Synthesis and Structural Characterization of $[W_2(O)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$, a Novel Binary Oxo-disulfido Anion of Tungsten(VI)

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Several soluble thiometallates of tungsten have been described and structurally defined: $W_3S_9^{2-}$ [1], $W_4S_{12}^{2-}$ [2], $W_3S_8^{2-}$ [3], $W_2S_{11}H^-$ [4], $W_2S_{11}^{2-}$ [5]. Our initial attempts to prepare new soluble metal sulfides of tungsten involved the acidification of WS_4^{2-} in non aqueous solvents. More recently [5], we have shown the need for $MnCl_2 \cdot 4H_2O$ to synthesize $W_2S_{11}^{2-}$ in an acidified mixture of CH_3CN and CH_3OH. Similarly we decided to utilize $(PPh_4)_2Mn(NCS)_4$ instead of the chloride in order to avoid the methanol. A new species has been isolated pertaining to the W–S–O system. Herein are described the preparation, crystal structure and spectral characterization of this new compound $(PPh_4)_2W_2S_9O_2$.

All manipulations were carried out in air; chemicals were used as purchased. $(PPh_4)_2Mn(NCS)_4$ was prepared by the literature method. A solution of 0.250 g (0.25 mmol) of $(PPh_4)_2WS_4$ in 25 ml of CH_3CN was prepared. After addition of a solution of 0.487 g (0.5 mmol) of $(PPh_4)_2Mn(NCS)_4$ in 17 ml of CH_3CN the mixture turned orange–brown. The resultant solution was stirred for 30 min, allowed to stand for *ca.* 1 h at room temperature and filtered to remove a cream precipitate. The filtrate was concentrated to *ca.* 20 ml by rapid evaporation under reduced pressure and cooled in a closed flask to −20 °C. After a few days well-formed light brown crystals were obtained together with a small amount of dark red crystals of $(PPh_4)_2W_2S_{11}$. The light brown crystals were not analyzed but a suitable one was chosen for a structure determination.

The unit cell dimensions and space group were determined from preliminary oscillations and Weissenberg photographs. The symmetry was orthorhombic and the systematic absences led to the *Pbcn* space group. A single crystal of dimensions 0.31 × 0.36 × 0.06 mm was selected and mounted on a Philips PW 1100 four circle diffractometer using graphite monochromatized Cu Kα radiation and a θ–2θ flying-step scan technique. Specific parameters pertaining to the data collection are reported in Table I. The intensities of three standard reflections were measured every hour and showed about 17% variation; corrections for decomposition were made based on the linear decay of the three standard intensities.

The structure was solved by normal heavy atom Patterson method and subsequent Fourier procedures. One of the phenyl rings of the PPh_4^+ cation was disordered over two orientations around the common pivot carbon atom; occupancies of the two orientations were constrained to 0.5. Final difference Fourier exhibits peaks that were attributed to a solvent molecule, CH_3CN. In the final stages of the refinements all atoms were anisotropically refined, the computations were performed by using SHELX-76 on a Gould Concept 32/87 computer.

Important bond distances and angles are given in Table II; the crystal structure of the complex consists of the dinuclear oxosulfide anion $W_2S_9O_2^{2-}$ and tetraphenylphosphonium counterions. A view of the dianion with the atomic labeling scheme is shown in Fig. 1. Both compounds $W_2S_9O_2^{2-}$ (1) and $W_2S_{11}^{2-}$ (2) [5] are structurally related. The geometry about each W(VI) atom is described as a pseudo-pentagonal pyramid, two η^2-S_2 ligands and the bridging sulfido ligand defining the basal plane, the apical position being occupied by a terminal oxygen atom. The two pyramidal subunits are related by a twofold axis passing through the S(1) atom. The central W atom is displaced about 0.49 Å from the basal plane toward the axial oxygen atom. The

TABLE I. Crystal Data for $(PPh_4)_2W_2S_9O_2$

Space group	*Pbcn*
a (Å)	27.176
b (Å)	9.473
c (Å)	21.743
U (Å^3)	5597
Z	4
Crystal dimension (mm)	0.31 × 0.36 × 0.06
μ (Cu Kα) (cm^{-1})	108.8
Trans. factors	0.34–0.74
Scan mode	θ–2θ
Scan range (2θ, °)	4–136
Scan rate (° s^{-1})	0.02
Scan width (°)	1.8
Standard (every 1 h)	$2\bar{4}0$, $\bar{4}\bar{4}\bar{6}$, $\bar{2}40$
No. reflections measured	5688
No. data used ($F_o^2 > 3\sigma(F_o^2)$)	3672
Final parameters varied	357
Final R	0.0664

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TABLE II. Interatomic Distances and Angles in the [$W_2S(S_2)_4O_2$] Anion^a

W–S(1)	2.534(4)	W–S(4)	2.371(5)
W–S(2)	2.398(3)	W–S(5)	2.398(5)
W–S(3)	2.363(4)	W–O	1.73(1)
S(2)–S(3)	2.045(5)	S(4)–S(5)	2.066(9)
W...W′	3.581(1)	W...S(2)′	2.816(3)
S(1)–W–S(2)	79.2(1)	S(2)–W–S(4)	138.0(2)
S(1)–W–S(3)	127.1(1)	S(2)–W–S(5)	151.8(1)
S(1)–W–S(3)	127.1(1)	S(2)–W–S(5)	151.8(1)
S(1)–W–S(4)	131.0(1)	S(3)–W–S(4)	88.9(2)
S(1)–W–S(5)	81.1(1)	S(3)–W–S(5)	135.4(2)
S(2)–W–S(3)	50.9(1)	S(4)–W–S(5)	51.3(2)
S(1)–W–O	102.8(4)	S(4)–W–O	100.1(3)
S(2)–W–O	99.5(3)	S(5)–W–O	104.3(4)
S(3)–W–O	101.6(4)	W–S(1)–W′	90.0(2)
S(3)–S(2)–W	63.7(1)	S(2)–S(3)–W	65.5(1)
S(5)–S(4)–W	65.0(2)	S(4)–S(5)–W	63.6(2)

^{a}Atoms related by the diad axis are primed.

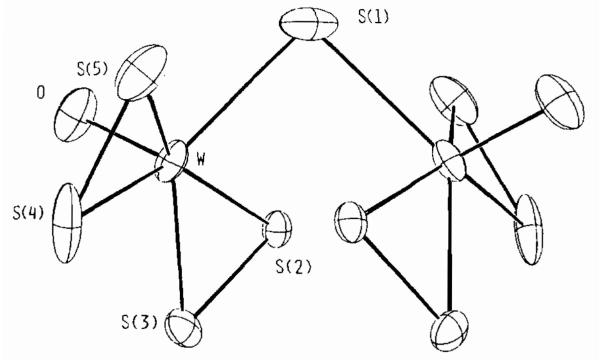

Fig. 1. Perspective view (50% ellipsoids) of the $W_2S_9O_2^{2-}$ anion showing the atom-labeling scheme. Half of the anion is generated through a binary axis passing through the S(1) atom.

dihedral angle between the basal planes of the two moieties is around 50° while the W–S(1)–W′ bridge is 90.0(2)°. All distances and angles within $W_2S_9O_2^{2-}$ closely resemble the analogous $W_2S_{11}^{2-}$ species. The W...W distance is 3.581(1) Å and the W–S(1) bridging distance is slightly longer than the corresponding distance in the sulfide 2. A similar binary oxo-disulfido molybdate(VI) anion [$((S_2)_2MoO)_2S$]$^{2-}$ has been reported [6]; each molybdenum atom achieves a pseudo-pentagonal bipyramidal environment, a terminal oxo ligand occupies an axial site, the other one being occupied through the approach of a sulfur from a disulfido-group bonded to the other molybdenum. The $W_2S_9O_2^{2-}$ anion can also adopt a similar geometry the basal planes being the same in the two descriptions while the axial positions are occupied by the oxo ligand and the S(2)′ sulfur atom (disulfido group S(2)′–S(3)′ of the symmetry-related tungsten W′ (S(2)′...W: 2.816(3) Å)).

Vibrational spectra of $W_2S_9O_2^{2-}$ are in accordance with its formulation; infrared W=O stretching vibration is found as strong absorption at 938 cm^{-1}. Bands associated with the W–S stretching vibrations of the W–S_2 unit are observed at 348(w), 326(w) and 311(w) cm^{-1}. Further evidence for the identity of **1** and **2** is available from electronic spectroscopy in CH_3CN. The spectra of **1** and **2** are very similar except for the blue shift in the bands of the former in the conversion of W=S to W=O. Pertinent values of λ_{max} (nm) are 450, 370, 330 for **1** and 470, 390, 340 for **2**. The two high energy absorptions are reasonably attributable to charge-transfer transitions of the type $S_2 \rightarrow$ metal [7].

Supplementary Material

Atomic coordinates, thermal parameters, mean planes, bond distances and bond angles are available from the authors on request.

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