

Novel Bonding Mode for WS_4^{2-} : Synthesis and Structure of $[Mo_2(O_2CPh)_2(WS_4)_2]^{2-}$

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The synthesis of $(Et_4N)_2[Mo_2(O_2CPh)_2(WS_4)_2]$ is reported; the structure reveals a novel bonding mode for the tetrathio tungstate ligands which bridge two quadruply-bonded molybdenum atoms.

Since their initial discovery nearly thirty years ago, quadruply-bonded metal dimers have received a great deal of attention and hundreds of such complexes have been prepared.¹ Similarly, tetrathio metallate species, MS_4^{x-} ($M = Mo, W, Re...$) have proved to be versatile synthetic species for preparing a wide range of multimetallic clusters.² Recently, a report appeared in which these two classes of synthons were combined, although no structural characterization of the products was reported.³ In this communication we report the synthesis and structural characterization of the first example of a quadruply-bonded metal dimer bridged by a tetrathio-metallate anion, WS_4^{2-} .

Slow addition of two equivalents of $(Pr_4N)_2(WS_4)$ in acetone to a stirred solution of $Mo_2(O_2CPh)_4$ in acetone produced a solution that slowly deposited a dark-maroon microcrystalline precipitate. The product, $(Pr_4N)_2[Mo_2(O_2CPh)_2(WS_4)_2]$, **1**, was isolated by filtration and washed with acetone and diethyl ether (yield *ca.* 75%).[†] Single crystals of $(Et_4N)_2[Mo_2(O_2CPh)_2(WS_4)_2]$, **2**, suitable for X-ray crystallography were prepared by layering of the two reactant solutions and allowing them to mix slowly by diffusion. $(Pr_4N)_2[Mo_2(O_2CMe)_2(WS_4)_2]$, **3**, can be similarly produced by substituting $Mo_2(O_2CMe)_4$ as a starting material.[†]

The electronic absorption spectrum of **1** in *N,N*-dimethylformamide contains maxima at λ/nm : 295 (ϵ $55 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 335 (40), 405 (26), 438 (21), 530 (4.4) and a shoulder at 620 (1.2). The absorption at 438 nm is likely the δ - δ transition arising from the presence of the Mo-Mo quadruple bond in **1**. This absorption is observed at 423 nm ($23.6 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in $Mo_2(O_2CPh)_4$.⁴ The

remaining absorptions are probably ligand-to-metal charge transfer bands originating on the WS_4^{2-} units.² The IR spectrum of **1** (KBr pellet) contains strong absorbances due to the benzoate ligand ring breathing modes (685, 721 cm^{-1}), terminal W-S stretch (495 cm^{-1}), and bridging Mo-S and W-S stretches (415, 420 cm^{-1}). Analogous electronic and IR absorption spectra are obtained for **2** and **3**.

The structure of **2** was determined by a single-crystal X-ray diffraction study and is illustrated in Fig. 1.[‡] The displacement of two benzoate groups by two WS_4^{2-} ligands in the $Mo_2(O_2CPh)_4$ starting material is clear. The molecule lies on a centre of inversion and the two WS_4^{2-} ligands are *trans* to each other and bent back along the S_2 - S_3 axis, such that the overall symmetry is C_{2h} . The Mo-Mo distance of 2.144(1) Å is slightly longer than that in $Mo_2(O_2CPh)_4$ [2.096(1) Å]⁵ indicating that the quadruple Mo-Mo bond remains intact. The WS_4^{2-}

[‡] Crystallographic data for **2**: $C_{30}H_{32}Mo_2N_2O_4S_8W_2$, $M_r = 1319$, monoclinic, space group, $P2_1/c$; $a = 21.885(6)$, $b = 10.286(2)$, $c = 22.666(5)$ Å, $\beta = 113.73(2)^\circ$, $V = 4671(2)$ Å³; $Z = 4$; $D_c = 1.875 \text{ g cm}^{-3}$; $\mu = 59.06 \text{ mm}^{-1}$ for Mo-K α radiation ($\lambda = 0.71069$ Å). A total of 6071 reflections having $2\theta < 50.0^\circ$ were collected at 25 °C on a Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-K α radiation. The structure was solved by direct methods utilizing the SHELX-76 direct methods package and the SDP refinement programs. The resulting structural parameters have been refined to $R = 0.056$, $R_w = 0.062$ for 5309 unique reflections [$I > 1\sigma(I)$] using full-matrix least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all non-hydrogen atoms. The intensity data were corrected empirically for absorption effects and were subjected to standard Lorentz and polarization corrections. The hydrogen atoms were not located. One of the cations showed disorder about two preferred orientations and the refinement was performed with both orientations being half occupied. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[†] Selected spectroscopic data for **1**: ¹H NMR: δ aromatic protons, 8.07, 8.04, 7.64, 7.44, 7.28; aliphatic, 3.33, 1.78, 0.96. Satisfactory elemental analyses were obtained for compounds **1** and **3**.

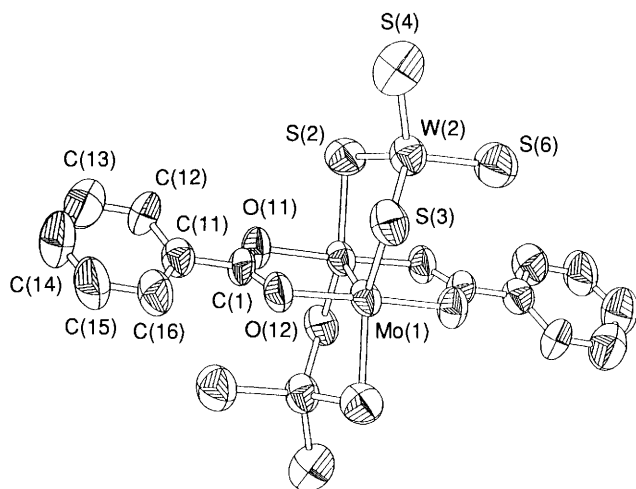


Fig. 1 Structure $[\text{Mo}_2(\text{O}_2\text{CPh})_2(\text{WS}_4)_2]^{2-}$. Key distances (\AA) are: Mo(1)–Mo(1') 2.144(1), Mo(1)–O(12) 2.109(4), Mo(1)–S(3) 2.416(2), W(2)–S(3) 2.253(2), W(2)–S(4) 2.137(2), W(2)–S(6) 2.128(2).

ligands withdrawal of electron density⁶ may be the cause of the observed Mo–Mo bond lengthening.⁷ The S–W–S angles in the WS_4^{2-} ligands are roughly tetrahedral [109.5(1), 105.2(1), 110.1(1) $^\circ$] being slightly opened for the bridging S(2)–W(2)–S(3) unit [117.7(1) $^\circ$]. The bridging [2.253(2), 2.257(2) \AA] and terminal [2.128(2), 2.137(2) \AA] W–S bond lengths are typical of a coordinated WS_4^{2-} .⁸ Overall, the structure can be viewed as composed of a quadruply-bonded molybdenum dimer that is bridged by a pair of benzoate ligands and a pair of WS_4^{2-} ligands.

Several unusual aspects of this structure are worth noting. First, this is a rare example of a stable complex containing two metals from the same group with such disparate oxidation states: Mo^{II} and W^{VI} . Secondly, although earlier workers had

postulated this mode of bridging by MS_4^{2-} across a Mo–Mo quadruple bond, they had no evidence to prefer this mode of binding over the alternative structure in which each MS_4^{2-} ligand binds in a bidentate mode to only one Mo in the dimer.³ Thirdly, the orientation of WS_4^{2-} within the molecule is peculiar in that it is decidedly tilted about the Mo–Mo quadruple bond such that one of the non-bridging sulfur atoms is directed at the aromatic ring of an adjacent benzoate ligand. The origin of this tilt is unclear.

Molecules in this class are potentially usable as building blocks in the construction of larger molecular networks. Various combinations of quadruply-bonded dimers with tetrathiometalate species should facilitate the synthesis of novel multimetallic supramolecular systems.

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