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Crystal Structure of the Barium Salt of the Binuclear Tungsten(V) Complex, Di-μ-oxo-μ-(N,N′)ethylenediaminetetra-acetato-bis[oxotungstate(V)], $Ba[W_2O_4(C_{10}H_{12}O_8N_2)]3.5H_2O$

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Whereas an extensive range of oxo(Mo(V) complexes containing MoO, Mo_2O_3 and Mo_2O_4 subunits have been prepared [1], the chemistry of W(V) is much less well understood and few analogues have been isolated. We here report the crystal structure of a W_2O_4 complex of W(V) which to date appears to be the only well characterised compound of this kind. A comparison of structural dimensions of compounds of W and Mo in different oxidation states is made.

Experimental

The sodium salt of the oxalato complex, reported to have the formula $Na_3[WO_2(C_2O_4)_2]3H_2O$, was used as a source of W(V) [3]. Details of the procedure for the conversion to orange–brown crystals of the title complex have already been described [4]. Analyses were in accordance with the formula $Ba[W_2O_4(edta)]3.5H_2O$ where edta = ethylenediaminetetra-acetate. The u.v.–visible spectrum of the complex in H_2O gave peak positions (nm) and absorption coefficient (M^{-1} cm^{-1}) at 275 (1.4×10^4), 340 (1100) and 423 (*ca.* 350).

Results and Discussion

The X-ray crystal structure was determined by conventional Patterson and Fourier synthesis, and refined by a full matrix least-squares method to a final R value of 0.059. A total of 4103 reflections was collected on an Enraf–Nonius CAD-4 diffractometer at room temperature using graphite crystal monochromatised Cu-Kα, radiation (λ 1.5405 Å) to $\theta = 70°$ with the ω–2θ scan technique. No absorption coefficient was made. The complex crystallises in the orthorhombic system, space group Ima2 with cell dimensions $a = 19.241$, $b = 14.852$, $c = 14.091$ Å and $Z = 8$. There are two independent and like binuclear W_2O_4 units, where the crystallographic unit cell contains four of each type. The first tungsten atom lies to one side of the crystallographic mirror plane forming, with its image and the bridging oxygens which lie in the mirror plane, the first anion. The second anion has a reverse arrangement with the two tungsten atoms lying in the mirror plane, while the bridging oxygens lie one on either side of this mirror plane, one being the image of the other. The tungsten atoms in each binuclear unit are coordinated by six atoms in a distorted octahedral environment (Figure). The two octahedra share a common edge containing the two bridging atoms. The ethylenediamine group of the edta also bridges the metal atoms.

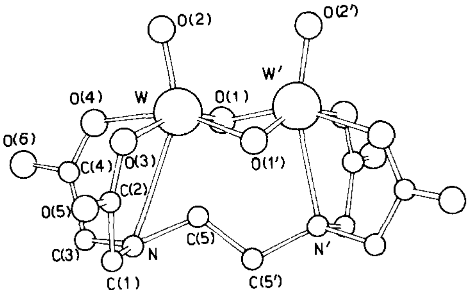

Figure.

The bridging oxygen atoms O(1) and O(1′) are an average of 1.91 Å from the two metal atoms. The W–W′ distance of 2.55 Å is consistent with metal–metal bonding and the observation that the complex is diamagnetic [4]. Bond lengths to the terminal oxo ligands, W–O(2) and W′–O(2′), average 1.72 Å. Each tungsten is displaced from the mean plane containing the bridging oxygen atoms by *ca.* 0.37 Å, giving a WO_2 dihedral angle of 147°. Comparable distances for five Mo_2O_4 type complexes average 1.92 Å ($Mo–O_{br}$), 2.55 Å (Mo–Mo) and 1.69 Å ($Mo{=}O_t$) [5]. Displacement of the Mo's is *ca.* 0.35 Å and the MoO_2 dihedral angle 140–150° in these complexes.

The present determination not only confirms the presence of the W_2O_4 unit, but again demonstrates the remarkable structural similarity of W and Mo in many (but not all) situations. The identical M–M distance (2.55 Å) for the V oxidation state complexes*, compares with M–M distances (Å) for the metal (Mo 2.73, W 2.74) [6, 7], for $M^{II}Cl_2$ cluster compounds (Mo 2.63, W 2.64) [6, 7], and in the oxides $M^{IV}O_2$ (Mo 2.51, W 2.49 [8, 9].

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*No crystal structure determination of the $[Mo_2O_4(edta)]^{2-}$ complex has yet been completed. In a preliminary investigation on the sodium salt an Mo–Mo distance of 2.5 Å has been obtained, but it was only possible to refine to $R = 0.15$. We are grateful to Professor Sawyer of the University of California, Riverside, for this information.

However, in the complexes $M_2^{III}Cl_9^{3-}$ (Mo 2.67, W 2.41) [10], a significantly shorter W–W bond is observed which is accounted for by strong bonding (one σ and two π) between the two tungsten atoms.

An aquo ion, yellow in colour, is obtained by reacting $[W_2O_4(edta)]^{2-}$ with 2–3 *M* HCl in air-free conditions [11]. The spectrum generated ($t_{1/2}$ = *ca.* 15 min in 3*M* HCl) has similar features to that of $[W_2O_4(edta)]^{2-}$ with peak positions at 262 (ϵ 6800 M^{-1} cm^{-1}), 345 and 430 nm, suggesting that the aquo ion is $W_2O_4^{2+}$ or a closely related species.

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