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A Novel Dimeric Tungsten Sulfido-Disulfido Complex Having an Unusual Geometry: $[P(C_6H_5)_4][W_2S_8OH_3]$

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Acidification of the thiotungstate series $(WO_xS_{4-x})^{2-}$ produces sulfur rich polynuclear complexes having characteristic geometries [1–4]. Regarding the interest of diatomic sulfur ligands in catalysis [5], we present here a structural study on a novel binuclear complex having both monoatomic (S^{2-}) and diatomic (S_2^{2-}) sulfur ligands. One of the S_2^{2-} groups functions simultaneously as a chelating and a bridging agent.

Experimental

A solution of HCl (2.5 mmol) in acetonitrile (5 ml) was added to a stirred solution of $WS_4(PPh_4)_2$ (0.4 mmol) in CH_3CN (45 ml). Upon HCl addition the colour of the solution changed from yellow to red. The solution was kept for one hour at 20 °C and then cooled to 0 °C. Dark red crystals deposited within 24 hours at 0 °C.

The main IR bands of the anion are observed at 960 cm^{-1} (s) (νs W_1 = 0), 515 cm^{-1} (s) (ν(SS))), 460 cm^{-1} (m) ($\nu s(W_2S_2)$), 340, 325, 305 and 295 cm^{-1} (m) (not yet attributed). The complex is diamagnetic at room temperature.

Results and Discussion

$W_2S_8OH_3PPh_4$, M = 982, monoclinic, space group Cc, a = 13.148 Å, b = 23.292 Å, c = 11.533 Å, β = 98.87°, V = 3498 Å^3, μ = 81.6 cm^{-1}, Z = 4. Intensity data were collected on a Philips PW 1100 four circle diffractometer with Mo-Kα radiation. The structure was solved by the heavy atom method and refined by least squares procedure to an actual R_1 = 0.105 for 2658 reflection ($2\theta \leqslant 46°$) without absorption correction. All atoms of the anion were refined anisotropically. The phenyl rings were considered as rigid groups.

A perspective view of the anion with atom labelling is shown in Fig. 1 with some selected distances. A salient structural feature of the molecule is the different coordination stereochemistry of each tungsten, resulting in an interesting example of dissymmetry. The geometry about the W_1 atom can be described as a very distorted tetragonal pyramid: the four S_3, S_4, S_7, S_8 sulfur atoms are approximately coplanar and a doubly bonded oxygen occupies the apex of the pyramid. The W_1 atom lies 0.70 Å above the sulfur basal plane. The octahedral environment of the W_2 atom is very distorted. A featuring detail

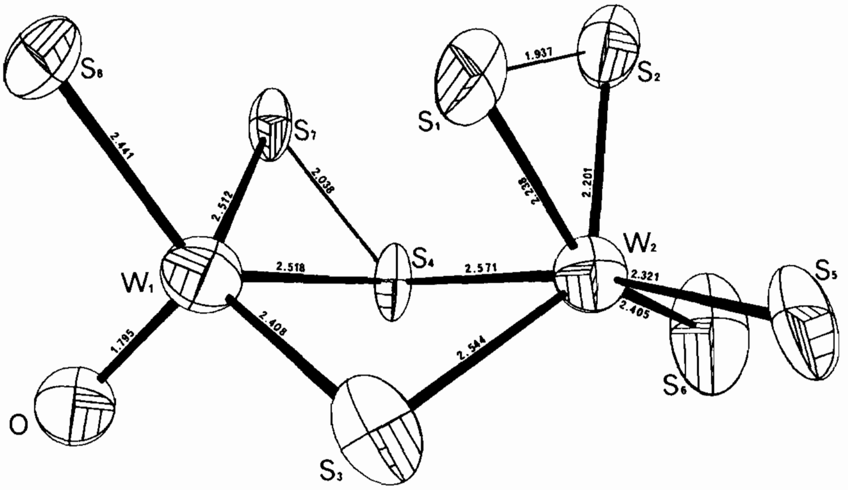

Fig. 1. Structure and labeling of the $(W_2S_8OH_3)^-$ anion. Thermal ellipsoids (50% of the probability distribution) are drawn by Johnson's ORTEP.

is the occurrence of monoatomic and diatomic sulfur ligands in the anion both as bridging and terminal groups. The average value of the S–S distances in the S_1–S_2 and S_4–S_7 is significantly shorter (1.998 Å) than the other S–S distances (*e.g.* S_{3-4} = 3.220 Å, S_5–S_6 = 3.516 Å). This S–S bond value is in good agreement with such reported S–S bond distance [5, 6]. The S_4 atom is triply bridged to the two W and the S_7 atoms. The three terminal sulfido groups are protonated (H NMR evidence). No direct bonding between the two W atoms is expected (distance 3.512 Å).

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