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A novel polyoxo(thio)molybdenum(V) sulfite compound: Synthesis and crystal structure of $\{[Mo_2^V(\mu\text{-}S)_2O_2]_6(\mu_3\text{-}SO_3)_4(\mu\text{-}SO_3)_{12}\}^{20-}$ anion

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The non-cyclic polyoxo(thio)molybdate(V)-sulfite $K_6(NH_4)_{14}\{[Mo_2^V(\mu\text{-}S)_2O_2]_6(\mu_3\text{-}SO_3)_4(\mu\text{-}SO_3)_{12}\}\cdot 7H_2O$ 1 was prepared by self-condensation of $[Mo_2^V(\mu\text{-}S)_2O_2]^{2+}$ building block in the presence of $(NH_4)_2SO_3$. Compound 1 was characterized by X-ray structure analysis as well as IR, UV-vis spectroscopies and thermogravimetric analysis.

Polyoxoanions of molybdenum, tungsten and vanadium are a large and rapidly growing class of compounds.[1] This family of metal-oxygen species (POMs) is unique for its molecular and electronic structural diversity and because of its potential applications in quite diverse disciplines *e.g.* catalysis,[2,3] materials science[4] and medicine.[1,5,6] During the last few years not only the number but also the size of many novel structures has been increasing dramatically. Two notable examples of gigantic POMs, $[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$ and $[As_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$ were reported by Muller *et al.*[7] and Pope *et al.*[8] respectively. In marked contrast to POMs, oxo(thio)metalates are far less common and of low sulfur content.[9] We are currently using the sulfite anion to prepare polyoxometalate-sulfite compounds.[10] The sulfite anion has C_{3v} symmetry and contains a nonbonding but stereochemically active pair of electrons and its non-centrosymmetric metal compounds may potentially display nonlinear optical (NLO) properties,[11] which are observed in the metal-selenites[12] and metal-iodates.[13] Furthermore, the molybdenum-sulfite chemistry is of great biological interest, since the enzyme sulfite oxidase, associated with the *in vivo* oxidation of SO_3^{2-} to SO_4^{2-}, contains a molybdenum atom in its active center.[14] In addition, metal-sulfite chemistry is very attractive in view of its potential for restricting the serious environmental problem of acid rain.[15] Inspired by the beautiful oxo(thio)metalate chemistry of Secheresse *et al.*[9] we decided to combine the $[M_2^V(\mu\text{-}S)_2O_2]^{2+}$ building block with the sulfite anion hoping to prepare some polyoxo(thio)-sulfite metalates.[16]

Herein we report the preparation,† X-ray crystal structure‡ and some properties of the first polyoxothiomolybdenum(V)-sulfite compound $K_6(NH_4)_{14}\{[Mo_2^V(\mu\text{-}S)_2O_2]_6(\mu_3\text{-}SO_3)_4(\mu\text{-}SO_3)_{12}\}\cdot 7H_2O$ **1**. Compound **1** exhibits a unique structural motif with a non-cyclic arrangement of the six $[Mo_2^V(\mu\text{-}S)_2O_2]^{2+}$.[9]

1 was prepared as follows:[9,16] $(Me_4N)_2[Mo_2^V(\mu\text{-}S)_2S_4O_2]$ (9 mmol) dissolved in aqueous KI 0.7 M (30 mL) was treated with an aqueous 1 M HCl solution (35 mL) containing iodine (18 mmol) and KI (48 mmol). The mixture was heated at 50 °C for 10 min and then it was cooled to 0 °C. The precipitate was removed by filtration, the pH of the solution was 0 and it contained the $[Mo_2^V(\mu\text{-}S)_2O_2(H_2O)_6]^{2+}$ species, and solid $(NH_4)_2SO_3$ (38 mmol) was added to the filtrate. Upon addition of the sulfite salt, the deep red color of the solution changed to orange-red and the pH became 6.4. The mixture was filtered and crystals of **1**, suitable for single-crystal X-ray structure analysis, were obtained after leaving the filtrate at ambient temperature (25 °C) for three days. Yield: 0.15 g (85%) based on molybdenum. Thus, it is evident that the sulfite anion performs the dual role of raising the pH of the solution, as well as acting as a template μ_3 and μ ligand in the self-assembly of the six $[Mo_2^V(\mu\text{-}S)_2O_2]^{2+}$ fragments. In marked contrast, addition of $(NH_4)_2SO_3$ (22.3 mmol) in water (10 mL) to a DMF solution (10 mL) containing the $[W_2^V(\mu\text{-}S)_2O_2]^{2+}$ building block[9f] (10.9 mmol) (final pH of the solution ~6) and then vapour diffusion of CH_3OH to it, resulted in the isolation of a yellow-orange crystalline material,† which proved to be by crystal structure analysis‡ the cyclic compound $[Me_4N]_2(NH_4)_2[W_9(OH)_8O_{13}S_8(H_2O)]\cdot 18H_2O$ **2** instead of an expected polyoxo(thio)tungsten(V)-sulfite species.[9d]

The X-ray structure of **1** exhibits a $\{[Mo_2^V(\mu\text{-}S)_2O_2]_6(\mu_3\text{-}SO_3)_4(\mu\text{-}SO_3)_{12}\}^{20-}$ cluster (Fig. 1), which contains 12 Mo^V centers within the main structural unit. Each molybdenum atom has octahedral coordination and is bonded to a terminal oxo group, two $\mu\text{-}S^{2-}$ ions and three sulfite (two μ- and one μ_3-) oxygen atoms. The twelve Mo^V atoms form six binuclear units $[Mo_2^V(\mu\text{-}S)_2O_2]^{2+}$ with a Mo^V–Mo^V separation of 2.828(7) Å (single bond). The six $[Mo_2^V(\mu\text{-}S)_2O_2]^{2+}$ moieties are connected to each other by sixteen sulfite ligands. Twelve of which have a μ-(2L, 2M) bonding mode, while the remaining four sulfite anions have a μ_3-(3L, 3M) mode of ligation (Fig. 1). The $\mu\text{-}SO_3^{2-}$ anions can be considered as outer groups and each of these anions bridges two $Mo_2^V(\mu\text{-}S)_2O_8$ dimeric moieties comprised of two edge-sharing $Mo^VO_4S_2$ octahedra, while the four $\mu_3\text{-}SO_3^{2-}$ anions are the "inner" groups and each of these

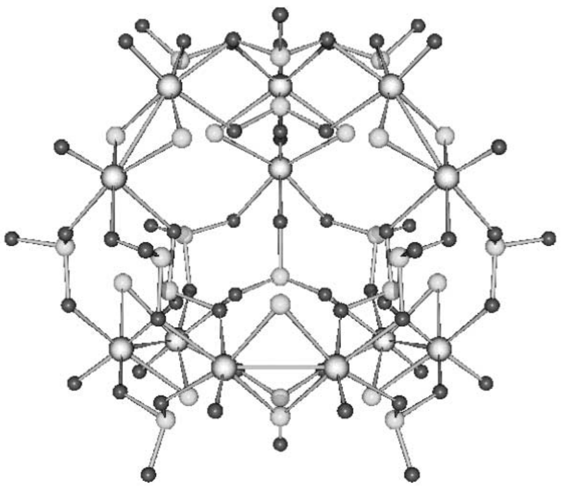

Fig. 1 Ball and stick representation of the anion of **1**; Mo: gray, S: smaller gray spheres, O: black; average bond lengths (Å): Mo=O 1.696(9), Mo–O (μ-O) 2.14(2), Mo–O (μ_3-O) 2.26(2), Mo–S 2.324(6), S=O 1.46(1), S–O ($\mu_3\text{-}SO_3^{2-}$) 1.54(2), S–O ($\mu\text{-}SO_3^{2-}$) 1.56(1), Mo–Mo 2.828(7).

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anions is connected to three $Mo^{V}_2(\mu\text{-}S)_2O_8$ dimeric moieties. Bond valence sum (BVS) calculations for the independent oxygen atoms gave values higher than 1.7 (non-protonated), while BVS calculations for the crystallographically independent molybdenum atoms gave values very close to 5.[17] X-Ray crystal structure analysis of **2** (ref. 18) exhibits a $[W_9O_9(\mu\text{-}S)_8(\mu_3\text{-}O)_4(\mu\text{-}OH)_8(H_2O)]^{4-}$ cluster associated with two Me_4N^+ and two NH_4^+ cations (Fig. 2). The latter cations were placed at crystallographically acceptable positions in order to bring the structural results to agreement with the elemental analysis of the sample; the N-atoms of NH_4^+ cannot be crystallographically distinguished from the O-atoms of interstitial H_2O molecules. The polyoxo(thio)tungstate anion consists of four $[W_2^{V}(\mu\text{-}S)_2O_2]^{2+}$ building units connected to each other through two μ-OH bridges to form a cyclic octamer encapsulating a *trans*-$[W^{VI}O(H_2O)(\mu_3\text{-}O)_4]^{4-}$ octahedron. BVS calculations[17] of **2** gave values higher than 1.7, 1.2 and 0.21 for the O^{2-}, OH^- and H_2O, respectively. BVS calculations for the tungsten atoms gave a value of 6 for the encapsulated tungsten and a value of 5 for the ring tungsten atoms, respectively (ref. 17).

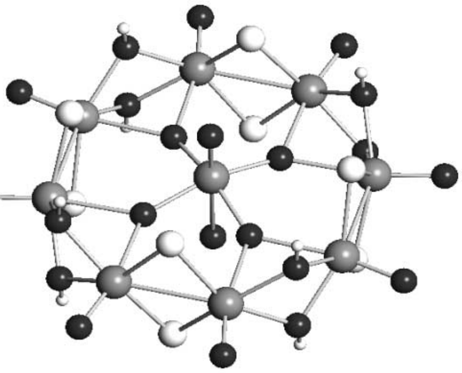

Fig. 2 Ball and stick representation of the anion of **2**; W: dark gray, O: black, S: light gray, H: white; average bond lengths (): W_A–W_A 2.8077(8), W_A–W_B 3.2063(9), W=O 1.716(7), W–O(OH) 2.095(5), W–S 2.329(2).

The infrared spectrum of **1** exhibited bands (cm^{-1}) at 3410s (br) [ν(O–H) from H_2O], 3153s (br) [ν(N–H) from NH_4^+], 1630m (br) [$\delta(H_2O)$], 1401s [$\delta(NH_4^+)$], 1035 [$\nu(SO_3^{2-})$], 968 (sh) [ν(Mo=O)], 947s [ν(Mo=O)], 900 (sh), 880vs [$\nu(SO_3^{2-})$], 677m [$\nu(SO_3^{2-})$], 456m [ν(Mo–S)]. The electronic spectrum of **1** in aqueous 1 M $(NH_4)_2SO_3$ consists of a peak and of a shoulder in the visible and two peaks and a shoulder in the ultraviolet region, namely: λ_{max}/nm (ε_M/M^{-1} cm^{-1}): 501 (670), 400 (sh) (3000), 284 (11 140) 250 (sh) (10 900) 230 (12 000). The UV-vis solid state reflectance spectrum of **1** contained the following bands (nm): 508, 390 (sh), 310 and 226. Thus, it is evident from the similarity of both spectra that **1** retains its integrity in 1 M aqueous $(NH_4)_2SO_3$ solution. The TGA curve for **1** was recorded in the presence of N_2 gas at a heating rate of 5 °C min^{-1} and shows four significant weight losses in the 25–600 °C temperature range. The first stage in the region 25–125 °C is endothermic and accounts for 10.3% of the weight loss and can be attributed to the loss of seven crystal water molecules and to the decomposition of fourteen NH_4^+ cations to NH_3 (the theoretical value for the loss of 7 H_2O and 14 NH_3 for **1** is 10.04%). The second stage between 125 and 355 °C accounts for 31.2% of the sample weight loss and consists of two not distinguished steps. The first step is attributed to the endothermic decomposition of sixteen sulfite groups and the removal of produced sulfur dioxide, while the second is attributed to dehydroxylation (the theoretical value for the loss of 16 SO_2 and 7 H_2O for **1** is 31.77%). A partial desulfurization took place in the third stage with a sharp exothermic peak at 413 °C. Then, as the temperature was raised, a gradual decrease of weight loss was observed up to 530 °C. The total weight loss for this stage was 5.3%. A new weight loss was observed up to 600 °C in the fourth endothermic stage. The weight loss was 2.2% and the peak maximum at 566 °C. The thermal behavior of **1** in the first two stages is very similar to that of the polyoxometalate–sulfite compounds reported very recently.[10]

In conclusion, the main finding of our work is the preparation, under mild conditions and characterization of the first polyoxo(thio)molybdenum(v)-sulfite compound **1**, by reacting the $[Mo_2^{V}(\mu\text{-}S)_2O_2]^{2+}$ building block with $(NH_4)_2SO_3$. The preparation of **1** emphasizes the great ability of the seemingly pedestrian sulfite anion to act as a template in the self-assembly of metal aggregates. Efforts to prepare polyoxo(thio)metal-sulfite species of higher nuclearity and increased sulfur content are in progress.

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Notes and references

† Elemental analysis for **1**: calcd. (%): N 5.4, H 1.9, S 24.7, Mo 31.7; found: N 5.5, H 2.1, S 24.9, Mo 31.9. Elemental analysis for **2**: calcd. (%): C 3.69, H 2.41, N 2.15, S 9.86, W 63.60; found: C 3.73, H 2.48, N 2.19, S 9.89, W 63.69.

‡ X-Ray crystal structure analysis for **1**: $K_6(NH_4)_{14}\{[Mo_2^{V}(\mu\text{-}S)_2O_2]_6(\mu_3\text{-}SO_3)_4(\mu\text{-}SO_3)_{12}\}\cdot 7H_2O$: $H_{70}N_{14}O_{67}S_{28}K_6Mo_{12}$, M_r = 3605.27, orthorhombic, space group *Pnma*, a = 30.260(4) Å, b = 23.199(3) Å, c = 16.6631(19) Å, V = 11697(2) Å^3, Z = 4, ρ_{calc} = 2.047 Mg m^{-3}, T = 125(2) K, R_1(final) = 0.0607, wR_2 = 0.1566, Index ranges = $-33 \le h \le 33$, $-25 \le k \le 25$, $-18 \le l \le 14$; Intensity data collection was carried out on a red crystal of 0.10 × 0.10 × 0.05 mm and refined by full-matrix least-squares, based on F^2. CCDC reference number 208245. See http://www.rsc.org/suppdata/dt/b3/b309473c/ for crystallographic data in CIF or other electronic format. X-Ray crystal structure analysis for **2**: $[Me_4N]_2(NH_4)_2[W_9(OH)_8O_{13}S_8(H_2O)]\cdot 8H_2O$: $C_8H_{58}N_4O_{30}S_8W_9$, M_r = 2601.71, tetragonal, space group *I*4/*m*, a = 15.762(2) Å, c = 11.375(2) Å, V = 2825.8(12) Å^3, Z = 2, ρ_{calc} = 3.058 Mg m^{-3}, T = 299(2) K, R_1(final) = 0.0281, wR_2 = 0.0797, Index ranges = $-14 \le h \le 20$, $-20 \le k \le 20$, $-14 \le l \le 10$; Intensity data collection was carried out on a red crystal of 0.18 × 0.16 × 0.14 mm and refined by full-matrix least-squares, based on F^2. CCDC reference number 208246. See http://www.rsc.org/suppdata/dt/b3/b309473c/ for crystallographic data in CIF or other electronic format.

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18 While we were preparing this manuscript the compound $Rb_3[W_8{}^{V}S_8O_8(OH)_8(H_3W^{VI}O_6)]\cdot 13H_2O$ appeared in the literature which has a μ_3-O^{2-} ligand protonated in the central unit $[WO(H_2O)(\mu_3\text{-}O)_3(\mu_3\text{-}OH)]^{3-}$ (See ref. 9*d*). In our case, the triply bridging oxygen atoms of the encapsulated tungsten $[W^{VI}O(H_2O)(\mu_3\text{-}O)_4]^{4-}$ unit gave a BVS value of ~1.5.