of the main axis and the staggered configuration of the equatorial carbonyl groups. The H atom (dotted circle) was not located but is presumed to be at the position indicated, in analogy with the known H position in the isoelectronic $HW_2(CO)_9(NO)$ (see ref. 3b).

planes, is 15° in $[HW_2(CO)_{10}]^-$ as compared to 29° in $HW_2(CO)_9(NO)$. The bridging hydrogen atom was not located, but is most probably situated, in analogy with $HW_2(CO)_9(NO)$, at a position such that the axial ligand—tungsten vector bisects the HWW angle [3]. The W—W distance of 3.391(1)Å compares well with those found in other compounds with bent W—H—W linkages: 3.329(1) Å in α-$HW_2(CO)_9(NO)$ [3], 3.330(3) Å in β-$HW_2(CO)_9(NO)$ [3], and 3.393(4) Å in $HW_2(CO)_8(NO)P(OMe)_3$ [4]. The $[(Ph_3P)_2N]^+$ cation is in the normal bent form, with P—N = 1.555(14), 1.575(13) Å, and P—N—P = 145.8(10)°.

The rather unexpected discovery of a bent and staggered $[HW_2(CO)_{10}]^-$ anion in $[(Ph_3P)_2N]^+$ $[HW_2(CO)_{10}]^-$ led us to speculate whether this remarkable anion might actually adopt different geometries in different crystalline salts. There was a strong reason to suspect this, for while the solid state Raman spectra of $[Et_4N]^+$ $[HCr_2(CO)_{10}]^-$ and $[Et_4N]^+$ $[HW_2(CO)_{10}]^-$ are extremely similar in the carbonyl stretching region*, that of $[(Ph_3P)_2N]^+$ $[HW_2(CO)_{10}]^-$ is quite different**. Accordingly, a sample of $[Et_4N]^+$ $[HW_2(CO)_{10}]^-$ was prepared [2] and crystallized. Analysis of the single-crystal diffraction pattern of the compound showed that it is isomorphous with its chromium analog [1]. This fact alone is almost sufficient proof for a D_{4h} geometry for the anion. Nevertheless, it was decided to complete the structure analysis to remove any vestigial uncertainty regarding the geometry of $[HW_2(CO)_{10}]^-$ in $[Et_4N]^+$ $[HW_2(CO)_{10}]^-$.

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*$[Et_4N]^+$ $[HCr_2(CO)_{10}]^-$: 1853 s, 1897 w, 1918 w, 1974 vs, 2068 s cm⁻¹; $[Et_4N]^+$ $[HW_2(CO)_{10}]^-$: 1852 s, 1894 w, 1919 w, 1964 vs, 2069 s cm⁻¹ [5].

**$[(Ph_3P)_2N]^+$ $[HW_2(CO)_{10}]^-$: 1873 m, 1882 s, 1947 w, 1962 vs, 2069 m cm⁻¹.

Crystal data: Space group $P\bar{1}$(triclinic), a = 6.891(2), b = 10.196(5), c = 8.950(5) Å, α = 102.25(3), β = 101.85(3), γ = 86.27(3)°, V = 601.3 Å^3, Z = 1. The completed structure analysis (final R factor = 6.0 % for 1411 non-zero reflections) confirms that $[Et_4N]^+$ $[HCr_2(CO)_{10}]^-$ and $[Et_4N]^+$ $[HW_2(CO)_{10}]^-$ are truly isostructural. The linearity of the anion and the eclipsed configuration of the equatorial carbonyl groups (Fig.2) are crystallographically required, due to the presence of an inversion center at the mid-point of the W—W bond. As in the case of the chromium complex [1], the H atom was not located but is presumed to be at the center of the W—W bond. It is interesting to note that, while the W—W distance in the linear form of $[HW_2(CO)_{10}]^-$ (3.504(1) Å) is longer than that in the bent form (3.391(1) Å), it is significantly shorter than expected. One would normally have expected to find in the linear form a W—W distance of 3.75 Å, which is twice the W—H (bridging) distance of 1.874(2) Å accurately known from recent neutron diffraction analyses*. This contraction of about 0.25 Å may be taken as an indication that substantial W—W interaction exists even in the linear form.

As far as is known, all salts of the $[HW_2(CO)_{10}]^-$ anion in solution exhibit the same simple three-band pattern of infrared carbonyl absorptions characteristic of the linear configuration. The fact that crystalline salts of both linear and bent form of the anion can be derived from this solution suggests that the M—H—M backbone of such species is quite flexible**. In this case, the flexibility is such that crystal-packing factors are probably responsible for determining the configuration of the anion in the solid state. Unlike other bridged species of the type M—X—M, whose geometries are more or less

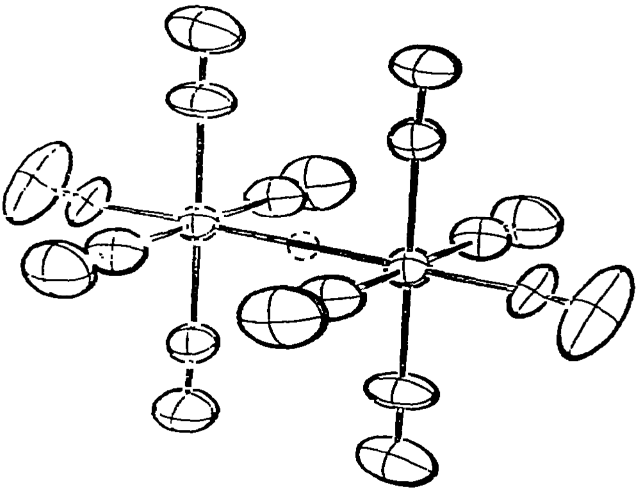

Fig.2. Geometry of the $[HW_2(CO)_{10}]^-$ anion in $[Et_4N]^+$ $[HW_2(CO)_{10}]^-$. The hydrogen atom position (dotted circle) is presumed.

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*The W—H (bridging) distance of 1.874 Å is obtained by averaging the W—H distances from several recent neutron diffraction analyses: 1.875(4) and 1.876(4) Å in α-$HW_2(CO)_9(NO)$ [3], 1.870(4) Å in β-$HW_2(CO)_9(NO)$ [3], 1.859(6) and 1.894(6) Å in $HW_2(CO)_8(NO)P(OMe)_3$ [4].

**Ironically, the $[(Ph_3P)_2N]^+$ cation itself is also known to exist in both bent and linear forms [6].

dictated by the hybridization preferences of the bridging atom X*, complexes with single M—H—M bridges should be more easily deformable, since there are no particular restraints (other than intramolecular or intermolecular steric effects) imposed on the M—H—M angle**.

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*An example would be the $[Cr_2(CO)_{10}I]^-$ anion, in which a Cr—I—Cr angle of 117.9(1)° was found [7].

**It has come to our attention that Prof. L.F. Dahl and his co-workers have independently discovered the bent geometry of the $[HW_2(CO)_{10}]^-$ anion in $[(Ph_3P)_2N]^+$ $[HW_2(CO)_{10}]^-$ [8].