



SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE TRIETHYLAMMONIUM MAGNESIUM β -OCTAMOLYBDATE(VI) SALT $[\text{Et}_3\text{NH}]_2[\text{Mg}(\text{H}_2\text{O})_6\text{Mo}_8\text{O}_{26}] \cdot 2\text{H}_2\text{O}$

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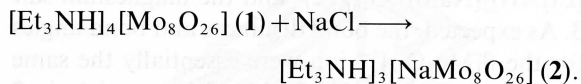
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(Received 21 December 1994; accepted 6 April 1995)

Abstract— $[\text{Et}_3\text{NH}]_4[\text{Mo}_8\text{O}_{26}]$ reacted with MgCl_2 and CaCl_2 giving the triethylammonium magnesium β -octamolybdate(VI) salt $[\text{Et}_3\text{NH}]_2[\text{Mg}(\text{H}_2\text{O})_6\text{Mo}_8\text{O}_{26}] \cdot 2\text{H}_2\text{O}$ (**3**) and the triethylammonium hydronium β -octamolybdate(VI) salt $[\text{Et}_3\text{NH}]_3[(\text{H}_3\text{O})\text{Mo}_8\text{O}_{26}] \cdot 2\text{H}_2\text{O}$ (**4**), respectively. A small amount of $[\text{Et}_3\text{NH}]_2[\text{Mo}_6\text{O}_{19}]$ was formed as a by-product. The salts **3** and **4** were characterized by X-ray crystallography. The $[\text{Mg}(\text{H}_2\text{O})_6\text{Mo}_8\text{O}_{26}]^{2-}$ moiety in **3** is polymeric, with each octahedral $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ ion sandwiched between two $\beta[\text{Mo}_8\text{O}_{26}]^{4-}$ ions, being hydrogen bonded to three terminal $\text{Mo}=\text{O}$ oxygen atoms on one face of each $\beta[\text{Mo}_8\text{O}_{26}]^{4-}$ 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 $\text{M}_x\text{O}_y^{n-}$ 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 $\text{M}-\text{O}-\text{M}-\text{O}-\text{M}$ and $\text{M}-\text{O}-\text{M}-\text{H}_2\text{O}-\text{M}-\text{O}-\text{M}$ bridges. Recently,² we reported the synthesis of the triethylammonium

β -octamolybdate(VI) salt $[\text{Et}_3\text{NH}]_4[\text{Mo}_8\text{O}_{26}]$ (**1**), and described its reaction with sodium chloride in aqueous solution to give the triethylammonium sodium salt $[\text{Et}_3\text{NH}]_3[\text{NaMo}_8\text{O}_{26}]$ (**2**):



The X-ray crystal structure of **2** showed it to be polymeric, with each Na^+ ion sandwiched between two $\beta[\text{Mo}_8\text{O}_{26}]^{4-}$ ions. Four oxygen atoms on one face of each $\beta[\text{Mo}_8\text{O}_{26}]^{4-}$ 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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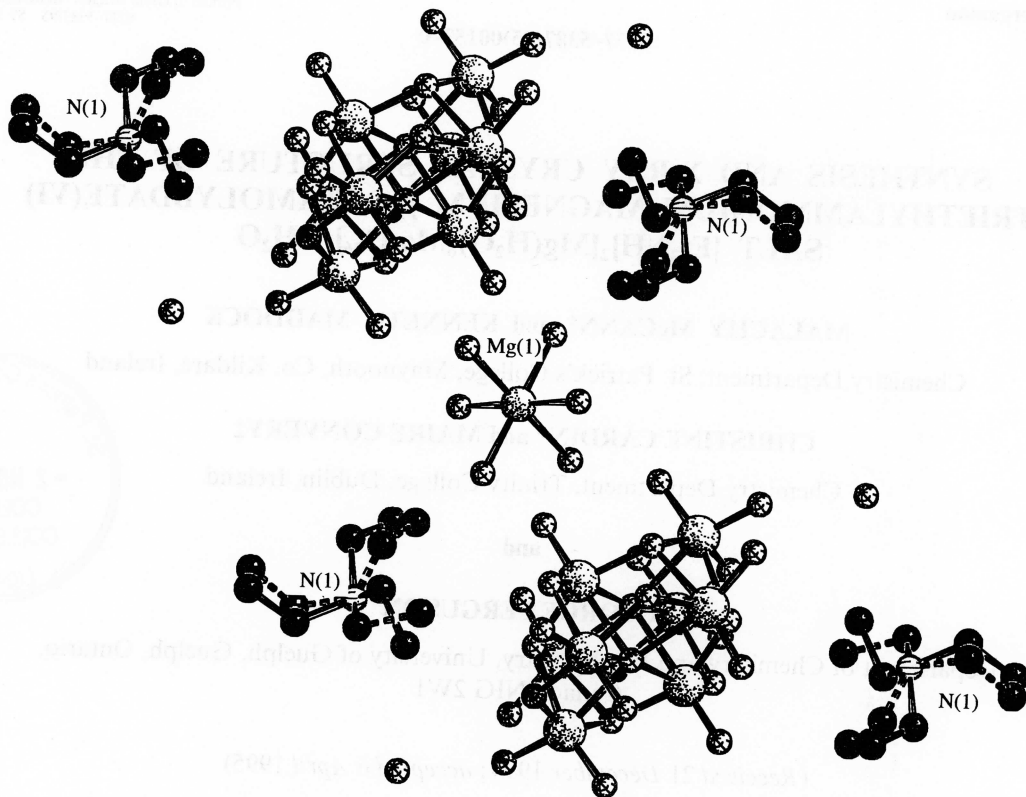


Fig. 1. The overall packing in the lattice of $[\text{Et}_3\text{NH}]_2[\text{Mg}(\text{H}_2\text{O})_6\text{Mo}_8\text{O}_{26}] \cdot 2\text{H}_2\text{O}$ (**3**).

RESULTS AND DISCUSSION

$[\text{Et}_3\text{NH}]_4[\text{Mo}_8\text{O}_{26}]$ (**1**) reacted with an excess of magnesium chloride to produce the colourless triethylammonium magnesium β -octamolybdate(VI) salt $[\text{Et}_3\text{NH}]_2[\text{Mg}(\text{H}_2\text{O})_6\text{Mo}_8\text{O}_{26}] \cdot 2\text{H}_2\text{O}$ (**3**) in good yield. A small quantity of the yellow triethylammonium hexamolybdate(VI) salt $[\text{Et}_3\text{NH}]_2[\text{Mo}_6\text{O}_{19}]^2$ 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 $[\text{Et}_3\text{NH}]_3[\text{NaMo}_8\text{O}_{26}]$ (**2**)² and the magnesium salt **3**. As expected, the bond distances and bond angles for the $\beta[\text{Mo}_8\text{O}_{26}]^{4-}$ ion were essentially the same in **2** and **3**. The $[\text{Mg}(\text{H}_2\text{O})_6\text{Mo}_8\text{O}_{26}]^{2-}$ moiety in **3** is polymeric, with each octahedral $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ ion sandwiched between two $\beta[\text{Mo}_8\text{O}_{26}]^{4-}$ ions, being hydrogen bonded to three terminal $\text{Mo}=\text{O}$ oxygen atoms on one face of each $\beta[\text{Mo}_8\text{O}_{26}]^{4-}$ 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 $[\text{Et}_3\text{NH}]_3[(\text{H}_3\text{O})\text{Mo}_8\text{O}_{26}] \cdot 2\text{H}_2\text{O}$ (**4**). Again, a small amount of $[\text{Et}_3\text{NH}]_2[\text{Mo}_6\text{O}_{19}]$ 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 $[(\text{H}_3\text{O})\text{Mo}_8\text{O}_{26}]^{3-}$ moiety. The hydronium ion H_3O^+ is sandwiched between two $\beta[\text{Mo}_8\text{O}_{26}]^{4-}$ anions and its oxygen atom makes eight contacts to four terminal $\text{Mo}=\text{O}$ oxygen atoms of each of the two anions. The hydrogen atoms of the hydronium ion were located from a difference map. Of the eight $\text{O} \cdots \text{O}$ contacts, one involves a simple $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond and four are associated with bifurcated $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. Crystallographic inversion symmetry transformations then give rise to a polymeric chain structure. The hydrogens of the two water molecules were located unequivocally and they take part in

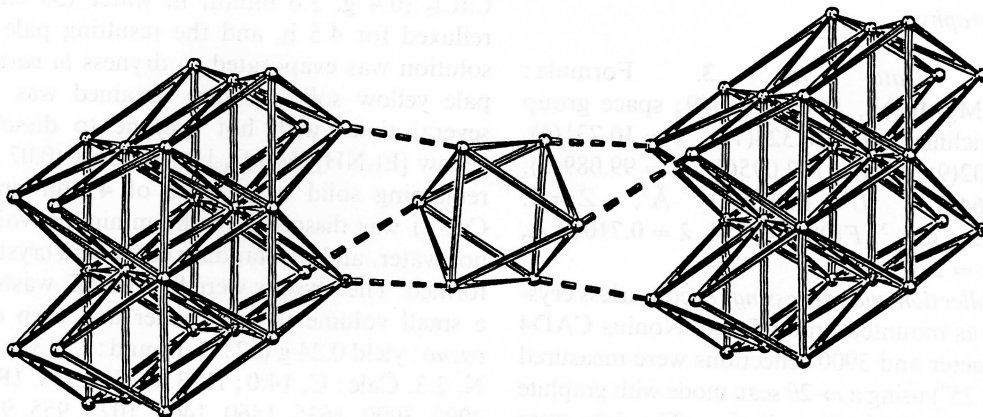
* X-ray crystallographic data associated with the present structure determination of **4** has been submitted as supplementary material with this paper.

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)		

^aSymmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x+1, -y, -z+1$.

^bSymmetry transformations used to generate equivalent atoms: #2 $-x+1, -y, -z+1$.


 Fig. 2. Hydrogen bonding between $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and $\beta[\text{Mo}_8\text{O}_{26}]^{4-}$ 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 cm² mol⁻¹, respectively,² the values obtained for **3** ($\Lambda_M = 421$ S cm² mol⁻¹) and **4** ($\Lambda_M = 512$ S cm² 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 attributable 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 Mg²⁺ ions produces the magnesium β -octamolybdate(VI) salt **3**, whilst Ca²⁺ 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 [Et₃NH]₂[Mo₂O₇] from water.⁴

EXPERIMENTAL

Chemicals were reagent grade and were used without further purification. [Et₃NH]₄[Mo₈O₂₆] (**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.

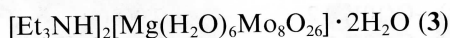
Crystallography

Crystal Data for 3. Formula: C₁₂H₄₈O₃₄MgMo₈N₂, $M = 1556.349$; space group $P-1$, triclinic, $a = 10.324(1)$, $b = 10.731(1)$, $c = 11.0302(9)$ Å, $\alpha = 107.095(5)$, $\beta = 99.089(5)$, $\gamma = 110.164(5)^\circ$, $U = 1049.6(2)$ Å³, $Z = 1$, $D_c = 2.472$ 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 ($1^\circ < \theta < 25^\circ$) using a ω - 2θ scan mode with graphite monochromated Mo-K α radiation. The data were merged to give 3686 unique reflections (R_{merge} of

0.0249), of which 3471 had $|F_{\text{obs}}| > 4\sigma|F_{\text{obs}}|$ 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).



A pale blue solution of [Et₃NH]₄[Mo₈O₂₆] **1** (0.4 g, 0.25 mmol) and MgCl₂ (0.4 g, 4.2 mmol) in water (50 cm³) 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 [Et₃NH]₂[Mo₆O₁₉] by-product (0.04 g). The remaining solid (a mixture of **3** and unreacted MgCl₂) 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.



A pale blue solution of **1** (0.4 g, 0.25 mmol) and CaCl₂ (0.4 g, 3.6 mmol) in water (50 cm³) 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 [Et₃NH]₂[Mo₆O₁₉] by-product (0.07 g). The remaining solid (a mixture of **4** and unreacted CaCl₂) 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.

Acknowledgement—G. F. thanks the NSERC (Canada) for Grants in Aid of Research.

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