Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Structure of the tri-(μ-hydroxo)hexacarbonylditungstate(0) trianion in the salt $K_3[W_2(OH)_3(CO)_6]\cdot 2H_2O$.

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(Received September 29th, 1970)

The structure of $[Mo(OH)(CO)_2(NO)]_4\cdot 4Ph_3PO$ has been recently described[1], the compound has to be formulated as the fourfold triphenylphosphine oxide adduct of tetrakis(μ_3-hydroxo)dicarbonylnitrosylmolybdenum(0). The parent diamagnetic compound having CO in place of NO, $[HMo(OH)(CO)_3]_4\cdot 4(OPPh_3)$, has been found strictly isomorphous with the previous complex[1]. The new and unexpected structural features of these compounds have prompted us to extend our structural work to other parent species of carbonyl derivatives of molybdenum and tungsten. In this note we report the structure of the salts $K_3[M_2(OH)_3(CO)_6]$ (M = Mo or W), the products of the alkaline hydrolysis of the carbonyls $M(CO)_6$ [2,3].

The tungsten compound crystallizes as $K_3[W_2(OH)_3(CO)_6]\cdot 2H_2O$ in yellow diamagnetic prisms. Crystal data are: $a = 8.85(1)$ Å, $b = 19.44(2)$ Å, $c = 9.25(1)$ Å, $\beta = 107°10'(10')$, $V = 1521$ Å^3, space group $P2_1/c$ (No. 14), $D_m = 3.23(2)\ g\cdot cm^{-3}$, $D_c = 3.24\ g\cdot cm^{-3}$ for $Z = 4$. The corresponding molybdenum compound is strictly isomorphous with this, but very unstable. The diffraction intensities, measured with a Pailred diffractometer in the range of $\sin\theta$ 0.07–0.38 ($\lambda = MoK\alpha_{1,2}$), have been corrected for Lp factors and for absorption ($\mu = 169\ cm^{-1}$). A set of 650 independent non-zero reflections with $\sigma(I)/I$ less than 0.28 has been used; the structure, solved with the aid of Patterson and Fourier maps, has been refined with the least-squares method up to a final reliability index R of 0.088.

The structure of the anion is illustrated in Fig.1. It conists of two metal atoms held together by three hydroxo groups forming regular bridges between them, and six CO groups terminally bonded to the metals. The idealized anion symmetry is D_{3h} and the coordination around each metal is trigonal antiprismatic (distorted octahedron).

The W–W distance is 3.230(5) Å; a similar distance, 3.22 Å, is bonding in the dimer $[\pi\text{-}C_5H_5W(CO)_3]_2$ [4], but in the present case the tungsten atoms complete their 18-shell without the need for a metal–metal bond. The intermetallic distance found in $[Mo(OH)(CO)_2(NO)]\cdot 4(OPPh_3)$, 3.429(3) Å, is 0.2 Å longer than the present one; this shortening may be due to the necessity of minimizing the O··O repulsions of the bridging OH groups; in fact the O··O contacts are 2.45 Å long, while the sum of the Van der Waals radii for the oxygen atom is 2.8 Å.

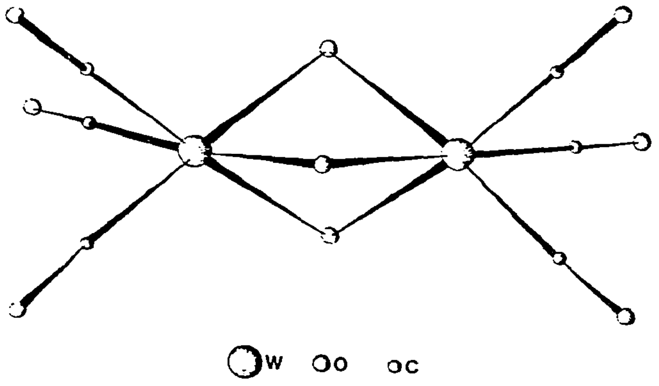

Fig.1. Perspective drawing of the trianion $[W_2(OH)_3(CO)_6]^{3-}$. Only the oxygen atoms of the μ-hydroxo groups are shown.

The μ-hydroxo groups are symmetrical within the ESD's and their bonding parameters have the following mean values: W–O = 2.16(2) Å, W–O–W = 97(1)°. The mean distances and angles for the six carbonyl groups are: W–C = 1.87(2) Å, C–O = 1.21(3) Å and W–C–O = 176(2)°. These distances indicate strong metal-to-ligand π-donation in agreement with the low frequencies of the CO stretching modes in the IR spectrum (1870–1700 cm^{-1})[5].

The K^+ cations exhibit contacts with the oxygen atoms of CO groups and H_2O molecules in the range 2.65–3.17 Å and the water molecules show an intricate net of hydrogen bonds with the CO and OH^- groups and among themselves with O–O distances in the range 2.77–3.15 Å.

Other structural determinations are in progress, in order to ascertain the molecular complexity of the hydridic products obtained on acidification of these salts[6].

ACKNOWLEDGEMENTS

This work has been financially supported by the Italian Consiglio Nazionale delle Ricerche. We thank Dr. U. Sartorelli who has prepared the crystals and furnished some chemical information. We also thank Dr. P.L. Bellon and Prof. V. Scatturin for their continued interest in this work.

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