A Tetrakis-(μ_3-hydroxometal) Group in the Crystal Structure of the Triphenylphosphine Oxide Adduct of $[Mo(OH)(CO)_2NO]_4$

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Summary The crystal structure of the adduct $[Mo(OH)(CO)_2NO]_4, 4(OPPh_3)$ and the probable structure of Hieber's acid and of its adduct with triphenylphosphine oxide are reported.

HIEBER has described an acid species, A, formulated as $H_3M_2(CO)_6(OH)_3$ (M = Mo or W), and a series of salts and derivatives of A containing dimethylsulphoxide, triphenylphosphine, and triphenylphosphine oxide.[1,2] Canziani *et al.* have replaced one CO by an NO group for each metal atom in A and in its derivatives, but not in the salts.[3] Typical members of both series of compounds are now under crystallographic investigation in our laboratory.

We report the crystal structure of an orange diamagnetic solid, B, which is obtained when a solution of A is allowed to react with NO at room temperature for 10 hr. and is subsequently treated with triphenylphosphine oxide, L, under the same conditions.[3]

Compound B is cubic. The crystal data are: $a = 16{\cdot}260(5)$ Å, $V = 4299(4)$ Å^3, $D_m = 1{\cdot}44$ g.cm.$^{-3}$, space group $P\bar{4}3n$ (No. 218). The molecular formula, obtained *a posteriori*, is $C_{20}H_{16}MoNO_5P$ and makes $Z = 8$ on the basis of D_m ($D_c = 1{\cdot}47$ g.cm.$^{-3}$).

The structure determination of B, in the case of the molybdenum compound, is based upon 210 independent reflections having a value of $\sigma(I)/I$ less than 0·25, measured on a PAILRED diffractometer in the range of $\sin\theta/\lambda$ 0·09—0·64 (λ = Mo-$K_{\alpha_{1,2}}$). After interpretation of the diffraction pattern with the aid of the Patterson function, the structure has been refined by full-matrix least squares with the phenyl rings constrained to rigid-body motion. The final reliability index R was 0·051.

B is a tetramer of $[Mo(OH)(CO)_2NO],L$ and is formulated as the fourfold adduct of the triphenylphosphine oxide of tetrakis-[μ_3-hydroxodicarbonylnitrosylmolybdenum(0)]. The structure, shown in the Figure without L groups, lies around and possesses the same site symmetry of positions (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) in the cell. This symmetry is T_d; the four C_3 axes pass through the four nonbonded pairs Mo–OH$^-$. The metal atoms are octahedrally co-ordinated and the tetramer results from the condensation of four octahedra sharing their OH$^-$–OH$^-$ edges. The C_3

axes are only statistical because they connect two CO groups and one NO which, therefore, are disordered.

The metal–metal interaction is definitely nonbonding, the edge of the Mo_4 tetrahedron being 3·43 Å. Other relevant bond angles and distances are given in the Figure.

A relevant feature of this structure is given by the four OH^- groups face-bonding on the metal tetrahedron, a situation which probably exists in other compounds (see, for instance, refs 4 and 5 and references cited therein). This is the second example of a μ_3-hydroxo-ligand; the first was reported by Cotton *et al.* in the crystal structure of a hexanuclear Ni^{II} species.[5]

The triphenylphosphine oxide molecules, not shown in the Figure, are connected to the tetramer through OH ··· O bridges. On the basis of the Patterson function and of a Fourier map we have refined the $OPPh_3$ groups as lying with the O–P vectors along the C_3 axes of the cell. The high thermal parameters ($B = 11{\cdot}0$ Å^2 or more) for all atoms of the group, apart from phosphorus, and also the value of the O–O distance in the hydrogen bond—which, apparently, is extremely short [2·44(3) Å]—suggest that this could be only a statistically mediated situation, the actual one being probably slightly disordered in such a way as to vary the orientation of O–P vector with respect to the threefold axes.

The species just described is strictly isomorphous with a yellow diamagnetic solid, C, that Hieber originally has formulated as $Mo(CO)_3L$. Not only are the space groups the same, but the cell edges are equal to within their experimental e.s.ds and the intensity distributions on the diffraction patterns are strictly equivalent.

Compound C, on the basis of its strict isomorphism with B, contains a similar adduct of a tetrakis-(μ_3-hydroxometal) compound with triphenylphosphine oxide. The correct formulation of C, which is diamagnetic, is that of a Mo^0 tetra-anion with H^+, H_3O^+, or even $H_5O_2^+$ cations in a more or less disordered situation. Evidence for the presence of hydroxonium ions in C has been obtained by Sartorelli.[6]

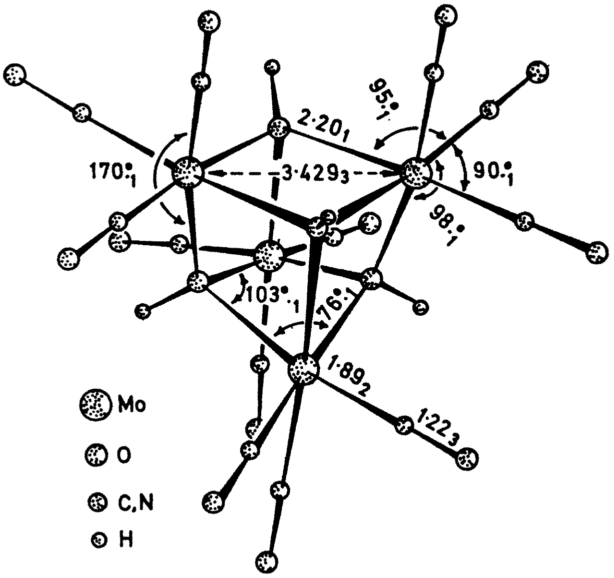

FIGURE. *Perspective view and relevant bond lengths and angles in* $[Mo(OH)(CO_2)(NO)]_4$.

It seems reasonable at this point, to re-formulate Hieber's acid, A, also as a tetramer $[M(OH)(CO)_3]_4,(H_3O)_4$.

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