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Deprotonation of an α-Hydroxy Group in 1-Hydroxyethylidenediphosphonic Acid and an Unusual Type of Dimeric Anion in the Structure of $Na_5[Mo_2O_6(L^*)]\cdot 14H_2O$

Inna A. Krol,[a] Zoya A. Starikova,[a] Vladimir S. Sergienko[b] and Elena O. Tolkacheva[a]

[a] *The scientific-industrial union 'IREA', 107258 Moscow V-76, USSR*
[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, 117907 GSP-1, Moscow V-71, USSR*

The synthesis and X-ray analysis of a complex containing a deprotonated α-hydroxy group, $Na_5[Mo_2O_6(L^*)]\cdot 14H_2O$, are presented; the dimeric anion has an unusual structure with a different number of terminal oxygen atoms in the 'yl' groups of the two moieties of the dimer (MoO_3 and MoO_2).

In most of the known complexes of 1-hydroxyethylidenediphosphonic acid (H_4L) with alkaline [1–5] and alkaline earth metals,[6] and with Cu^{II} [7,8] and Er^{III},[7] the OH-group remains protonated.

NMR studies of the complexation of Cu^{II} by H_4L in aqueous solution[9] have revealed the formation of the binuclear anion $[Cu_2L^*]^-$† in which the α-hydroxy group is deprotonated and the O(C) atom of this group is a bridging atom bonded to both Cu atoms. In the hexameric anion $[Mo_6O_{17}(HL^*)_2]^{6-}$ studied by X-ray analysis[10] the α-hydroxy group was found to be protonated and coordinated to one of the Mo atoms.

We now report the synthesis and X-ray analysis of another complex containing a deprotonated α-hydroxy group, $Na_5[Mo_2O_6(L^*)]\cdot 14H_2O$ **1**. Compound **1** was obtained by the reaction of Na_2MoO_4 and H_4L in a ratio 2:1 at pH 9.0 and with an Mo concentration of ~ 1 mol dm^{-3}.

The crystal is built up of Na^+ cations, dimeric complex anions $[Mo_2O_6(L^*)]^{5-}$ and water molecules of crystallization.‡ The dimeric anion has an unusual structure (see Fig. 1), in which the 1-hydroxyethylidenediphosphonic acid anion L^{*5+} is fully deprotonated, including the α-hydroxy group. Both Mo atoms possess a distorted octahedron coordination but differ in their ligand environments. Mo(1) is coordinated by three terminal oxo-atoms (O_t), one bridging oxo-atom (O_b), one oxygen atom of the PO_3^{2-} group [O(P)] of L* and atom O(C) of the deprotonated α-hydroxy group. Mo(2) is coordinated by two O_t atoms, two O(P) atoms, one O_b atom and one O(C) atom. The octahedra in the dimer share a common edge O_b—O(C). The Mo—Mo distance is 3.404(1) Å, and the bond angles are Mo(1)—O_b—Mo(2) 112.1(1) and Mo(1)—O(C)—Mo(2) 99.1(1)°.

Such a structural type with a different number of terminal oxygen atoms in the 'yl' groups of the two moieties of the dimer (MoO_3 and MoO_2) is unique for oxo complexes of group 5–7 d^0 metals and, in particular, for dimeric Mo^{VI} compounds. The latter, as a rule, have two MoO_2^{2+} dioxo groups united by

† L* denotes an anion in which the α-hydroxy group is deprotonated while for the usual type of 1-oxyethylidenediphosphonic acid anion the notation L is used. The anion charges are L^{*5-} and L^{4-}, respectively.

‡ *Crystal data* for **1**: $Na_5Mo_2O_{13}P_2C_2H_3\cdot 14H_2O$, triclinic, space group $P\bar{1}$, $a = 9.503(3)$, $b = 16.703(5)$, $c = 8.563(5)$ Å, $\alpha = 97.20(4)$, $\beta = 97.75(4)$, $\gamma = 84.03(2)°$, $U = 1330(2)$ Å^3, $M = 856.1$, $Z = 2$, $D_x = 2.128$ g cm^{-3}, $\lambda = 0.7107$ nm, μ(Mo-Kα) = 12.2 cm^{-1}, $F(000) = 856$, $T = 300$ K. Intensity data were collected on an Enraf–Nonius CAD-4-SDP diffractometer by the ω–θ scan method in the range $2 \leq 2\theta \leq 52°$. The structure was solved by the Patterson method and refined by full-matrix least-squares procedures (all non-H atoms anisotropic, H atoms isotropic). The final residuals R and R_w are 0.036 and 0.0415 ($w = A/\sigma^2F + bF^2$, $A = 0.5940$, $b = 0.002086$) for 3989 observed reflections with $I \geq 3\sigma(I)$. All calculations were carried out on a PDP-11/55t computer and a UNIPAC PC-256 personal computer using the Enraf–Nonius ENX-SDP and SHELX76 program packages.[11] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1 of *J.C.S. Chem. Commun.*

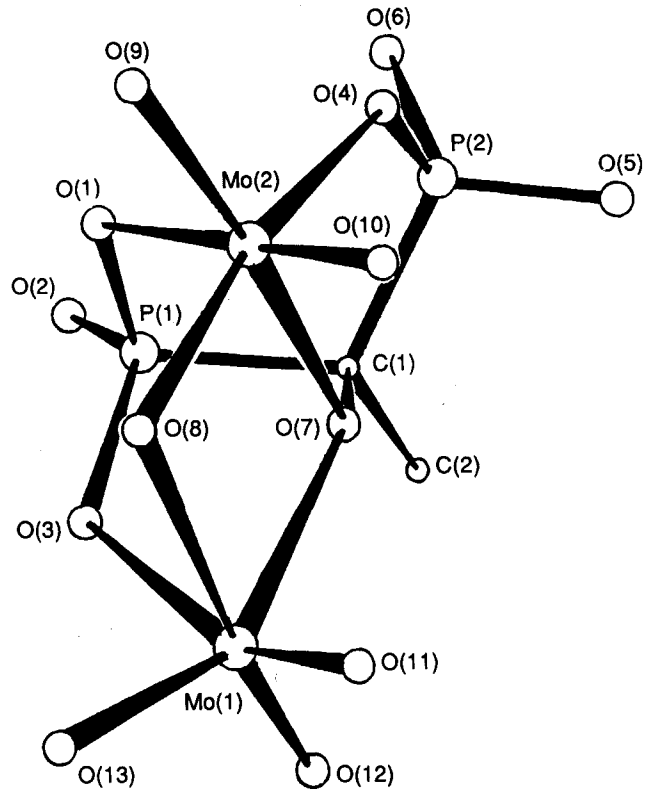

Fig. 1 Structure of the dimeric anion $[Mo_2O_6(L^*)]^{5-}$. Bond lengths: Mo(1)—O(3) 2.232(3), Mo(1)—O(7) 2.189(3), Mo(1)—O(8) 2.289(4), Mo(1)—O(11) 1.750(3), Mo(1)—O(12) 1.741(3), Mo(1)—O(13) 1.745(4), Mo(2)—O(1) 2.247(3), Mo(2)—O(4) 2.064(3), Mo(2)—O(7) 2.283(3), Mo(2)—O(8) 1.803(4), Mo(2)—O(10) 1.742(3), Mo(2)—O(9) 1.724(3), P(1)—O(1) 1.542(4), P(1)—O(2) 1.500(4), P(1)—O(3) 1.546(4), P(1)—C(1) 1.838(5), P(2)—O(4) 1.565(4), P(2)—O(5) 1.523(4), P(2)—O(6) 1.493(4), P(2)—C(1) 1.834(5), C(1)—O(7) 1.463(3), C(1)—C(2) 1.509(7)

oxo-bridges (sometimes in combination with chelate-bridging organic ligands). In these complexes coordination octahedra of Mo atoms in the dimer are united in different ways (sharing a common vertex, edge or face).

The oxygen bridge O_b is markedly asymmetric, and the O_b atom plays the part of a multiply bonded ligand with respect to the Mo(2) atom. The three O_b atoms bonded to Mo(1), and the two O_t atoms and one O_b atom bonded to Mo(2) are on the common face of the MoO_6 octahedron. The distances Mo—O(P) and Mo—O(C), *trans* to Mo—O_t, are lengthened (to 2.189–2.289 Å) owing to the *trans* effect of the multiply bonded oxo-ligands O_t. The Mo(2)—O(P) bond, *trans* to Mo(2)—O_b, is somewhat lengthened (to 2.064 Å) compared with the Mo—O(P) bonds, *cis* to Mo—O_t, in the structures of $(NH_4)_3[MoO_2(H_3L_2)]\cdot 6.75H_2O$,[12] $(NH_4)_5[MoO_2(HL)_2]\cdot 5H_2O$[13] and $Na_4(NH_4)[MoO_2(HL)_2]\cdot 15H_2O$[14] (1.958–1.988 Å). This indicates the presence of a multiply bonded pseudo-trioxo group $Mo(O_t)_2O_b$ at Mo(2).

In the completely deprotonated tetradentate chelate-bridging ligand L^{*5-}, Mo(1) and Mo(2) are linked to three O(P) atoms from the two phosphoryl groups and to one O(C) atom exhibiting an unusual bridging function. It might be assumed that 1-hydroxyethylidenediphosphonic acid, on titration with alkali (to pH 12), would behave as a tetrabasic acid H_4L, and this is confirmed by potentiometric titration data.[15,16] In the process of complex formation with transition metals the elimination of the fifth proton from the aliphatic hydroxy group of the pentabasic acid H_5L^* is possible.

Comparing the structures of dimeric, hexameric and monomeric anions $[Mo_2O_6(L^*)]^{5-}$, $[Mo_6O_{17}(HL^*)_2)]^{6-}$, $[MoO_2(H_3L_2)]^{3-}$ and $[MoO_2(HL)_2]^{5-}$, one can conclude that the strength of the P—O bonds whose atoms are coordinated to the metal atoms is primarily determined by the position of the O(P) atom in the MoO_6 octahedron. The P—O bonds whose coordinated atoms are in a position *trans* to the Mo—O_t are shorter than the analogous bonds which are *cis* to Mo—O_t (the average values are 1.538 and 1.563 Å, respectively).

The bond lengths of the P—O bonds formed by the non-coordinated O atoms are 1.493, 1.500 and 1.523 Å in **1**. The Na^+ cations are octahedrally and square-pyramidally coordinated by the O atoms of the water-molecules of crystallization and those of the MoO_3, MoO_2 and PO_3 groups of the anion [Na—O 2.288–2.688(5) Å].

The structural units in the crystal are united by a branched system of hydrogen bonds in which all the oxygen atoms of the anion [with the exception of O(C) and the terminal atom O(10)] and those of all the H_2O molecules are involved (O···O 2.709–3.095, O···H 1.73–2.41 Å, angles OHO 132–178°). The terminal atom O(10) is a bridging atom between two Na atoms.

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