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$[Mo_9S_8O_{12}(OH)_8(H_2O)_2]^{2-}$: a novel polyoxothiomolybdate with a Mo^{VI} octahedron encapsulated in a reduced Mo^{V} cyclic octanuclear core

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The novel polyoxothioanion $[Mo_9S_8O_{12}(OH)_8(H_2O)_2]^{2-}$ was prepared from the acido-basic condensation of four $\{Mo^{V}_2S_2O_2\}$ building units around a central $\{Mo^{VI}O_6\}$ octahedron, the anion was characterized by X-ray diffraction as a tetramethylammonium salt.

The field of polyoxometalates, although explored for several years, still attracts significant attention,[1] because of its large number of potential applications, especially in the domain of heterogeneous catalysis.[2] We are currently interested in the synthesis of sulfur-containing polyoxoanions, a first step towards the design of sulfur-containing (possibly microporous) three dimensional frameworks. We thus developed a strategy based on the acido-basic condensation of the oxothio building block $\{Mo_2S_2O_2\}$. The efficiency of this method was recently[3] evidenced by the preparation of $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$, a cyclic oxothio compound prepared from the one-step self-condensation of $[Mo_2S_2O_2]^{2+}$. The condensation reaction was performed by controlled addition of potassium hydroxide to an acidic aqueous solution of the thiocation.† $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$ appeared to be a convenient starting material for further syntheses because of its ability to regenerate straightforwardly the $\{Mo_2S_2O_2\}$ unit either in acidic solution, as the $[Mo_2S_2O_2(H_2O)_6]^{2+}$ dithiocation,[3] or in basic solution. Indeed, there is strong evidence that $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$ hydrolyses, at pH > 11, into the dark red, air sensitive, $[Mo_2S_2O_2(OH)_4(H_2O)_2]^{2-}$ dianion.‡ In this way, the condensation of the $\{Mo_2S_2O_2\}$ building blocks occurs when the pH of the solution is lowered. Accordingly, in the absence of any other reactants, the cyclic compound $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$ is reformed, around pH = 1.5. This procedure is convenient when the reactants are unstable in acidic media; this is the case, for example, for MoO_4^{2-}, which can self condense to give various types of oxoanions.[4]

We thus report here the results of the reaction of MoO_4^{2-} with $[Mo_2S_2O_2(OH)_4(H_2O)_2]^{2-}$, at pH about 5. The synthesis§ is quite straightforward, starting from MoO_4^{2-} and a solution of the dianion. Four building units condense around the central $[MoO_4(H_2O)_2]^{2-}$ anion, which serves as a template, to form the novel polyoxothio anion $[Mo_9S_8O_{12}(OH)_8(H_2O)_2]^{2-}$. This compound has been fully characterized by IR spectroscopy, microanalysis and single crystal X-ray diffraction.¶

The molecular structure of the compound is shown in Fig. 1. The anion has crystallographically imposed inversion symmetry. It can be described as an eight-membered ring encapsulating an $Mo^{VI}O_6$ octahedron. As already observed[3] the $\{Mo_2S_2O_2\}$ unit has a strong tendency to form cyclic arrangements. This eight-membered ring compares well with the one obtained by the condensation of the oxo analog $[Mo_2O_4]^{2+}$ in the presence of oxalic acid.[5] The Mo^V atoms have a slightly distorted octahedral coordination: they are connected to a terminal oxygen atom, two hydroxo and two sulfido bridging ligands; the coordination sphere of the Mo centers is completed by a bridging oxygen bound to the central Mo^{VI} atom. The octahedra within the $\{Mo_2S_2O_2\}$ building blocks share edges but they are connected by faces as shown in Fig. 1. Short (*ca.* 2.8 Å) Mo–Mo distances characteristic of a single Mo^V–Mo^V bond alternate with longer (*ca.* 3.2 Å) Mo–Mo distances within the ring. The inner Mo^{VI} atom is disordered over four positions around the inversion centre, with a 25% occupancy,[6] this disordered Mo atom exhibits a distorted octahedral coordination [Mo–O distances from 1.745(7) to 2.391(7) Å]. In this mixed-valence compound, the electrons are thus strictly localized, as demonstrated by the absence of the blue colour characteristic of electron delocalization in the so-called ‘molybdenum blue’ species.[4,7]

In conclusion, the synthesis and isolation of the tetramethylammonium salt of the novel polyoxo anion $[Mo_9S_8O_{12}(OH)_8(H_2O)_2]^{2-}$ is straightforward, with a good yield, by simply mixing starting materials which are readily available. The complexity of the anions can be increased by replacing the central MoO_6^{2-} octahedron with a more sophisticated anionic template. The synthesis of $[Mo_9S_8O_{12}(OH)_8(H_2O)_2]^{2-}$ there-

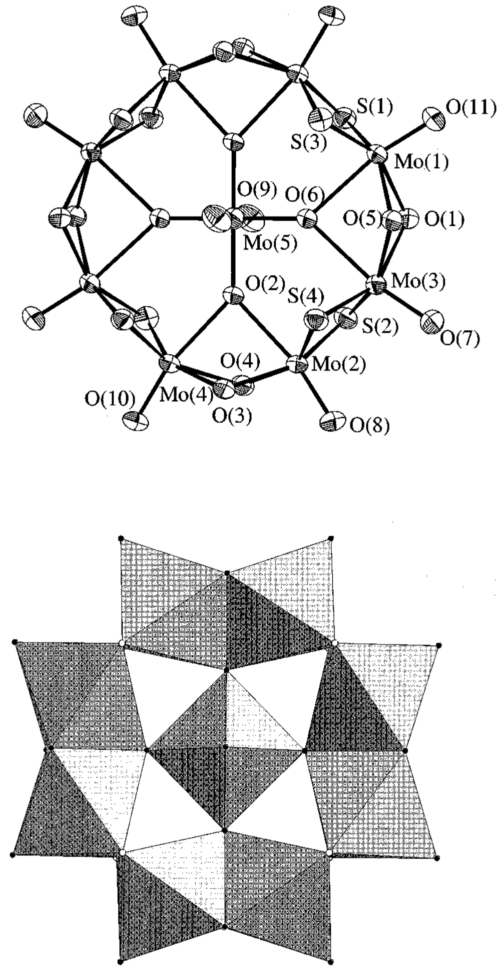

Fig. 1 Molecular structure of the polyoxothioanion $[Mo_9S_8O_{12}(OH)_8(H_2O)_2]^{2-}$. Top: ball-and stick model showing the eight-membered ring and the central $\{MoO_6\}$ octahedra. Thermal ellipsoids are drawn at the 50% probability level. For clarity, the disordered Mo(5) atom has been located at its mean position on the inversion centre, with a mean isotropic factor. Bottom: polyhedral representation showing the connectivity of the building blocks.

fore demonstrates that the acido-basic condensation of the $\{Mo_2S_2O_2\}$ fragments, either starting from an acidic solution or a basic solution, is a promising approach for the preparation of a variety of polyoxothio compounds.

Notes and references

† It should be noted that the crude product, obtained by the synthetic procedure described in ref. 3, before recrystallization has the composition $K_{2.6}(NMe_4)_{0.4}I_3[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]\cdot 30H_2O$ as shown by elemental microanalysis: Calc. (Found) C 0.62(1.23); I 12.31(12.13); K 3.29(3.27); Mo 37.23(36.71); N 0.18(0.40); S 12.42(12.72)%.

‡ $[Mo_2S_2O_2(OH)_4(H_2O)_2]^{2-}$ was precipitated as a potassium salt from a 1 M KOH solution, and isolated as a dark red powder. Elemental microanalysis confirmed the molecular formula $K_2[Mo_2S_2O_2(OH)_4(H_2O)_2]\cdot 13H_2O$: Calc. (Found) K 15.85(15.34); Mo 38.88(38.75); S 12.97(13.45)%.

§ As the intermediate $[Mo_2S_2O_2(OH)_4(H_2O)_2]^{2-}$ dianion is sensitive to air oxidation, the synthesis has to be carried out under a constant flow of N_2 gas. 20 ml of 1 M NaOH was first degassed for 10 min and 1 g (0.33 mmol) of $K_{2.6}(NMe_4)_{0.4}I_3[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]\cdot 30H_2O$ was added. The solution was stirred vigorously until the yellow powder dissolved to give a dark red solution of the $[Mo_2S_2O_2(OH)_4(H_2O)_2]^{2-}$ dianion. 0.16 g (0.66 mmol) of $Na_2MoO_4\cdot 2H_2O$ was then rapidly added and the pH was adjusted to 4.5 with a solution of 4 M HCl. The precipitation of the polyoxothio anion was achieved by the addition of 0.44 g (4.4 mmol) of $[NMe_4]Cl$ and gave 0.76 g of a thin yellow powder [yield = 86% (based on Mo)]. This powder was collected by filtration, washed with water and ethanol and dried with diethyl ether. IR spectra (KBr pellet, ν/cm^{-1}) gave absorptions at *ca.* 1480s, 1446w, 948s, 830m, 745m, 512s, 415w, 348w. Elemental microanalysis confirmed the molecular formula $[N(CH_3)_4]_2[Mo_9S_8O_{12}(OH)_8(H_2O)_2]\cdot 8H_2O$: Calc. (Found) C 5.46 (5.94); H 2.96 (2.79); Mo 49.09 (48.61); N 1.59 (1.61); S 14.55 (14.26)%. A few single crystals, suitable for X-ray diffraction, were grown in a solution containing only a small amount of tetramethylammonium cations.

¶ *X-Ray crystal structure analysis* for $[N(CH_3)_4]_2[Mo_9S_8O_{12}(OH)_8(H_2O)_2]\cdot 5H_2O$: Intensity data collection was carried out on a yellow crystal of 0.28 × 0.18 × 0.02 mm, with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector, using monochromatized λ(Mo-Kα) = 0.71073 Å. T = 293 K. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program[8] based on the method of Blessing.[9] *Crystal data* for $C_8H_{24}Mo_9N_2O_{27}S_8$: a = 15.0752(2), b = 12.9951(2), c = 12.6676(1) Å, β = 113.530(1)°, U = 2275.3(5) Å^3, Z = 2, M = 1700.22, D_c = 2.505 g cm^{-3}, monoclinic, space group $P2_1/c$ (no. 14), μ = 28.40 cm^{-1}, index ranges $-12 \leqslant h \leqslant 20$, $-17 \leqslant k \leqslant 17$, $-17 \leqslant l \leqslant 13$; total data 15389; unique data 5817 (R_{int} = 0.037), data with $I_o > 2\sigma(I_o)$ 4419. The structure was solved by direct methods and refined by full matrix least-squares, based on F^2, using the SHELX-TL software package.[10] All non-hydrogen atoms were refined anisotropically except for the disordered molybdenum atom and the water oxygen atoms. No. of variables, 242; final $R(F)$ = 0.040, $wR(F^2)$ = 0.098; GOF 1.08; minimum and maximum peak in difference electron density map -0.96 and 1.57 e Å^{-3}. CCDC 182/1006.

1 See for example the special issues on polyoxometalates of *Chem. Rev.* 1998, **98** and *C. R. Acad. Sci. Paris, Sér. IIc*, 1998.

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