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$[Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]$: a novel decameric molecular ring showing supramolecular properties

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The new decameric $[Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]$ oxo–thio ring was prepared by self-condensation of $[Mo_2S_2O_2]^{2+}$ upon addition of hydroxide ion; crystals were obtained in dimethylformamide in the presence of tetrabutylammonium iodide; X-Ray diffraction analysis reveals a 10-membered ring-shaped cluster; the cyclic architecture exhibits a supramolecular assembly resulting from hydrogen bonding between two iodide anions and inner water molecules of the open cavity of the Mo_{10}-ring.

The synthesis of large and discrete species resulting from transition metal and sulfur combinations is an exciting challenge for the inorganic chemist. Indeed, transition metal sulfides represent a prominent class of compounds involved in many areas of chemistry.[1] Especially, such systems are studied extensively for their implications in both biological and industrial catalytic processes. The nuclearity of the thiometalates is generally low with topologies often limited to a restricted number of archetypal architectures.[2] These features contrast with polyoxometalates which have now reached the nanometric scale with spectacular examples such as the 'big wheel' for molybdenum blues[3] and the 'giant butterfly' for heteropolytungstates.[4] We reported in a previous work the characterization of the first oxo–thio molecular ring with high nuclearity[5] and we have now indications that other derived compounds might be synthesized through the original and convenient route of synthesis we are developing. The $[Mo_2S_2O_2(H_2O)_6]^{2+}$ precursor (aqua ion) reacts rapidly with hydroxo ions to give cyclic polymeric oxo–thio molecules, the first compound (solid **1**) isolated at pH <3 from concentrated potassium iodide solution, leading after crystallization in water to $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$ (denoted Mo_{12}) a cyclic iodide-free dodecameric neutral cluster **2**.[5]† The Mo_{12} ring-shaped molecule results from the cyclic linking of six $\{Mo_2S_2O_2\}$ fragments by face-shared connections. We have demonstrated that the six water molecules lining the inner ring are labile enough to be exchanged by small anions such as phosphate or arsenate ions.[6] These exchange properties arising from the cationic character of the central open cavity hold much promise for the elaboration of a new generation of 'multicomponent systems' based on host–guest chemistry. In the presence of anionic structuring agents, such as oxalate[7] or even metalates such as molybdate,[8] the self-condensation of $[Mo_2S_2O_2]^{2+}$ produces an octameric $\{Mo_8S_8O_8(OH)_8\}$ ring encapsulating the structuring anion. With more concentrated phosphate or arsenate solutions, the condensation leads exclusively to the hexameric $[(HXO_4)_4Mo_6S_6O_6(OH)_3]^{5-}$ anion (X = As, P)[9] in which three building units $\{Mo_2O_2S_2\}$ condense around a central phosphate group through hydroxo and peripheral phosphato bridges.

The structural characterization of the new $[Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]$ ring-shaped cluster **3** (denoted Mo_{10}), obtained from **1** in a DMF solution containing tetrabutylammonium iodide represents a nice illustration of the self-condensation process. The synthesis is straightforward and consists of the dissolution of the reactants in dimethylformamide, leading to the crystallization of **3**‡ which has been fully characterized by X-ray diffraction, IR spectroscopy and elemental analysis.§

The results of the X-ray crystallographic investigation are shown in Figs. 1 and 2. The asymmetric unit contains one molecular Mo_{10}-ring, associated with two iodide anions and two tetrabutylammonium cations. The $[Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]$ molecular ring consists of five $\{Mo_2S_2O_2\}$ units connected to each other by hydroxo double bridges to form a cyclic neutral decamer. Two types of Mo–Mo distances are observed: short Mo–Mo distances [2.835(2)–2.847(2) Å] within the $\{Mo_2S_2O_2\}$ building block and long Mo–Mo interblock distances (3.314–3.324 Å). A terminal oxygen atom and two bridging sulfur atoms, both belonging to the preformed building block, complete the coordination of the Mo^V centers. Five oxygen atoms located in the open cavity of the $\{Mo_{10}S_{10}O_{10}(OH)_{10}\}$ ring bridge two neighboring Mo atoms through long Mo–O distances (2.572–2.630 Å). This arrangement confers an overall zero charge to the cluster. The presence of two iodide anions symmetrically located on both sides of the mean plane defined by the ten Mo atoms is a remarkable feature of the molecular structure (Fig. 2). The distances between iodides and the five inner water molecules are short enough (3.570–3.622 Å) to suggest that the stability of the bis-halide complex is directly related to hydrogen bonds. The hydrogen atoms of the five inner water molecules are symmetrically distributed on each side of the ring cluster, in two planes parallel to those defined by the ten molybdenum atoms. The five

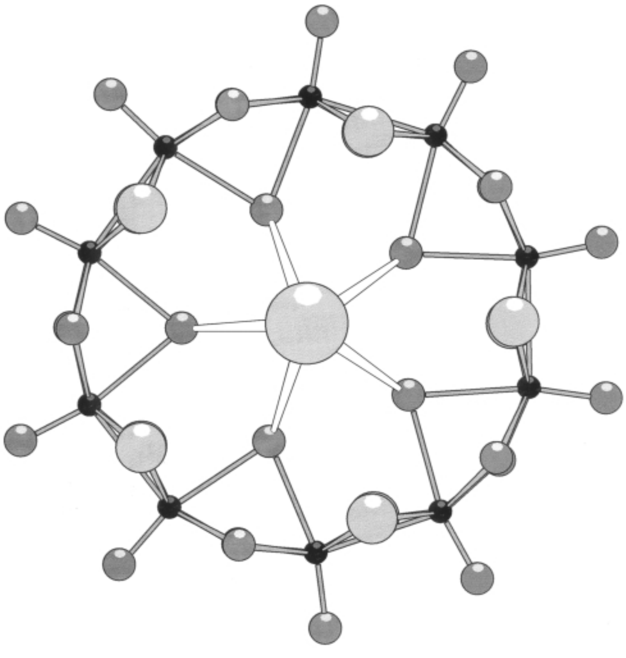

Fig. 1 Molecular structure of $[I_2Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]^{2-}$: ball and stick model showing the 10 membered ring with the central iodide anions (black spheres: Mo, light grey spheres: S, dark grey spheres: O, light grey central sphere: I).

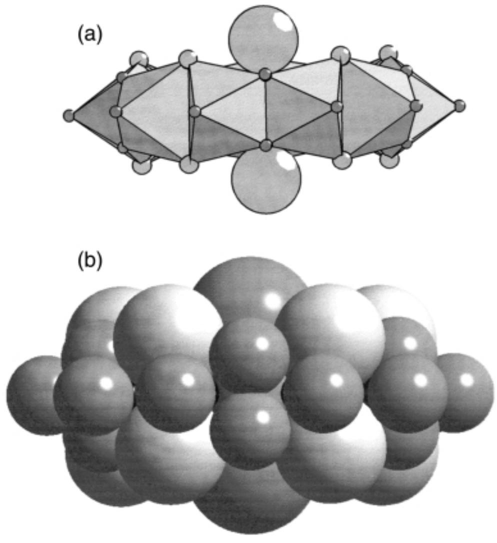

Fig. 2 Side view of $[I_2Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]^{2-}$ showing the two symmetric iodide anions floating over the cavity of the Mo_{10} ring-shaped cluster through hydrogen interactions: (a) polyhedral representation; (b) space-filling sketch with ionic radii of the elements ($O^{2-} = 1.32$ Å, $S^{2-} = 1.84$ Å, $I^- = 2.20$ Å).

$[I^- \cdots H–O–H \cdots I^-]$ interactions provoke a pronounced shortening of the $I \cdots I$ distances (4.783 Å), rather close to the sum of the ionic radii (4.40 Å). The electrostatic balance in the crystal is ensured by two tetrabutylammonium cations.

In conclusion, this work illustrates the flexibility and the versatility of the cyclic oxo–thio architecture: in water, **1** leads to the dodecamer $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$ **2** while in iodide containing DMF solution, **1** gives the cyclic decamer $[Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]$ **3**. The solid state structure of **3** reveals a remarkable bis-halide complex resulting from the electrostatic interactions of two iodide ions with the inner cavity of the Mo_{10}-cluster. Such promising results demonstrate that supramolecular chemistry of anions can be considered in those inorganic systems.

Notes and references

† The crude product **1**, obtained by the synthetic procedure described in ref. 5 is a mixed $K^+–NMe_4^+$ salt of a neutral oxo–thio-cluster which incorporates iodide in the solid state. The elemental and thermogravimetric analysis for **1** led to the empirical molecular composition $\{K_{0.40}(NMe_4)_{0.1}I_{0.5}[Mo_2S_2O_2(OH)_2(H_2O)]\cdot 6.3H_2O\}_n$ with no direct evidence for the determination of the nuclearity *n*.

‡ *Synthesis of* $[NBu_4]_2I_2[Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]\cdot H_2O\cdot 13DMF$ **3**. 1 g of **1** and tetrabutylammonium iodide (2.8 g, 7.6 mmol) were dissolved in 15 mL of DMF. After filtration, the solution was allowed to stand at room temperature for crystallization. After a week, well shaped orange crystals, suitable for X-ray diffraction were collected [yield: 41% (based on Mo)]. IR spectra (KBr pellet, ν/cm^{-1}) gave absorptions at *ca*. 1488w, 1434w, 1411w, 1388m, 1257m, 1150w, 1101m, 1063w, 968s, 876w, 666m, 533s, 413m, 378m. Crystals are strongly hygroscopic and not stable in air. Such a behavior explains the difference between the number of water molecules found in the solvate by X-ray diffraction (1.0 H_2O) and those determined by elemental analysis after hydration of the solid (18 H_2O). Anal. for $[NBu_4]_2I_2[Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]\cdot 18H_2O\cdot 13DMF$. Calc.(Found): C, 23.40 (24.85); I, 6.86 (6.91); Mo, 25.96 (26.47); N, 5.67 (5.31); S, 8.65 (8.58)%.

§ *X-Ray crystal structure analysis* for $[NBu_4]_2I_2[Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]\cdot H_2O\cdot 13DMF$ **3**. Intensity data collection was carried out on an orange crystal of 0.30 × 0.30 × 0.40 mm mounted in a glass tube, with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector, using monochromatized wavelength λ(Mo-Kα) = 0.71073 Å, at T = 293 K. An absorption correction was made in the data set using the SADABS program[10] based on the method of Blessing.[11] The asymmetric unit is composed of one Mo_{10}-ring, two iodide anions and two $[NBu_4]^+$ cations. Among the 13 DMF molecules per Mo_{10}-ring obtained by microanalysis, only 10 were located, the others being disordered in the lattice. *Crystal data* for $H_{185}C_{71}I_2Mo_{10}N_{15}O_{39}S_{10}$: a = 21.573(2), b = 21.075(2), c = 30.190(5) Å, β = 97.766(8)°, U = 13600(3) Å^3, Z = 4, M = 3405, D_c = 1.663 g cm^{-3}, monoclinic, space group $P2_1/c$, μ = 15.67 cm^{-1}, index ranges $-26 \leqslant h \leqslant 30$, $-15 \leqslant k \leqslant 23$, $-30 \leqslant l \leqslant 41$; total data 44152; unique data 29602 (R_{int} = 0.056), data with $I_0 > 2\sigma(I_o)$ 12749. The structure was solved by direct methods and refined by full matrix least squares, based on F^2, using the SHELX-TL software package.[12] All the non-hydrogen atoms were refined anisotropically except the water oxygen atoms, nitrogen, oxygen and carbon atoms of the DMF molecules and the three terminal carbon of the four alkyl chains in the two NBu_4^+ cations. No. of variables, 855; final $R(F) = 0.0782$, $wR_2(F^2)$ = 0.1790; GOF 1.074; minimum and maximum peak in difference electron density map −1.761 and 1.415 e Å^{-3}. CCDC 182/1517. See http://www.rsc.org/suppdata/cc/a9/a909024j/ for crystallographic files in .cif format.

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