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Synthesis, IR Study and Crystal Structure of a Novel Mononuclear Tungsten(VI) Oxo Complex with 1-Hydroxyethylidenediphosphonic Acid, Exhibiting a WO_3 Core

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The synthesis and IR spectroscopic and X-ray diffraction studies of $[C(NH_2)_3]_5[WO_3(L^*)]\cdot 4.5H_2O$,† the first W^{VI} monomeric compound to contain a WO_3 group, have been carried out and an unusual structure (with ratio M:L*=1:1) has been observed for both independent complex anions: the tungsten atoms have *fac*-octahedral coordination with three terminal oxo-atoms (O_t), two O(P) atoms and one O(C) atom of the tridentate ligand L* in the *trans* position to O_t.

Tungsten(VI) oxo complexes have been poorly investigated as compared with the analogous molybdenum(VI) compounds. The structure of Mo^{VI} mononuclear compounds containing not only one or two oxo groups, but up to three oxo groups have been studied, whereas structures containing only one or two terminal oxo ligands are known for the monomeric W^{VI} complexes. Tungsten(VI) trioxo compounds are extremely unstable in solution, and often can not be isolated in the solid state.[1,2] Stable in water and alcohols, trioxo tungstates of cyclic triamines obtained in the solid state are an exception, but these compounds have only been characterized by chemical analysis and IR spectroscopy.[3,4]

Systematic studies on complex formation have previously been carried out by us for the $M^+/H^+–MoO_4^{2-}–H_2L^{2-}$ system.[5] The crystal structure of a number of the compounds derived from this system in the form of crystal hydrates has been studied by X-ray diffraction. The H_4L ligand was shown to stabilize compounds containing complex anions in various degrees of oligomerisation: mononuclear, $[MoO_2(H_nL_2)]^{n-6}$, $n = 0$[6], 1[7,8] and 3[9] (Mo:L = 1:2); binuclear, $[Mo_2O_6(L^*)]^{5-}$ [10–12] (Mo:L* = 2:1); trinuclear, $[Mo_3O_9(L^*)]^{5-}$ [13,14] (Mo:L* = 3:1); hexanuclear anions, $[Mo_6O_{17}(H_nL^*)_2]^{2n-8}$, $n = 0$[15] and 1[16] (Mo:L* = 6:2). However, attempts to synthesize the mono-

† The form of the anion in which the α-hydroxy group is deprotonated is denoted by L^{*5-}, while the L^{4-} notation is used for the usual type of 1-hydroxyethylidenediphosphonic acid anion.

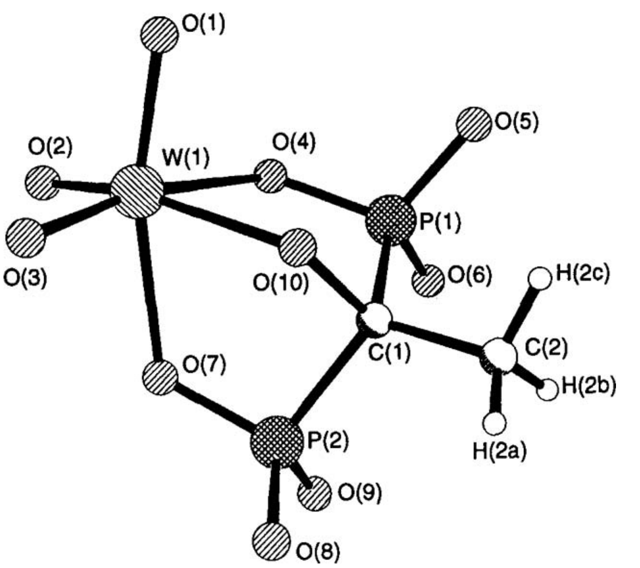

Fig. 1 The structure of one of two independent complex anions $[WO_3(L^*)]^{5-}$; interatomic bond lengths (Å) and angles (°): W(1)–O(1) 1.76(1), W(1)–O(2) 1.774(8), W(1)–O(3) 1.77(1), W(1)–O(4) 2.215(8), W(1)–O(7) 2.209(8), W(1)–O(10) 2.052(8), P(1)–O(4) 1.550(7), P(1)–O(5) 1.51(1), P(1)–O(6) 1.524(9), P(1)–C(1) 1.83(1), P(2)–O(7) 1.533(8), P(2)–O(8) 1.510(9), P(2)–O(9) 1.512(9), P(2)–C(1) 1.83(1), O(10)–C(1) 1.46(1), C(1)–C(2) 1.51(1) Å, O(1)–W(1)–O(2) 101.0(4), O(1)–W(1)–O(3) 101.3(5), O(2)–W(1)–O(3) 100.8(4), O(4)–W(1)–O(7) 79.9(3), O(4)–W(1)–O(10) 76.8(3), O(7)–W(1)–O(10) 75.8(3), O(1)–W(1)–O(7) 165.7(4), O(2)–W(1)–O(10) 155.2(4), O(3)–W(1)–O(4) 168.3(4)°

nuclear complex, ratio Mo:L(L^*) = 1:1, have not been successful.

We have recently begun a structural investigation of a class of W^{VI} complexes with H_4L (H_5L^*), previously unknown. The $[C(NH_2)_3]_5[W_2O_6(L^*)]\cdot 3H_2O$[17] compound, which is isostructural to the Mo^{VI} analogue,[12] contains a $[W_2O_6(L^*)]^{5-}$ (W:L^* = 2:1) binuclear complex anion.

The results of synthesis and IR spectroscopic and X-ray studies of the novel complex $[C(NH_2)_3]_5[WO_3(L^*)]\cdot 4.5H_2O$ **1** are presented in this article. The composition of complex **1** has been determined in an X-ray diffraction study.‡

Single crystals of **1** were obtained by slow evaporation of an aqueous solution containing $Na_2WO_4\cdot 2H_2O$ and $H_4L\cdot H_2O$ (1:2 molar ratio) and $[C(NH_2)_3]_2CO_3$ at pH ~ 7.5. The initial concentration was *ca.* 1 mol dm^{-3}.

Four intense absorption bands (779, 812, 882 and 930 cm^{-1}) in the M–O bond stretch region were observed in the IR spectrum of **1**. We had assumed initially that the compound had a polymeric structure because two intensive bands in the IR spectra of transition metal oxo compounds in the range 800–1000 cm^{-1} [18,19] can be attributed to the M=O multiple bond vibrations, and additional broad bands could be assigned to M-O-M[18] bridging bond vibrations. However, this assumption was not supported by an X-ray diffraction study. The complex anion in compound **1** has a mononuclear structure and contains a WO_3 fragment. The bands in the region *ca.* 870 and 820 cm^{-1} are usually assigned to ν_s (MO_3) and ν_{as} (MO_3) stretching frequencies, respectively. It is probable that the occurrence of four absorption bands instead of two in the IR spectrum of compound **1** is a consequence of the presence of two crystallographically independent $[WO_3(L^*)]^{5-}$ complexes.

Two crystallographically non-equivalent $[WO_3(L^*)]^{5-}$ complexes have a similar structure (Fig. 1). The corresponding bond lengths and bond angles differ by *ca.* 0.03 Å and 3.7° in two independent complexes. Both tungsten atoms have distorted octahedral coordination with an arrangement typical for trioxo complexes of d^0 metals with terminal oxo atoms (O_t) placed on one face of the octahedron. Two O(P) atoms of two PO_3 groups and the O(C) atom of the deprotonated α-hydroxy group of tridentate chelate ligand L^* occupy a *trans* position with respect to the O_t atoms.

The monomeric complex anions $[WO_3(L^*)]^{5-}$ in structure **1** are unique in their metal:ligand ratio (1:1) and also in the nature of the deprontonation of 1-hydroxyethylidendiphosphonic acid. In the monomeric complexes studied previously the initial acid acted as tetrabasic H_4L; completely deprotonated L^{*5-} ligand was found only in the oligomeric (bi-, tri- and hexanuclear) structures of the anions. As mentioned above, H_5L^* acid is deprotonated completely and its O(C) atom is coordinated by the metal atom in the complex anion of **1**.

The W=O_t mean distance in **1** (1.769 Å) is similar to the value found for the terminal trioxo group in $[W_2O_6(L^*)]^{5-}$ [17] binuclear anion **2** (1.762 Å). The W=O_t bonds in the WO_3 group of **1** and **2** are longer, on the average, by 0.02–0.05 Å than the corresponding distances in mono-, bi- and trinuclear molybdenum complexes (Mo=O_t 1.715–1.747 Å).[10–14,20–26] The elongation of the M=O_t bonds in going from Mo^{VI} trioxo complexes to the analogous W^{VI} compounds indicates that the extent of localization of π-interaction on the M=O bonds decreases in the case of tungsten. The W–O_{trans} bond lengths are not equal in structure **1**: the W–$O(P)_{ch}$ mean bond length is greater than W–$O(C)_{ch}$ by 0.149 Å. The W–$O(P)_{ch}$ bond lengths in structure **1** (2.204 Å) are comparable to the analogous bond lengths in complex **2** (2.190 Å), whereas the W–$O(C)_{ch}$ bonds in structure **1** are noticeably shorter than the W–$O(C)_{chb}$ bonds *trans* to the M=O_t bonds of the MO_3 fragment in W^{VI} binuclear complex **2** (2.222 Å).

It is possible that such non-equivalence of the W–O bond lengths arises from the greater rigidity of the O(P) atoms as compared with O(C) [*i.e.* a consequence of less effective negative charge on the O(P) atoms] because of the delocalization of electron density over three P–O bonds of the PO_3^{2-} phosphonic group (and, hence, because the manifestation of the *trans* effect is facilitated). Anotber possible reason for the effect is the rigid position of the central O(C) atom in the bicyclic chelate system.

In L^* ligands, P–O bonds with oxygen atoms of chelate cycles (O_{ch}) are longer than P–O bonds with a terminal oxygen atom (O_t): the mean P–O_{ch} bond length is 1.548 Å, mean P–O_t bond length is 1.513 Å.

The complex anions, guanidinum cations and water molecules in **1** are united by a branched system of N–H···O and O–H···O ordinary and bifurcated hydrogen bonds involving all oxygen atoms from two independent anions (the shortest contacts are N···O 2.78, O···O 2.59, H···O 1.79 Å, and the range of NHO bond angles is 112–175°.

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‡ Crystal data for **1**: $WP_2O_{10}N_{15}C_7H_{21}\cdot 4.5H_2O$, triclinic, space group $P\bar{1}$, a = 10.094(3), b = 17.125(6), c = 18.915(5) Å, α = 109.26(3), β = 102.66(2), γ = 100.94(3)°, V = 2887(2) $Å^3$, M = 620.8, Z = 4, D_x = 1.873 g cm^{-1}, λ = 0.7107 nm, μ(Mo-K_α) = 42.8 cm^{-1}, $F(000)$ = 1636, T = 294 K. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using an ω scan method ($2\theta_{max}$ = 50°). An empirical absorption correction was applied by a ψ-scanning method. The structure was solved by the heavy-atom method and refined by full-matrix least-squares in an isotropic approximation for water oxygen atoms and an anisotropic one for all other non-hydrogen atoms. The coordinates and thermal parameters of the hydrogen atoms of guanidinium cations and methyl groups were fixed (U_H 0.05 $Å^2$, C–H 1.00, N–H 1.00 Å). The population factors of the positions of O(W8)–O(W11) atoms are 0.5. Final values of R and R_w are 0.037 and 0.045, respectively (w = 1), S = 4.35 for 5701 observed reflections with $I \geqslant 2\sigma(I)$. All the calculations were performed on an IBM PC/AT using SHELX76 programs. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Centre, see Notice to Authors, *Mendeleev Commun.*, 1993, issue 1.

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