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SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE TRIETHYLAMMONIUM MAGNESIUM β-OCTAMOLYBDATE(VI) SALT $[Et_3NH]_2[Mg(H_2O)_6Mo_8O_{26}] \cdot 2H_2O$

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Abstract—$[Et_3NH]_4[Mo_8O_{26}]$ reacted with $MgCl_2$ and $CaCl_2$ giving the triethylammonium magnesium β-octamolybdate(VI) salt $[Et_3NH]_2[Mg(H_2O)_6Mo_8O_{26}] \cdot 2H_2O$ (**3**) and the triethylammonium hydronium β-octamolybdate(VI) salt $[Et_3NH]_3[(H_3O)Mo_8O_{26}] \cdot 2H_2O$ (**4**), respectively. A small amount of $[Et_3NH]_2[Mo_6O_{19}]$ was formed as a by-product. The salts **3** and **4** were characterized by X-ray crystallography. The $[Mg(H_2O)_6Mo_8O_{26}]^{2-}$ moiety in **3** is polymeric, with each octahedral $[Mg(H_2O)_6]^{2+}$ ion sandwiched between two $\beta[Mo_8O_{26}]^{4-}$ ions, being hydrogen bonded to three terminal Mo=O oxygen atoms on one face of each $\beta[Mo_8O_{26}]^{4-}$ ion. The X-ray crystal structure of **4** corresponds to that reported previously. IR and conductivity data are given for **3** and **4**.

Heteropolyoxometalate(VI) salts are commonly found with alkali metal cations coordinated to some of the oxygen atoms that form part of the exterior wall of the $M_xO_y^{n-}$ cluster.[1] In addition, the alkali metals *M* in these salts are normally also bonded to a number of water molecules, overall producing an intricate three-dimensional framework stitched together through M—O—*M*—O—M and M—O—*M*—H_2O—*M*—O—M bridges. Recently,[2] we reported the synthesis of the triethylammonium β-octamolybdate(VI) salt $[Et_3NH]_4[Mo_8O_{26}]$ (**1**), and described its reaction with sodium chloride in aqueous solution to give the triethylammonium sodium salt $[Et_3NH]_3[NaMo_8O_{26}]$ (**2**):

$$[Et_3NH]_4[Mo_8O_{26}]\,(\mathbf{1}) + NaCl \longrightarrow [Et_3NH]_3[NaMo_8O_{26}]\,(\mathbf{2}).$$

The X-ray crystal structure of **2** showed it to be polymeric, with each Na^+ ion sandwiched between two $\beta[Mo_8O_{26}]^{4-}$ ions. Four oxygen atoms on one face of each $\beta[Mo_8O_{26}]^{4-}$ ion were coordinated to an Na^+ ion, and four oxygens from the opposite face were bonded to the next Na^+ ion in the polymer chain.

As an extension to this work we now report on the reaction of **1** with the alkaline earth metal dications Mg^{2+} and Ca^{2+}.

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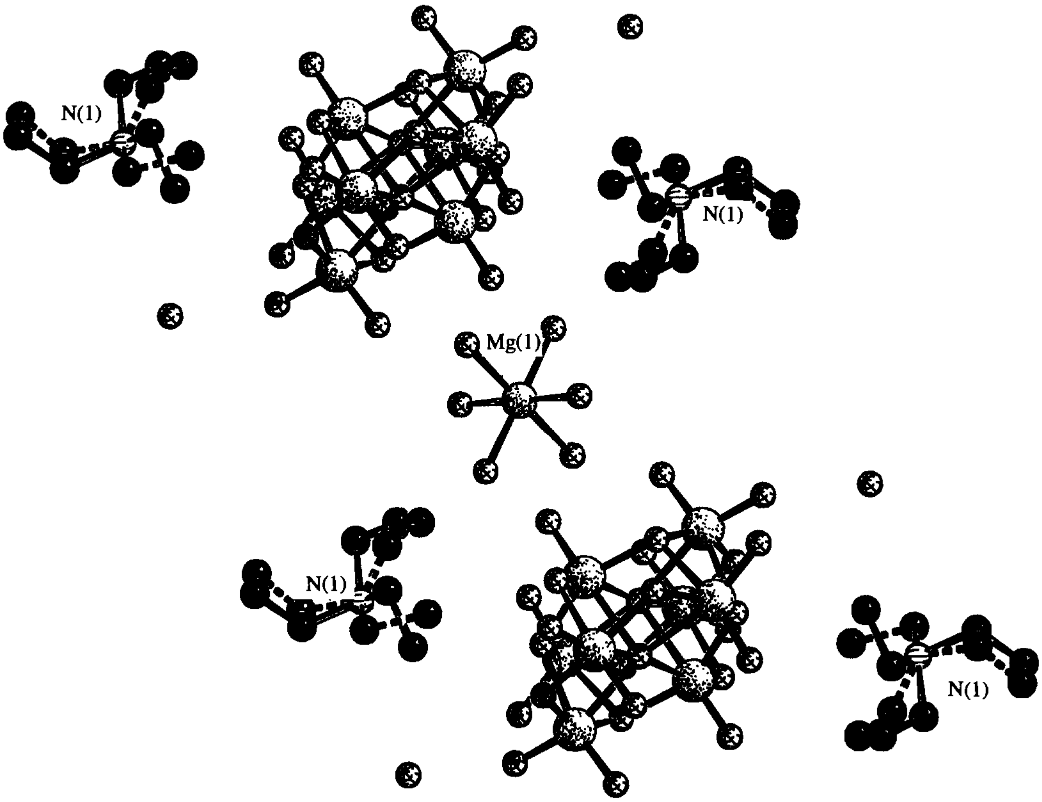

Fig. 1. The overall packing in the lattice of $[Et_3NH]_2[Mg(H_2O)_6Mo_8O_{26}]\cdot 2H_2O$ (3).

RESULTS AND DISCUSSION

$[Et_3NH]_4[Mo_8O_{26}]$ (**1**) reacted with an excess of magnesium chloride to produce the colourless triethylammonium magnesium *β*-octamolybdate(VI) salt $[Et_3NH]_2[Mg(H_2O)_6Mo_8O_{26}]\cdot 2H_2O$ (**3**) in good yield. A small quantity of the yellow triethylammonium hexamolybdate(VI) salt $[Et_3NH]_2[Mo_6O_{19}]$[2] formed as a by-product in the reaction. The X-ray crystal structure of **3** is shown in Fig. 1, and the more important bond distances and bond angles are listed in Table 1. There are a number of similarities between the structure of the sodium salt $[Et_3NH]_3[NaMo_8O_{26}]$ (**2**)[2] and the magnesium salt **3**. As expected, the bond distances and bond angles for the $\beta[Mo_8O_{26}]^{4-}$ ion were essentially the same in **2** and **3**. The $[Mg(H_2O)_6Mo_8O_{26}]^{2-}$ moiety in **3** is polymeric, with each octahedral $[Mg(H_2O)_6]^{2+}$ ion sandwiched between two $\beta[Mo_8O_{26}]^{4-}$ ions, being hydrogen bonded to three terminal Mo═O oxygen atoms on one face of each $\beta[Mo_8O_{26}]^{4-}$ ion (Fig. 2).

In contrast to the reaction of **1** with $MgCl_2$ to give the triethylammonium magnesium *β*-octamolybdate(VI) salt **3**, $CaCl_2$ reacts with **1** to produce the triethylammonium hydronium *β*-octamolybdate(VI) salt $[Et_3NH]_3[(H_3O)Mo_8O_{26}]\cdot 2H_2O$ (**4**). Again, a small amount of $[Et_3NH]_2[Mo_6O_{19}]$ was formed during the reaction. The structure of **4** was confirmed by X-ray crystallography and it corresponded with that reported previously by Ohashi *et al.*[3] for this salt. The crystallographic data obtained from our analysis* were slightly better than those of Ohashi *et al.* and allowed a more accurate interpretation of the complex hydrogen bonding within the $[(H_3O)Mo_8O_{26}]^{3-}$ moiety. The hydronium ion H_3O^+ is sandwiched between two $\beta[Mo_8O_{26}]^{4-}$ anions and its oxygen atom makes eight contacts to four terminal Mo═O oxygen atoms of each of the two anions. The hydrogen atoms of the hydronium ion were located from a difference map. Of the eight O···O contacts, one involves a simple O—H···O hydrogen bond and four are associated with bifurcated O—H···O hydrogen bonds. Crystallographic inversion symmetry transformations then give rise to a polymeric chain structure. The hydrogens of the two water molecules were located unequivocially and they take part in

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* X-ray crystallographic data associated with the present structure determination of **4** has been submitted as supplementary material with this paper.

Table 1. Selected molecular dimensions for **3**

Bond lengths (Å)[a]			
Mo(1)—O(3)	1.695(4)	Mo(1)—O(6)	1.706(4)
Mo(1)—O(8)	1.880(4)	Mo(1)—O(7)	1.997(4)
Mo(1)—O(55)	2.286(4)	Mo(1)—O(5)	2.327(4)
Mo(1)—Mo(4)	3.2009(7)	Mo(2)—O(2)	1.694(5)
Mo(2)—O(11)	1.707(5)	Mo(2)—O(10)	1.917(4)
Mo(2)—O(8) #1	1.926(4)	Mo(2)—O(1)	2.299(4)
Mo(2)—O(55) #1	2.448(4)	Mo(3)—O(4)	1.695(4)
Mo(3)—O(9)	1.697(4)	Mo(3)—O(10) #1	1.897(4)
Mo(3)—O(5) #1	1.998(4)	Mo(3)—O(7) #1	2.336(4)
Mo(3)—O(55)	2.352(4)	Mo(4)—O(12)	1.695(4)
Mo(4)—O(1)	1.742(4)	Mo(4)—O(7)	1.942(4)
Mo(4)—O(5) #1	1.947(4)	Mo(4)—O(55)	2.155(4)
Mo(4)—O(55) #1	2.360(4)	O(5)—Mo(4) #1	1.947(4)
O(5)—Mo(3) #1	1.998(4)	O(7)—Mo(3) #1	2.336(4)
O(8)—Mo(2) #1	1.925(4)	O(10)—Mo(3) #1	1.897(4)
O(55)—Mo(4) #1	2.360(4)	O(55)—Mo(2) #1	2.448(4)
Mg(1)—O(102)	2.046(4)	Mg(1)—O(102) #2	2.046(4)
Mg(1)—O(101) #2	2.068(4)	Mg(1)—O(101)	2.068(4)
Mg(1)—O(103)	2.080(4)	Mg(1)—O(103) #2	2.080(4)
Intermolecular contact distances:			
O(3)—O(102)	2.726	O(12)—O(101)	2.947
O(2)—O(103)	2.836		
Bond angles (°)[b]			
O(102)—Mg(1)—O(102) #2	180.0	O(102)—Mg(1)—O(101) #2	92.3(2)
O(102) #2—Mg(1)—O(101) #2	87.7(2)	O(102)—Mg(1)—O(101)	87.7(2)
O(102) #2—Mg(1)—O(101)	92.3(2)	O(101) #2—Mg(1)—O(101)	180.0
O(102)—Mg(1)—O(103)	88.7(2)	O(102) #2—Mg(1)—O(103)	91.3(2)
O(101) #2—Mg(1)—O(103)	89.6(2)	O(101)—Mg(1)—O(103)	90.4(2)
O(102)—Mg(1)—O(103) #2	91.3(2)	O(102) #2—Mg(1)—O(103) #2	88.7(2)
O(101) #2—Mg(1)—O(103) #2	90.4(2)	O(101)—Mg(1)—O(103) #2	89.6(2)
O(103)—Mg(1)—O(103) #2	180.0(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x+1, -y, -z+1$.

[b] Symmetry transformations used to generate equivalent atoms: #2 $-x+1, -y, -z+1$.

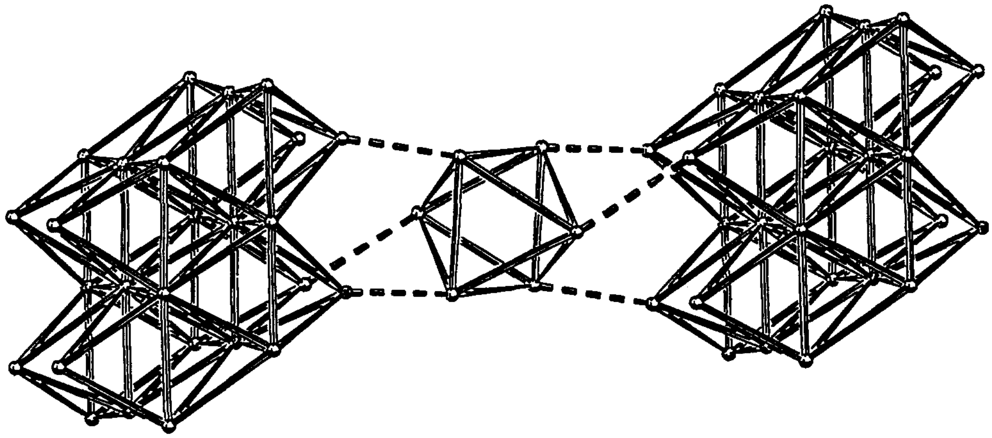

Fig. 2. Hydrogen bonding between $[Mg(H_2O)_6]^{2+}$ and $\beta[Mo_8O_{26}]^{4-}$ ions in **3**.

O—H · · · O hydrogen bonding to terminal Mo=O oxygens.

The salts **1–4** were soluble only in water and in DMSO. Whereas the molar conductivities of **1** and **2** in water were 815 and 885 S cm^2 mol^{-1}, respectively,[2] the values obtained for **3** ($\Lambda_M = 421$ S cm^2 mol^{-1}) and **4** ($\Lambda_M = 512$ S cm^2 mol^{-1}) were significantly smaller, implying that **3** and **4** do not ionize in aqueous solution to the same extent as **1** and **2**. The IR spectra of **1–4** are very similar in the region 3200–300 cm^{-1} and contain bands attributible to the Mo=O and Mo—O—Mo vibrations, as well as those associated with the triethylammonium cations. In addition, the spectra of **3** and **4** show strong O—H bands around 3400 cm^{-1} associated with the water molecules in these salts.

In conclusion, it is evident that the nature of the reaction product isolated from the interaction of **1** with alkaline earth metal salts is quite unpredictable. Reaction of **1** with Mg^{2+} ions produces the magnesium β-octamolybdate(VI) salt **3**, whilst Ca^{2+} ions promote the formation of the hydronium β-octamolybdate(VI) salt **4**. Furthermore, Ohashi *et al.*[3] obtained the same hydronium β-octamolybdate(VI) salt **4** by the entirely different route of recrystallizing the triethylammonium dimolybdate salt $[Et_3NH]_2[Mo_2O_7]$ from water.[4]

EXPERIMENTAL

Chemicals were reagent grade and were used without further purification. $[Et_3NH]_4[Mo_8O_{26}]$ (**1**) was prepared by the literature method.[2] IR spectra (as KBr discs) were recorded in the region 4000–200 cm^{-1} on a Perkin–Elmer 783 grating spectrometer, and conductivity readings (10^{-3} M aqueous solutions; 25°C) were taken with a WTW model LF9 conductivity meter.

Crystallography

Crystal Data for **3**. Formula: $C_{12}H_{48}O_{34}MgMo_8N_2$, $M = 1556.349$; space group $P-1$, triclinic, $a = 10.324(1)$, $b = 10.731(1)$, $c = 11.0302(9)$ Å, $\alpha = 107.095(5)$, $\beta = 99.089(5)$, $\gamma = 110.164(5)°$, $U = 1049.6(2)$ $Å^3$, $Z = 1$, $D_c = 2.472$ g cm^{-3}, $F(000) = 754$, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 2.37$ mm^{-1}.

Data collection and processing. A colourless crystal of **3** was mounted on an Enraf–Nonius CAD4 diffractometer and 3900 reflections were measured ($1° < \theta < 25°$) using a ω–2θ scan mode with graphite monochromated Mo-K_α radiation. The data were merged to give 3686 unique reflections (R_{merg} of 0.0249), of which 3471 had $|F_{obs}| > 4\sigma|F_{obs}|$ and were used for structure solution.

Structure solution and refinement. The structure was solved by the direct methods routine of SHELXS-86, followed by difference Fourier synthesis and refined by full-matrix least squares, both using SHELXL to $R = 0.0376$. The non-hydrogen atoms of the molybdenum and magnesium ions were refined with anisotropic temperature factors along with the oxygen of the co-crystallized water. The triethylammonium ion was found to be disordered, two positions were located for all of the carbon atoms, one more prominent than the other (60% occupancy). These positions were refined with fixed hydrogen atoms. SHELXS-86 and SHELXL were used with the kind permission of G. M. Sheldrick (Universität Göttingen).

$[Et_3NH]_2[Mg(H_2O)_6Mo_8O_{26}]\cdot 2H_2O$ (3)

A pale blue solution of $[Et_3NH]_4[Mo_8O_{26}]$ **1** (0.4 g, 0.25 mmol) and $MgCl_2$ (0.4 g, 4.2 mmol) in water (50 cm^3) was refluxed for 12 h, and the resulting pale yellow solution was evaporated to dryness *in vacuo*. The pale yellow solid mixture obtained was washed several times with hot acetone to dissolve the yellow $[Et_3NH]_2[Mo_6O_{19}]$ by-product (0.04 g). The remaining solid (a mixture of **3** and unreacted $MgCl_2$) was dissolved in the minimum volume of hot water, and on standing colourless crystals of **3** deposited. The crystals were filtered off, washed with a small volume of cold water and then dried *in vacuo*; yield 0.24 g (61%). Found: C, 9.9; H, 3.3; N, 2.2; Mg, 1.7. Calc: C, 9.3; H, 3.1; N, 1.8; Mg, 1.6%. IR: 3400, 3060, 3000, 1645, 1470, 1400, 1030, 955, 915, 840, 700, 655, 520, 400, 360 cm^{-1}.

$[Et_3NH]_3[(H_3O)Mo_8O_{26}]\cdot 2H_2O$ (4)

A pale blue solution of **1** (0.4 g, 0.25 mmol) and $CaCl_2$ (0.4 g, 3.6 mmol) in water (50 cm^3) was refluxed for 4.5 h, and the resulting pale yellow solution was evaporated to dryness *in vacuo*. The pale yellow solid mixture obtained was washed several times with hot acetone to dissolve the yellow $[Et_3NH]_2[Mo_6O_{19}]$ by-product (0.07 g). The remaining solid (a mixture of **4** and unreacted $CaCl_2$) was dissolved in the minimum volume of hot water, and on standing colourless crystals of **4** formed. The crystals were filtered off, washed with a small volume of cold water and then dried *in vacuo*; yield 0.24 g (62%). Found: C, 13.5; H, 3.9; N, 2.3. Calc: C, 14.0; H, 3.6; N, 2.7%. IR: 3400, 3090, 3000, 1635, 1460, 1400, 1025, 955, 915, 840, 715, 655, 520, 400, 360 cm^{-1}.

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