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Formation and Structure of the Tetranuclear Mixed Valence Anion $[W_2^{(VI)}W_2^{(V)}S_{12}]^{2-}$

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In recent years, considerable interest has grown concerning sulfur-containing polynuclear complexes with respect to the biochemical implications of their redox behaviour [1]. Emphasis has been placed on μ-sulfido and di-μ-sulfido Mo(V) species [2–5] but there is up to now little information on complexes of tungsten with such a high sulfur content [6–8]. This paper describes the structure of the first tetranuclear complex with two $W^{(VI)}$ and two $W^{(V)}$ atoms ligated by double bridged sulfur atoms. The two different valence state metals have two different coordination geometries.

Experimental

The tungsten(VI) tetrathiotungstate $[P(C_6H_5)_4]_2(WS_4)$ (0.5 mmol) was reacted with 100 ml of a CH_2Cl_2 solution of acetic acid (3.5 mol l^{-1}) for three days. Dark red crystals were isolated by filtration and washed with ether (yield 96%). The formula determined from analysis data is $[(P(C_6H_5)_4)(WS_3)_2]_n$ (Found: W = 40.8%, S = 20.9%, C = 32.1%). The 'n' value was determined from X-Ray data. The IR solid state spectrum shows a strong band at 495 cm^{-1} ($W–S_{terminal}$), whereas the 465 cm^{-1} one was attributed to W–S–W bridges.

Crystals were examined by X-Ray diffraction methods at room temperature.

Crystal Data

M = 1798, triclinic, space group $P\bar{1}$ (from structure analysis) a = 19.278(1) Å, b = 21.244(2) Å, c = 14.929(6) Å, α = 89.43(6)°, β = 89.73(6)°, γ = 78.23(1)°, V = 5985 Å^3, μ = 8.62 mm^{-1}, Z = 4, d_m = 2.00 g cm^{-3}, d_c = 1.996 g cm^{-3}. The intensities of 11187 independent reflections with $2\theta \leqslant 40°$ were recorded by four circle diffractometry using Mo-Kα radiation (0.71069 Å). The structure was solved by direct methods [9] and refined by least squares procedure (phenyl rings were considered as rigid groups). Refinements are not achieved; the conventional R value to date is 0.108.

A perspective view of the anion with selected distances is shown in Fig. 1. The anion consists of two central edge linked pyramids sharing basal edge with two terminal WS_4 tetrahedra. As reported previously [2], two isomers are possible for two pyramids sharing a basal edge. The molecule described here adopts the syn conformation. The dihedral angle between the two pyramids is 147.5° as previously found [2].

The tetrahedral environment on W(1) and W(4) is slightly distorted. The average values of the four bonds in the WS_4 groups are respectively 2.204 Å and 2.191 Å. 2.195 Å is reported for W–S bonds in $(Zn(WS_4)_2)^{2-}$ and $(WO(WS_4)_2)^{2-}$ anions [6, 7, 10]. A (+VI) valence state is expected for the W(1) and W(4) atoms since tetrahedral coordination is a feature of hexavalent tungsten. The geometries about W(2) and W(3) are similar. Four sulfur atoms form the basal plane and a thio group lies on the apex of the tetragonal pyramid. The W(2) and W(3) atoms are

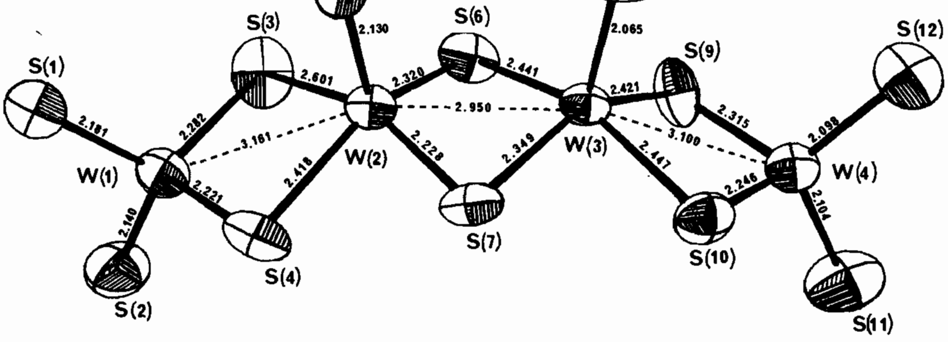

Fig. 1. View of the anion with 50% thermal ellipsoids.

located 0.708 Å and 0.739 Å respectively above the sulfur basal plane. No ligand *trans* to the thio groups is observed. The charge of the anion determined by chemical titrations and the presence of two hexavalent tungstens lead to expect a (+V) formal valence state for each pyramidal tungsten. The anion is found diamagnetic in solid state with no ESR signal; then the anion is likely stabilized by W–W interactions. This view is supported by a 2.95 Å short W(2)–W(3) distance.

References

1 E. I. Stiefel, *Prog. Inorg. Chem., 22,* 1 (1977).
2 G. Bunzey, J. H. Enemark, J. K. Howie, D. T. Sawyer, *J. Am. Chem. Soc., 99,* 4168 (1977).
3 K. Menneman, R. Mattes, *J. Chem. Research,* 100 (1979).
4 I. G. Dance, A. G. Wedd, I. W. Boyd, *Aust. J. Chem., 31,* 519 (1978).
5 G. Bunzey, J. H. Enemark, *Inorg. Chem., 17,* 682 (1978).
6 F. Sécheresse, G. Lavigne, Y. Jeannin, J. Lefebvre, *J. of Coord. Chem.,* in press.
7 A. Muller, R. G. Bhattacharyya, R. Koniger-Ahlborn, R. C. Sharma, W. Rittner, A. Neuman, *Inorg. Chim. Acta, 37,* L493 (1979).
8 E. Koniger-Ahlborn, A. Muller, *Angew. Chem., 87,* 598 (1975).
9 The following programs were used in solution and refinement of the structure: MULTAN, G. Germain, P. Main, M. M. Woolfson; Iber's NUCLS; FORDAP, A. Zalkin; ORFFE, Busing, Martin, Levy; ORTEP, C. K. Johnson; Local Programs.
10 I. Paulat-Boshen, B. Krebs, E. Koniger-Ahlborn, H. Dornfeld, H. Shultz, *Chem. 17,* 1440 (1978).