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LETTER

Hydrothermal synthesis and crystal structure of $(NH_4)_5Na_4\{Na[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]_2\}\cdot 6H_2O$

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TABLE 1. Summary of crystal data and the details of structure refinement for **1**

Formula	$C_{48}H_{78}N_5O_{60}Na_5P_8Mo_{12}$
Molecular weight	3199.2
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	31.254(7)
b (Å)	30.441(6)
c (Å)	13.455(3)
β (°)	112.87(2)
V (Å^3)	11795(2)
Z	4
D_{calc} (g/cm^3)	1.80
μ(Mo Kα) (cm^{-1})	15.01
Scan method	ω
Maximum 2θ (°)	45
No. reflections measured	4215
No. unique data, $I > 3.00\sigma(I)$	2162
No. parameters refined	312
R_a	0.069
$R_w{}^b$	0.075

$^aR = \Sigma||F_o| - |F_o||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_o|)^2/\Sigma w(F_o)^2]^{1/2}$.

The solid phases of the metal organophosphonate system have received considerable contemporary attention because of their unusual structural chemistry and their real and potential applications. Layered metal phosphonates may serve as sorbents, catalysts and catalyst supports, and ion exchangers [1–3]. Furthermore, the organophosphonate group has also been shown to form molecular anion clusters with molybdenum [4] and vanadium [5, 6]. As part of our continuing studies of the coordination chemistry of polyoxometalates, we have synthesized by hydrothermal techniques and structurally characterized a novel polyoxomolybdenum(V) organophosphonate species $(NH_4)_5Na_4\{Na[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]_2\}\cdot 6H_2O$ (**1**). While this work was in progress the anion core was also isolated in the solid phase, $[(C_2H_5)_4N]_2Na_3H_{10}\{Na[Mo_6O_{15}(O_3PC_6H_5)_4]_2\}\cdot xH_2O$ (7).

Experimental

Synthesis of $(NH_4)_5Na_4\{Na[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]_2\}\cdot 6H_2O$

A mixture of $Na_2MoO_4\cdot 2H_2O$, MoO_3, $H_2O_3PC_6H_5$, KCl, NH_4Cl and H_2O in the mole ratio 6:6:10:10:5:300 was placed in a Teflon-lined acid digestion bomb and heated for 4 days at 180 °C and autogenous pressure. After cooling the reaction mixture to room temperature, bright red crystals were collected from the brown mother liquor and air dried (yield 60%). Since crystals removed from the mother liquor turn opaque after several hours, the sample used for the X-ray study was kept in contact with the mother liquor. The crystal chosen for study was immediately immersed in the cold stream of the low temperature device at −60 °C. IR (KBr pellet, cm^{-1}): 1435(s), 1260(s), 1142(s), 1120(m), 1058(m), 1014(m), 955(vs), 799(s), 737(s), 721(m), 694(m), 572(vs), 484(s). Satisfactory elemental analyses were obtained.

X-ray data collection, structure solution and refinement of 1

Intensity data were collected on a Rigaku AFC5S diffractometer. All calculations was performed using the PC version of SHELXTL. The molybdenum positions were located by direct methods and all other non-hydrogen atoms were located from subsequent different Fourier maps. The molybdenum and phosphorus atoms were refined anisotropically, while all other atoms were refined using isotropic temperature factors. Due to the relative paucity of data, the phenyl rings were refined as rigid groups. The water molecules of crystallization were in several cases highly smeared; the formula unit thus contains approximately six water molecules. One sodium cation, Na2, is disordered about a mirror plane, resulting in a highly disordered associated hydration sphere. Crystal data and the details of data collection, structure solution and refinement are summarized in Table 1.

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Results and discussion

The hydrothermal reaction of $Na_2MoO_4 \cdot 2H_2O$, MoO_3, $C_6H_5PO_3H$, KCl, NH_4Cl and H_2O in the mole ratio 6:6:10:10:5:300 at 180 °C and autogenous pressure for 4 days yielded dark red crystals of **1** in 60% yield. The IR spectrum exhibits bands at 1142 and 1058 cm^{-1} attributed to ν(P–O) of the organophosphonate groups and a strong feature at 955 cm^{-1} characteristic of ν(Mo=O). Thermogravimetric analysis was consistent with the presence of *c.* six H_2O of crystallization.

The X-ray structural study revealed the presence of discrete NH_4^+ and Na^+ cations, H_2O molecules of crystallization and the unusual molecular anion $\{Na[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]_2\}^{9-}$ (**1a**), shown in Fig. 1(a). The structure of the molecular anion consists of two hexanuclear oxomolybdenum(V)–organophosphonate clusters linked by a sodium cation. The hexamolybdenum unit $\{Mo_6O_{24}\}$ forms a cyclic core, constructed from edge-sharing of $\{MoO_6\}$ octahedra. The Mo(V) centers of the core are associated in strongly interacting pairs so as to produce an alternating pattern of short and long Mo...Mo contacts, characterized by

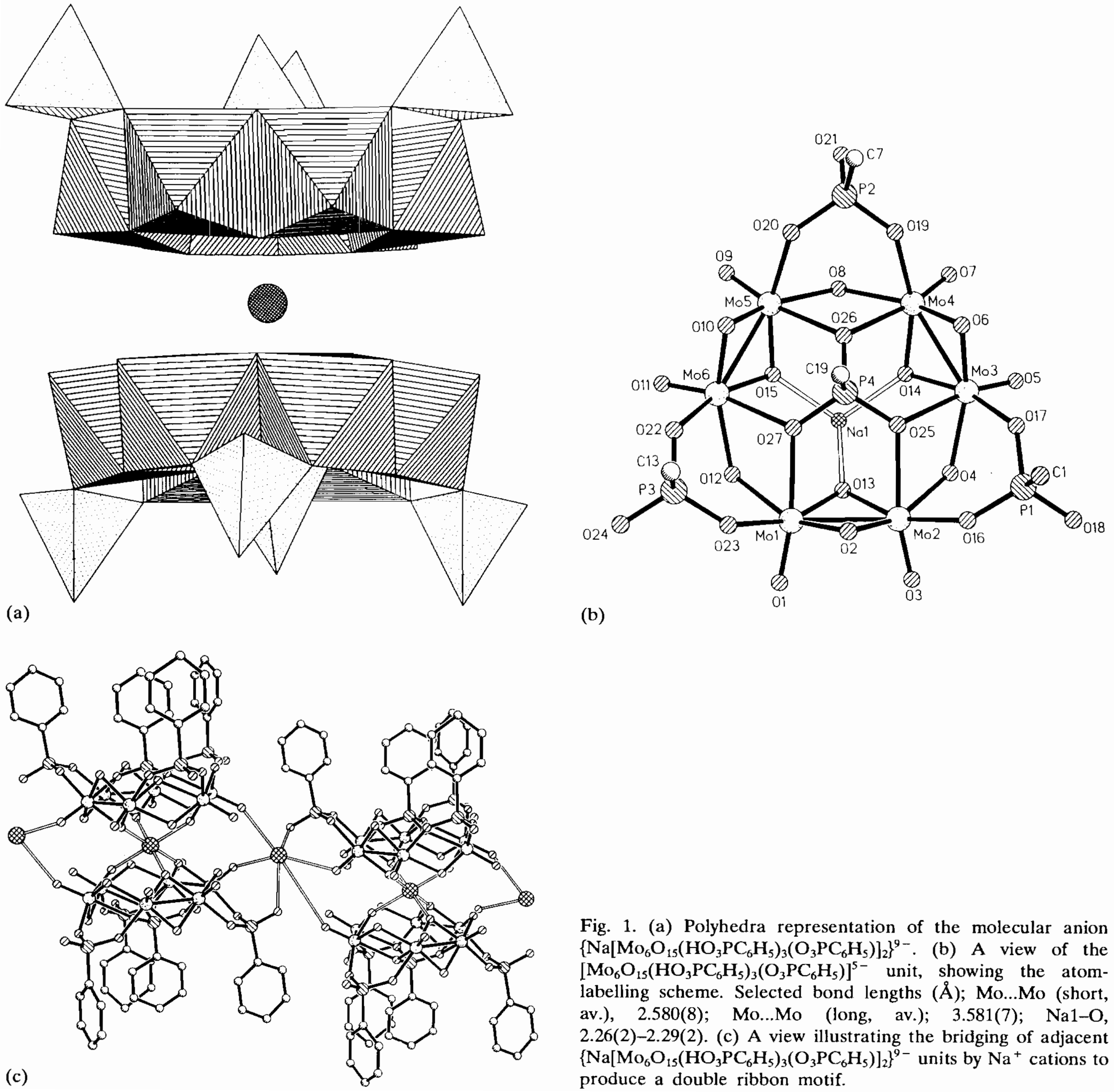

Fig. 1. (a) Polyhedra representation of the molecular anion $\{Na[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]_2\}^{9-}$. (b) A view of the $[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]^{5-}$ unit, showing the atom-labelling scheme. Selected bond lengths (Å); Mo...Mo (short, av.), 2.580(8); Mo...Mo (long, av.); 3.581(7); Na1–O, 2.26(2)–2.29(2). (c) A view illustrating the bridging of adjacent $\{Na[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]_2\}^{9-}$ units by Na^+ cations to produce a double ribbon motif.

distances of 2.58 and 3.58 Å, respectively. This cyclic core is reminiscent of the Anderson structure with the central atom removed [8] and appears to be a recurrent theme of the structural chemistry of reduced oxomolybdenum clusters, having been previously observed in the oxomolybdenum phosphate $(Et_4N)_6Na_2[Na_{12}(H_3PO_4)\{Mo_6O_{15}(HPO_4)(H_2PO_4)_3\}_4 \cdot xH_2O$ [9] and in $(Me_3NH)_2(Et_4N)Na_4[Na(H_2O)_3H_{15}Mo_{42}O_{109}\{(OCH_2)_3CCH_2OH\}_7] \cdot 15H_2O$ [10]. As shown in Fig. 1(b), there are two types of organophosphonate groups associated with this hexamolybdenum core in the $[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]^{5-}$ unit. The central $RPO_3{}^{2-}$ group provides three oxygen bridges so as to span each pair of Mo centers with long Mo...Mo distances. The three remaining organophosphonate groups assume μ_2-$O_2P(OH)R$ geometry so as to bridge pairs of non-bonded Mo centers; the uncoordinated oxygen of these units has been protonated. As shown in Fig. 1(a), the organophosphonate groups assume a *syn* conformation relative to the hexamolybdenum plane, an orientation which results in a double layer of polyhedra: one layer of phosphonate tetrahedra and a second of molybdenum octahedra.

One Na^+ cation is sandwiched between a pair of $[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]^{5-}$ moieties, which present the faces defined by the hexamolybdenum rings in a staggered orientation so as to provide an octahedral cavity for the Na^+ cation. The Na–O distances associated with this site are relatively short, suggesting that the formation of the sandwiched cation core is crucial to isolation of the polyanion. As illustrated in Fig. 1(c), a second Na^+ cation serves to bridge adjacent pairs of $\{Na[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]_2\}^{9-}$ units to generate double ribbons with the phenyl groups disposed about the exterior. Attempts to replace the Na^+ cation with other cations have thus far proved unsuccessful. However, it is clear that a variety of organic and inorganic cations may substitute for the large concentration of other cations in the lattice.

Supplementary material

Further data may be obtained from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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