Preparation, Structure and Properties of Mixed-Metal Trinuclear Complex: $(Pr_4N)_2[MoO(WS_4)_2]$

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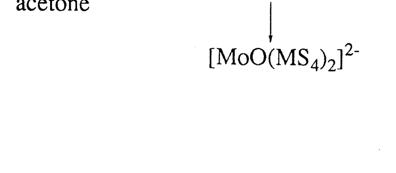
A mixed-metal trinuclear complex, $(Pr_4N)_2[MoO(WS_4)_2]$, has been prepared for the first time in pure form and characterized by several physical methods, including X-ray crystallography.

Tetrathio- and oxothiometalate anions are known to be versatile starting materials as they act as bidentate ligand to give wide variety of di- and trinuclear complexes.[1] Recently, reports appeared on the compounds in which tetrathiometalate anion acts as a bridging ligand across a Mo-Mo quadruple bond.[2,3] In the course of reinvestigation of the reaction of $[Mo_2(PhCO_2)_4]$ with $(Pr_4N)_2WS_4$ as reported by Greaney and Stiefel,[3] we encountered a formation of the title compound, $(Pr_4N)_2[MoO(WS_4)_2]$ (**1**), which provides the first successful preparation of a mixed-metal complex of the type, $[ME(M'S_4)_2]^{2-}$ (M, M' = Mo, W; E = O, S). Furthermore similar reaction of $[Mo_2(PhCO_2)_4]$ with $(Pr_4N)_2MoS_4$ successfully gave $(Pr_4N)_2[MoO(MoS_4)_2]$ (**2**). Although the X-ray structural analyses of the mixed-crystal compound with approximate composition of $(PPh_4)_2[Mo_{1.4}W_{1.6}O_{1.3}S_{8.3}]$[4] and $(PPh_4)_2[MoO(MoS_4)_2]$[5,6] have been reported previously, physical properties of the complex anions of **1** and **2** have remained still unknown. In this communication we report the preparation and structural characterization of the new mixed-metal trinuclear complex, $(Pr_4N)_2[MoO(WS_4)_2]$, whose physical properties provide various new insight into the electronic state of this type of complexes.

Preparation of **1** was conducted according to the procedure reported for $[Mo^{II}_2(PhCO_2)_2(WS_4)_2]^{2-}$ by Greaney and Stiefel.[3] To an acetone solution of $[Mo_2(PhCO_2)_4]$ (200 mg/50 cm^3) four equivalents of $(Pr_4N)_2WS_4$ in acetone (810 mg/30 cm^3) were added and stirred at room temperature under an argon atmosphere. After several hours, dark-maroon precipitate separated out which was identified as $(Pr_4N)_2[Mo_2(PhCO_2)_2(WS_4)_2]$. Further stirring of the suspension gave an orange solution, which was concentrated to ca. 10 cm^3.[7] Brown-orange precipitate was collected, washed with ether, and dried in vacuo. Yield 394 mg (60%).[8] The reaction of the isolated $(Pr_4N)_2[Mo_2(PhCO_2)_2(WS_4)_2]$ with WS_4^{2-} in acetone also gave **1**. Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_3CN/ether. This preparative method was applied for the reaction of $[Mo_2(PhCO_2)_4]$ with $(Pr_4N)_2MoS_4$. The reaction proceeded similarly with the precipitation of brown intermediate species which is presumably $[Mo_2(PhCO_2)_2(MoS_4)_2]^{2-}$,[9] and redissolution to give **2** finally.

The complex **1** involves two crystallographically independent molecules in the unit cell. Each complex anion is disordered around the center of inversion belonging to different Wyckoff position in the crystal.[10] A perspective view of one of the complex anions is given in Figure 1 and indicates that each anion consists of a central square pyramidal Mo sharing edges with two WS_4 tetrahedra. The occupancies of Mo and O atoms are 1/2. This type of disorder can often be found in comparable trinuclear thiometalates.[4,11-14] The corresponding bond lengths and bond angles in each complex anion in the crystal are similar to each other though the distortion of square pyramidal environment of Mo(1) is slightly larger than that of Mo(2). The central Mo(1) and Mo(2) atoms are displaced 0.54 and 0.68 Å, respectively, from the basal plane toward the axial O atom. The Mo-O distances of 1.67(2) and 1.63(2) Å indicate no oxygen-sulfur disorder on this position.[11] The Mo···W distances (2.808-3.077 Å) are in good agreement with other comparable trinuclear thiometalates.[4-6,11-14] The $W-S_b$ distances (2.231-2.248 Å) are longer than $W-S_t$ distances (2.121-2.149 Å). The tetrahedral environment of W(1) and W(2) are also slightly distorted; the S_b-W-S_b angles is smaller and S_t-W-S_t angle is larger than S_b-W-S_t angles in each anion. These structural features are common in comparable trinuclear thiometalates.[4-6,11-14]

Trinuclear complexes, **1** and **2**, exhibit two or three irreversible reduction processes between +0.5 and -2.5 V vs. Ag/AgCl, as is seen for the related complexes, $[MoS(MoS_4)_2]^{2-}$, $[WS(WS_4)_2]^{2-}$ and $[WO(WS_4)_2]^{2-}$.[15] If the reduction scan is reversed before the second reduction occurs, the first reduction corresponds to a quasi-reversible one-electron reduction process ($E_{1/2}$ = -2.12 and -1.83 V vs. $Fc^{+/0}$ for **1** and for **2**, respectively; $E_{1/2}(Fc^{+/0})$ = +0.53 V vs. Ag/AgCl). Comparison of the first reduction potentials of **1** and **2** with the related



$$[Mo_2(PhCO_2)_4] \xrightarrow[\text{acetone}]{MS_4^{2-}\ (M = W,\ Mo)} [Mo_2(PhCO_2)_2(MS_4)_2]^{2-} \longrightarrow [MoO(MS_4)_2]^{2-}$$

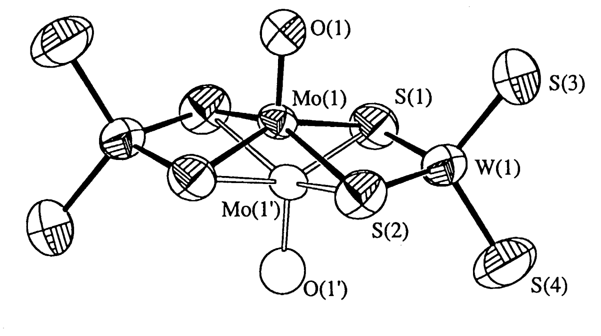


Figure 1. A perspective view of the complex anion of **1**. Selected bond distances (Å) and angles (°): [Molecule 1]: Mo···W, 3.077(3); Mo-O, 1.67(2); $Mo-S_b$, 2.443(5), 2.548(5); $W-S_b$, 2.231(5), 2.240(5); $W-S_t$, 2.141(6), 2.121(6); W-Mo-W', 158.72(9); $O-Mo-S_b$, 102.9(7), 103.1(7); S_b-Mo-S_b, 90.4(2); $Mo-S_b-W$, 82.2(2), 79.7(2); S_b-W-S_b, 104.8(2); S_t-W-S_t, 111.8(3); [Molecule 2]: Mo···W, 2.979(3); Mo-O, 1.63(2); $Mo-S_b$, 2.453(5), 2.376(5); $W-S_b$, 2.241(4), 2.248(5); $W-S_t$, 2.136(5), 2.149(5); W-Mo-W', 153.60(9); $O-Mo-S_b$, 105.5(8), 104.7(8); S_b-Mo-S_b, 94.0(2); $Mo-S_b-W$, 78.6(1), 80.2(2); S_b-W-S_b, 103.8(2); S_t-W-S_t, 111.3(2).

complexes gave the order of $[MoS(MoS_4)_2]^{2-}$ (-1.60 V vs. $Fc^{+/0}$) > $[MoO(MoS_4)_2]^{2-}$ (**2**) (-1.83 V) > $[WS(WS_4)_2]^{2-}$ (-1.88 V) > $[MoO(WS_4)_2]^{2-}$ (**1**) (-2.12 V) > $[WO(WS_4)_2]^{2-}$ (-2.14 V).[16] It indicates that the reduction potential of the trinuclear complexes is affected mainly by the difference of terminal metal ion ((MoS_4) > (WS_4)), secondary by the difference of terminal atom coordinated to the central metal ion (S > O), and lastly by the difference of central metal ion (Mo > W). Thus it is noted that while $[WO(WS_4)_2]^{2-}$ is reduced at a similar potential as $[MoO(WS_4)_2]^{2-}$, it is significantly more difficult to reduce than $[WS(WS_4)_2]^{2-}$. One-electron reduction indicates the strong electronic communication over the whole trinuclear systems.

The X-ray photoelectron spectra were measured for **1**, **2**, and $(Pr_4N)_2MS_4$ (M = Mo, W).[17] Binding energies of metal ions of **1** and **2** are slightly higher than those of $(Pr_4N)_2MS_4$. The single component of Mo($3d_{5/2}$) for **2** is noted, the peak width of which is similar to that (1.3 eV) for $(Et_4N)_2Mo_3S_9$.[18]

The ^{183}W and ^{95}Mo NMR spectra were measured for **1** and **2**. We could not observe the signal of the central Mo atom of both compounds presumably due to quadrupolar line broadening owing to a strongly noncubic environment. **1** and **2** show ^{183}W and ^{95}Mo signals of terminal MS_4 fragments at +2735 and +1614 ppm, respectively.[19] These resonances are shielded with respect to the corresponding MS_4^{2-} anions. The ratio of the chemical shifts of ^{183}W and ^{95}Mo for **1** and **2** ($\delta(^{183}W):\delta(^{95}Mo)$ = 1.69) is in good agreement with the ratio of 1.67 ± 0.03 which is found for the series of $[MO_{4-n}S_n]^{2-}$ (M = Mo, W) and related compounds.[20]

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7 When the reaction was conducted in more diluted condition, no precipitation of $(Pr_4N)_2[Mo_2(PhCO_2)_2(WS_4)_2]$ was observed and the solution of **1** was obtained directly.

8 Anal. Found: C, 26.21; H, 5.02; N, 2.53; S, 23.10%. Calcd for $C_{24}H_{56}MoN_2OS_8W_2$: C, 26.00; H, 5.09; N, 2.53; S, 23.13%. IR (KBr)/cm^{-1}: ν(Mo=O) 966, ν(W=S) 495, ν(W-S-Mo) 473, 439. UV-vis (CH_3CN)/nm (ε/$mol^{-1}dm^3cm^{-1}$): 247 (30600), 266 (31500), 314 sh (11400), 382 (25600).

9 Yield 40%. Anal. Found: C, 36.43; H, 5.28; N, 2.29; S, 20.12%. Calcd for $C_{38}H_{66}Mo_4N_2O_4S_8$: C, 36.36; H, 5.30; N, 2.23; S, 20.43%. IR (KBr)/cm^{-1}: δ(C-H) 719, 682, ν(Mo=S) 514, 496, ν(Mo-S-Mo) 428. UV-vis (DMF)/nm (ε/$mol^{-1}dm^3cm^{-1}$): 316 (24700), 336 sh (19900), 375 (15800), 475 (6500), 519 (6200), 707 (1200).

10 Crystal data for **1**: $C_{24}H_{56}MoN_2OS_8W_2$, FW = 1108.84, monoclinic, space group $P2_1/c$; a = 15.436(2) Å, b = 17.563(3) Å, c = 14.932(2) Å, β = 96.79(1)°, V = 4020.0(9) $Å^3$, Z = 4, D_c = 1.83 g cm^{-3}, μ(MoKα) = 65.6 cm^{-1}. The structure was solved by direct method using SIR88 and other crystallographic software package in teXsan (Molecular Structure Corporation). The final R value was 0.046 (R_w = 0.048) for 3106 reflections with $I > 4\sigma(I)$ measured on a Rigaku AFC-5R diffractometer up to $2\theta = 50°$ (Mo Kα radiation, λ = 0.71073 Å).

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