

only one geometric situation (and its mirror image) compared to the continua of situations exhibited by the skew-lines systems.

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are indebted to this working party for help in various ways; in particular, we thank K. Yamasaki for suggesting the symbols Δ and Λ (cf. Figure 4). The material has also been briefly presented to the Commission itself at its 1980 annual meeting; the Commission decided that it would not attempt to use it to make any new recommendations regarding chirality descriptors at that time but suggested that we meanwhile publish the basic ideas for assessment by the community. T.D. acknowledges support from the Danish Natural Science Research Council (Grant No. 11-0608).

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Structure and Bonding of Melaminium β -Octamolybdate

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Only a few of the known organoammonium isopolymolybdates have been subjected to an X-ray crystal structure analysis. The only organoammonium or amine β -octamolybdate to have its crystal structure determined is 3-ethylpyridinium β -octamolybdate.¹ The other structure determinations of β -Mo₈O₂₆⁴⁻ have been made on the hydrated ammonium β -octamolybdate.²⁻⁵ The structure of melaminium β -octamolybdate reported here is the first octamolybdate structure containing a multifunctional complex cation. It also represents the first melaminium isopolymolybdate to be reported in the open literature. Melaminium β -octamolybdate crystallizes in the triclinic system with space group $P\bar{1}$ and $Z = 1$ ($R = 0.028$). The unit cell dimensions are $a = 10.286 \text{ \AA}$, $b = 10.706 \text{ \AA}$, $c = 10.209 \text{ \AA}$, $\alpha = 115.75^\circ$, $\beta = 85.58^\circ$, and $\gamma = 93.11^\circ$. The β -Mo₈O₂₆⁴⁻ anions in the melaminium, pyridinium,¹ and ammonium⁴ molybdates, while similar, show significant differences in several bond lengths and angles. These differences appear to be related to major differences in the cation-molybdate interactions. This structure, the first reported for the melaminium cation, contains ring-protonated melamine rings, similar to the ring-protonated cyclotriphosphazanium rings in a cyclophosphazanium hexamolybdate.⁶ This confirms the prediction from an early UV spectroscopic study⁷ that the endocyclic ring nitrogen atoms in melamine are more basic than the exocyclic nitrogen atoms. The distinguishing feature of the melaminium β -octamolybdate structure is its extensive hydrogen bonding. All 12 nitrogens of the two non-symmetry-related melaminium rings are positioned to be able to form hydrogen bonds with either molybdate oxygen atoms or nitrogen atoms on adjacent rings. The closest approach distances associated with 11 of these potential hydrogen bonds vary from 2.73 to 3.12 \AA . The proposed strong hydrogen-bonding interactions appear to stabilize the structure and explain its high thermal stability.

Introduction

Melaminium octamolybdate, (Hmel)₄Mo₈O₂₆, is the first amine isopolymolybdate based on a multifunctional cation to have its crystal structure determined. Because each melaminium cation contains six nitrogen atoms, it seemed likely that the crystalline structure will be characterized by very extensive hydrogen bonding between melaminium nitrogen atoms and molybdate oxygen atoms, as well as between adjacent melaminium cations. In fact, hydrogen-bond formation has been shown to exist in the two octamolybdates based on monofunctional cations (ammonium⁴ and 3-ethylpyridinium¹) with known structures.

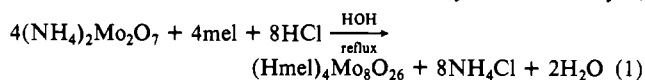
Besides studying the hydrogen-bonding interactions between the melaminium cations and the molybdate anions, this structure determination was made to unambiguously identify the structure of the octamolybdate anion. For example, the IR spectrum of (Hmel)₄Mo₈O₂₆⁸ in the Mo-O absorption regions is significantly different from the published IR spectra of known molybdates containing either the β - or α -Mo₈O₂₆⁴⁻ anions.

Another important goal of this structural study was to determine the structure of the melaminium cations. No crystal structures of melaminium salts are published. Specifically, the identification of the protonation site of the melaminium cation should unambiguously determine whether the ring nitrogen atoms are more basic than the exocyclic nitrogen atoms.

(Hmel)₄Mo₈O₂₆ was first isolated from an aqueous solution study of the formation of melaminium isopolymolybdates.⁸ It is a white crystalline solid with exceptional thermal and chemical stabilities compared to the other known melaminium isopolymolybdates. (Hmel)₄Mo₈O₂₆ is insoluble in all common polar and nonpolar solvents. It will dissolve, with decomposition, in cold caustic soda and in a hot mixture of sulfuric and nitric acids. It is stable in air up to $\sim 260^\circ\text{C}$. Above 260°C it slowly discolors and evolves ammonia.

Experimental Section

Synthesis of (Hmel)₄Mo₈O₂₆. Melaminium β -octamolybdate is prepared by the reaction of either ammonium dimolybdate or ammonium paramolybdate and melamine in aqueous HCl solution as described in reaction 1.⁸ It was characterized by elemental analysis,



IR spectroscopy, and powder XRD.⁸ The subsequent X-ray structure determination confirmed it to be formulated as (C₃H₆N₇)₄ β -Mo₈O₂₆ or (Hmel)₄ β -Mo₈O₂₆, where Hmel represents the melaminium(1+) cation. The (Hmel)₄Mo₈O₂₆ is insoluble in water and organic solvents.

- (1) Roman, P.; Jaud, J.; Galy, J. Z. *Kristallogr.* **1981**, *154*, 59.
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- (5) Weakley, T. J. R. *Polyhedron* **1982**, *1*, 17.
- (6) Allcock, H. R.; Bissell, E. C.; Shaw, E. T. *Inorg. Chem.* **1973**, *12*, 2963.
- (7) Hirt, R. C.; Schmitt, R. G. *Spectrochim. Acta* **1958**, *12*, 127.
- (8) Kroenke, W. J. "Proceedings of the Climax Fourth International Conference on the Chemistry and Uses of Molybdenum"; Barry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum Co.; Ann Arbor, MI, 1982; pp 102-106.

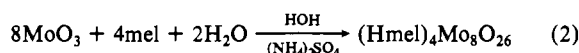
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Table I. Crystal Data and Final Refinements for $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$

mol formula	$\text{C}_{12}\text{H}_{28}\text{N}_{24}\text{Mo}_8\text{O}_{26}$	molecules/cell	4
color	colorless	cell vol, Å^3	1009.3 (4)
cryst dimens, mm	$0.10 \times 0.16 \times 0.44$	density, g/cm^3	2.784
cryst class	triclinic	wavelength, Å	0.71069
space group	$P\bar{1}$	mol wt	1692.02
cell dimens		linear abs coeff	24.8
a , Å	10.286 (2)	reflens with	2698
b , Å	10.706 (3)	$F > 3\sigma(F)$	
c , Å	10.209 (2)	final residuals	
α , deg	115.75 (2)	R	0.028
β , deg	85.58 (2)	R_w	0.034
γ , deg	93.11 (2)		

Single crystals of $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$ suitable for a single-crystal XRD study were prepared by reacting a pressed pellet of MoO_3 with an unstirred aqueous solution of melamine and ammonium sulfate maintained at $\sim 90^\circ\text{C}$. Large, well-formed crystals of $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$ grew from the surface of the MoO_3 pellet. The synthesis is represented by reaction 2.



X-ray Structural Studies. A columnar crystal with a diamond cross section (acute angle $\sim 37^\circ$) was selected for the data collection (see Table I). This transparent crystal showed uniform extinction when viewed through a polarizing microscope. The X-ray data were obtained with a Syntex $P2_1$ automatic four-circle diffractometer. Standard Syntex programs for crystal centering and indexing were used with graphite crystal monochromatic $\text{MoK}\alpha$ radiation. Lattice parameters (25°C) were calculated from the angular settings of 15 well-centered reflections. They indicated a triclinic cell. The data for final analysis were collected with $5 \leq 2\theta \leq 50^\circ$ by using the θ - 2θ scan technique with variable scan rates from $2.0^\circ/\text{min}$ to $29.5^\circ/\text{min}$. The scan count was corrected for background, and standard reflections were monitored every 50 reflections throughout the data collection process. The usual Lorentz-polarization and decay factor corrections were made, but the data were not corrected for absorbance. The collected data set was consistent with $P\bar{1}$ space group.

Solution and Refinement of the Structure. Programs used in the solution and refinement of the structure have been previously described.⁹ The positions of the eight molybdenum atoms were found from a full-cell three-dimensional Patterson synthesis by identifying the vectors that describe the parallelepiped formed by the molybdenums. Subsequent refinement and Fourier map generation readily revealed all of the non-hydrogen atoms. The final full-matrix isotropic refinement gave $R = 0.054$ and $R_w = 0.067$ (with unit weights and 2709 data). Two cycles of full-matrix anisotropic refinement using a statistical weighting scheme were followed by a difference Fourier map that clearly revealed the positions of all the hydrogen atoms. Because not all of the hydrogen positions would refine, a final anisotropic refinement was made by using the hydrogen positions from the difference Fourier and permitting only the carbon and nitrogen atoms positions to vary. The final residuals are $R = 0.028$ and $R_w = 0.034$. Table I summarizes the crystal data and final refinement of the structure. Tables II-IV summarize the atomic positions, bond distances, and angles. Figure 1 is an ORTEP drawing of the $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ anion while Figure 2 is a PLUTO¹⁰ stereoview that illustrates the packing arrangement of the melaminium cations around the $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ anion. Anisotropic thermal parameters and structure factor tables are available as supplementary material. The supplementary material also contains a labeled PLUTO drawing of the melaminium cation and an ORTEP stereoview of the $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ anion.

Results and Discussion

The β -Octamolybdate Anion. The $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ anion as shown in the structural studies of $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26}^{2-5}$ and $(3\text{-Etpy})_4\text{Mo}_8\text{O}_{26}^1$ consists of very distorted molybdenum-oxygen octahedra linked together by bridging oxygen atoms. This distortion is emphasized in the PLUTO drawings of the four

Table II. Atom Coordinates

atom	x	y	z
Mo ₁	0.58091 (5)	0.63727 (6)	0.79358 (6)
Mo ₂	0.66853 (5)	0.51982 (6)	0.45359 (6)
Mo ₃	0.56436 (5)	0.21314 (6)	0.39619 (6)
Mo ₄	0.46901 (5)	0.33010 (6)	0.74243 (6)
O ₁	0.7320 (4)	0.5921 (4)	0.8131 (5)
O ₂	0.8169 (4)	0.4866 (4)	0.4927 (4)
O ₃	0.7165 (4)	0.1899 (4)	0.4373 (4)
O ₄	0.6220 (4)	0.2950 (4)	0.7742 (4)
O ₅	0.3632 (4)	0.2709 (4)	0.8390 (5)
O ₆	0.4711 (4)	0.5265 (4)	0.8597 (4)
O ₇	0.5577 (4)	0.7978 (4)	0.9315 (4)
O ₈	0.6278 (4)	0.6901 (4)	0.6297 (4)
O ₉	0.7018 (4)	0.6018 (4)	0.3399 (4)
O ₁₀	0.6144 (4)	0.3396 (4)	0.3042 (4)
O ₁₁	0.5278 (4)	0.0647 (4)	0.2490 (4)
O ₁₂	0.4599 (4)	0.1886 (4)	0.5450 (4)
O ₁₃	0.5489 (3)	0.4390 (4)	0.5796 (4)
C ₁	0.8408 (6)	0.3791 (6)	0.0517 (6)
C ₂	0.9270 (6)	0.2621 (6)	0.1614 (6)
C ₃	0.7675 (5)	0.1532 (6)	0.0108 (6)
C ₄	0.9556 (6)	0.8813 (6)	0.2225 (7)
C ₅	0.1247 (6)	0.9763 (6)	0.3621 (6)
C ₆	0.0405 (6)	0.7562 (6)	0.3223 (7)
N ₁	0.8324 (5)	0.4884 (5)	0.0225 (6)
N ₂	0.9230 (5)	0.3803 (5)	0.1454 (5)
N ₃	0.0155 (5)	0.2587 (5)	0.2494 (6)
N ₄	0.8508 (5)	0.1477 (5)	0.0980 (5)
N ₅	0.6842 (5)	0.0470 (5)	0.9434 (6)
N ₆	0.7620 (5)	0.2663 (5)	0.9802 (5)
N ₇	0.8654 (5)	0.8935 (5)	0.1408 (7)
N ₈	0.0407 (5)	0.9895 (5)	0.2800 (5)
N ₉	0.2164 (6)	0.0758 (6)	0.4229 (7)
N ₁₀	0.1241 (5)	0.8640 (5)	0.3920 (6)
N ₁₁	0.0449 (6)	0.6460 (6)	0.3512 (7)
N ₁₂	0.9548 (5)	0.7600 (5)	0.2336 (5)

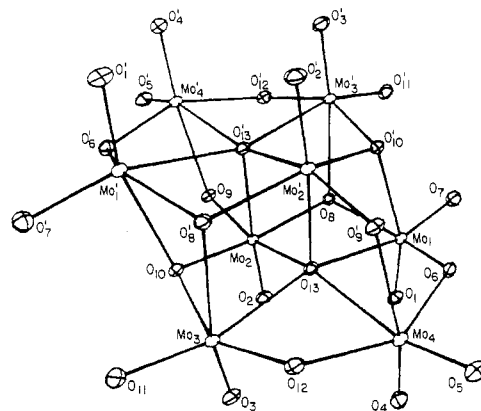


Figure 1. ORTEP drawing of the β -octamolybdate anion, $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ (50% probability thermal ellipsoids).

non-symmetry-related octahedra included in the Mo-O bond lengths and angles table (Table III). The orientations of the octahedra shown in Table III are similar to their orientations in the $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ anion shown in Figure 1. The distortion is seen in the PLUTO stereoview (Figure 2). The Mo-O bond lengths vary from 1.691 Å for one of the nonbridging Mo-O bonds to 2.483 Å for one of the bonds to the unusual 5-coordinate oxygen atom that sets near the center of each Mo_4O_{13} half of the anion, in the plane of the four molybdenum atoms.

Table V provides a comparison of the Mo-O bond lengths in $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$, $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26} \cdot 4\text{H}_2\text{O}$,⁴ and $(3\text{-Etpy})_4\text{Mo}_8\text{O}_{26}$.¹ It is obvious that there are significant differences in the bond lengths (and bond angles) in the $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ anions from these three compounds. As suggested by Klemperer et al.,¹¹ the $\text{Mo}_8\text{O}_{26}^{4-}$ cluster can be viewed,

(9) Chen, H. W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 22.

(10) PLUTO is a program for plotting molecular and crystal structures. The version used was written by S. Motherwell (Cambridge), modified by D. A. Pensak (Du Pont, May 15, 1979), and finally by R. G. Getts (BFGoodrich, April 30, 1982).

(11) Day, V. W.; Frederich, M. F.; Klemperer, W. G.; Shum, W. J. *Am. Chem. Soc.* **1977**, *99*, 952.

Table III. Molybdenum-Oxygen Bond Lengths (Å) and Angles (deg) in Melaminium β -Octamolybdate

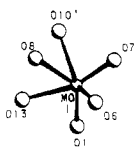
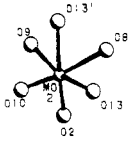
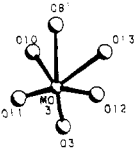
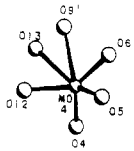
β -Mo ₈ O ₂₆ octahedra	Mo-O bond lengths			O-Mo-O bond angles ($\pm 0.2^\circ$)				
	O ₁	1.703 (5)	O ₁ -O ₆	102.0	O ₆ -O ₇	101.5	O ₇ -O ₈	99.3
	O ₁₀	2.382 (4)	O ₁ -O ₇	105.2	O ₆ -O ₁₀	82.6	O ₇ -O ₁₃	160.1
	O ₇	1.699 (3)	O ₁ -O ₈	98.2	O ₆ -O ₁₃	77.7	O ₈ -O ₁₃	73.6
	O ₈	2.005 (5)	O ₁ -O ₁₃	94.2	O ₆ -O ₈	145.9	O ₈ -O ₁₀	71.1
	O ₁₃	2.322 (3)	O ₁ -O ₁₀	163.8	O ₇ -O ₁₀	88.8	O ₁₃ -O ₁₀	71.4
	O ₆	1.889 (4)						
	O ₂	1.700 (4)	O ₂ -O ₁₃	98.7	O ₁₃ -O ₈	79.0	O ₈ -O ₉	95.5
	O ₁₃	2.380 (4)	O ₂ -O ₈	99.8	O ₁₃ -O ₁₃	75.2	O ₈ -O ₁₀	150.3
	O ₈	1.962 (3)	O ₂ -O ₉	105.2	O ₁₃ -O ₁₀	78.4	O ₉ -O ₁₀	97.3
	O ₉	1.740 (5)	O ₂ -O ₁₀	102.5	O ₁₃ -O ₉	156.1	O ₉ -O ₁₃	80.9
	O ₁₀	1.954 (3)	O ₂ -O ₁₃	173.7	O ₈ -O ₁₃	77.8	O ₁₀ -O ₁₃	77.9
	O ₁₃	2.128 (4)						
	O ₃	1.709 (5)	O ₃ -O ₁₂	100.8	O ₁₂ -O ₁₃	77.4	O ₁₃ -O ₁₀	73.1
	O ₈	2.365 (4)	O ₃ -O ₁₃	94.2	O ₁₂ -O ₈	82.8	O ₁₃ -O ₁₁	160.5
	O ₁₃	2.332 (3)	O ₃ -O ₁₀	98.1	O ₁₂ -O ₁₁	100.8	O ₁₀ -O ₁₁	101.3
	O ₁₀	1.983 (5)	O ₃ -O ₁₁	105.2	O ₁₂ -O ₁₀	145.8	O ₁₀ -O ₈	71.9
	O ₁₁	1.695 (4)	O ₃ -O ₈	164.2	O ₁₃ -O ₈	71.6	O ₁₁ -O ₈	88.9
	O ₁₂	1.897 (5)						
	O ₄	1.724 (5)	O ₄ -O ₅	105.5	O ₅ -O ₆	102.9	O ₆ -O ₁₃	73.3
	O ₉	2.286 (4)	O ₄ -O ₆	98.7	O ₅ -O ₉	90.1	O ₆ -O ₁₂	143.5
	O ₆	1.915 (4)	O ₄ -O ₁₃	95.1	O ₅ -O ₁₂	103.5	O ₁₃ -O ₁₂	73.1
	O ₁₃	2.483 (5)	O ₄ -O ₁₂	98.1	O ₅ -O ₁₃	159.4	O ₁₃ -O ₉	69.3
	O ₁₂	1.930 (3)	O ₄ -O ₉	164.4	O ₆ -O ₉	77.9	O ₁₂ -O ₉	77.2
	O ₅	1.691 (5)						

Table IV. Comparison of Bond Lengths and Angles in the Two Crystallographically Independent Melaminium Cations

melaminium cation 1		melaminium cation 2	
Bond Lengths, Å			
C ₁ -N ₁	1.335 (10)	C ₆ -N ₁₁	1.339 (11)
C ₁ -N ₂	1.320 (9)	C ₆ -N ₁₂	1.326 (9)
C ₁ -N ₆	1.367 (7)	C ₆ -N ₁₀	1.360 (7)
C ₂ -N ₂	1.347 (9)	C ₄ -N ₁₂	1.352 (9)
C ₂ -N ₃	1.340 (9)	C ₄ -N ₇	1.341 (10)
C ₂ -N ₄	1.350 (7)	C ₄ -N ₈	1.353 (7)
C ₃ -N ₄	1.303 (9)	C ₅ -N ₈	1.304 (9)
C ₃ -N ₅	1.344 (7)	C ₅ -N ₉	1.347 (8)
C ₃ -N ₆	1.380 (10)	C ₅ -N ₁₀	1.363 (10)
Bond Angles, deg			
C ₁ -N ₂ -C ₂	115.7 (4)	C ₆ -N ₁₂ -C ₄	114.0 (4)
N ₂ -C ₂ -N ₄	126.4 (4)	N ₁₂ -C ₄ -N ₈	127.0 (5)
C ₂ -N ₄ -C ₃	115.6 (4)	C ₄ -N ₈ -C ₅	115.1 (4)
N ₂ -C ₃ -N ₆	122.1 (4)	N ₈ -C ₅ -N ₁₀	122.4 (5)
C ₃ -N ₆ -C ₁	118.3 (4)	C ₅ -N ₁₀ -C ₆	118.4 (4)
N ₂ -C ₁ -N ₆	121.6 (4)	N ₁₀ -C ₆ -N ₁₂	122.5 (5)
N ₁ -C ₁ -N ₆	117.5 (4)	N ₁₁ -C ₆ -N ₁₀	116.8 (5)
N ₁ -C ₁ -N ₂	121.0 (4)	N ₁₁ -C ₆ -N ₁₂	120.6 (5)
N ₃ -C ₂ -N ₂	116.5 (4)	N ₇ -C ₄ -N ₁₂	116.4 (5)
N ₃ -C ₂ -N ₄	117.1 (4)	N ₇ -C ₄ -N ₈	116.5 (5)
N ₅ -C ₃ -N ₄	121.4 (4)	N ₉ -C ₅ -N ₈	120.6 (5)
N ₅ -C ₃ -N ₆	116.5 (4)	N ₉ -C ₅ -N ₁₀	116.9 (5)

(Figures 1 and 2) as consisting of two (O²⁻)(Mo₄O₁₂) subunits by breaking bonds with lengths that exceed 2.22 Å and therefore have bond orders less than 0.2. Such a viewpoint may be helpful in understanding some of the transformations and reactivities of the β -Mo₈O₂₆⁴⁻ anion in solution.

Figures 1 and 2 also show that the β -Mo₈O₂₆⁴⁻ anion contains eight nonequivalent oxygen positions. This has been verified by Klemperer et al. from ¹⁷O-enriched NMR studies.¹¹ Unfortunately, no meaningful relationships could be found between the Mo-O bonds involving these nonequivalent oxygens in the three different β -Mo₈O₂₆⁴⁻ structures (Table V). A discussion of the distortions between the three separately determined β -Mo₈O₂₆⁴⁻ structures will be deferred to the section concerned with hydrogen bonding.

Melaminium Cations. A comparison of the bond lengths and angles of the two crystallographically independent me-

Table V. Comparison of Bond Lengths (Å) in Three β -Octamolybdates

bonds ^a	(Hmel) ₄ Mo ₈ O ₂₆	(NH ₄) ₄ Mo ₈ O ₂₆ ^b	(3-Etpy) ₄ Mo ₈ O ₂₆ ^c
Mo ₁ -O ₁	1.703 (5)	1.712 (5)	1.688 (3)
Mo ₁ -O ₁₀	2.382 (4)	2.327 (4)	2.348 (3)
Mo ₁ -O ₇	1.699 (3)	1.707 (5)	1.706 (4)
Mo ₁ -O ₈	2.005 (5)	1.995 (4)	1.981 (3)
Mo ₁ -O ₁₃	2.322 (3)	2.310 (4)	2.313 (4)
Mo ₁ -O ₆	1.889 (4)	1.901 (4)	1.884 (3)
Mo ₂ -O ₂	1.700 (4)	1.702 (4)	1.683 (3)
Mo ₂ -O ₁₃	2.380 (4)	2.346 (3)	2.409 (3)
Mo ₂ -O ₈	1.962 (3)	1.954 (4)	1.945 (4)
Mo ₂ -O ₉	1.740 (5)	1.751 (4)	1.746 (3)
Mo ₂ -O ₁₀	1.954 (3)	1.937 (4)	1.949 (3)
Mo ₂ -O ₁₃	2.128 (4)	2.182 (4)	2.147 (3)
Mo ₃ -O ₃	1.709 (5)	1.717 (4)	1.698 (4)
Mo ₃ -O ₈	2.365 (4)	2.334 (4)	2.337 (4)
Mo ₃ -O ₁₃	2.332 (3)	2.299 (4)	2.298 (4)
Mo ₃ -O ₁₀	1.983 (5)	2.011 (4)	1.984 (4)
Mo ₃ -O ₁₁	1.695 (4)	1.709 (5)	1.710 (4)
Mo ₃ -O ₁₂	1.897 (5)	1.892 (5)	1.886 (4)
Mo ₄ -O ₄	1.724 (5)	1.689 (6)	1.707 (3)
Mo ₄ -O ₉	2.286 (4)	2.323 (4)	2.286 (3)
Mo ₄ -O ₆	1.915 (4)	1.924 (4)	1.916 (4)
Mo ₄ -O ₁₃	2.483 (5)	2.482 (4)	2.444 (4)
Mo ₄ -O ₁₂	1.930 (3)	1.929 (5)	1.923 (4)
Mo ₄ -O ₅	1.691 (5)	1.692 (6)	1.688 (4)

^a Atoms labeled as in (Hmel)₄Mo₈O₂₆. ^b Reference 4. ^c Reference 1.

laminium cations is shown in Table IV. The PLUTO stereoview (Figure 2) illustrates their planarity. The planarity was confirmed by least-squares plane calculations. Although the two rings are very similar, there is a statistically significant difference between the C₁-N₂-C₂ (ring 1) and C₆-N₁₂-C₄ (ring 2) endocyclic bond angles. This difference, first observed in the preliminary full-matrix isotropic refinement, persisted through the final anisotropic refinement. There also is a large difference (0.017 Å) between the C₃-N₆ (ring 1) and C₅-N₁₀ (ring 2) bond lengths. However, this difference is not statistically significant.

The data in Table IV show that the exocyclic C-N bonds are neither consistently elongated nor shortened compared to

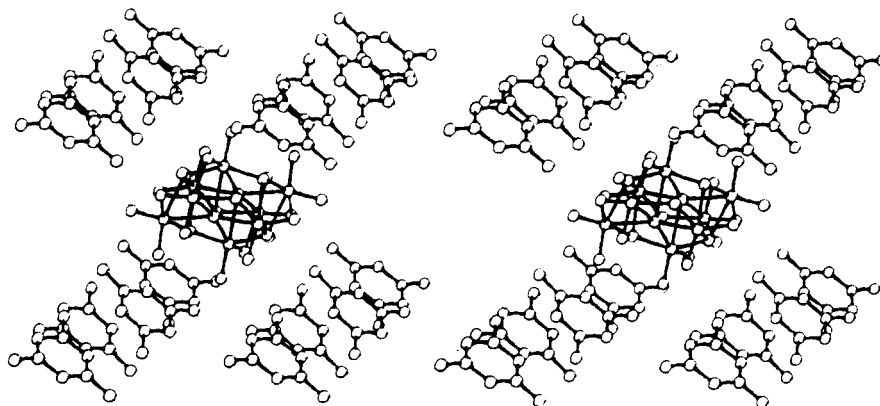


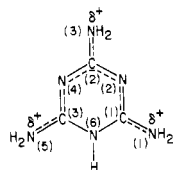
Figure 2. PLUTO stereoview of $(\text{Hmel})_4\text{-}\beta\text{-Mo}_8\text{O}_{26}$ parallel to the c axis.

Table VI. Potential Hydrogen Bonding: Suitably Oriented Intermolecular Closest Approach Distances

melaminium cation 1			melaminium cation 2		
bonds	length, Å	atom type	bonds	length, Å	atom type
$\text{N}_2\text{-N}_{11}$	2.984 (7)	exocyclic N	$\text{N}_{12}\text{-N}_1$	3.043 (6)	exocyclic N
$\text{N}_4\text{-N}_7$	2.951 (9)	exocyclic N	$\text{N}_8\text{-N}_3$	3.057 (9)	exocyclic N
$\text{N}_6\text{-O}_4$	2.769 (8)	nonbridged O	$\text{N}_{10}\text{-O}_3'$	2.733 (8)	nonbridged O
$\text{N}_3\text{-O}_2'$	3.284 (6) ^a	nonbridged O	$\text{N}_7\text{-O}_5'$	2.910 (7)	nonbridged O
$\text{N}_3\text{-N}_8$	3.057 (9)	endocyclic N	$\text{N}_7\text{-N}_4$	2.951 (9)	endocyclic N
$\text{N}_5\text{-O}_{11}'$	2.895 (7)	nonbridged O	$\text{N}_9\text{-O}_8'$	3.121 (8)	dbl-bridged O
$\text{N}_5\text{-O}_7$	2.862 (7)	nonbridged O	$\text{N}_9\text{-O}_{12}$	2.852 (7)	bridged O
$\text{N}_1\text{-O}_1$	3.066 (9)	nonbridged O	$\text{N}_{11}\text{-O}_2$	3.018 (9)	nonbridged O
$\text{N}_1\text{-N}_{12}$	3.043 (6)	endocyclic N	$\text{N}_{11}\text{-N}_2$	2.984 (7)	endocyclic N

^a Too long to permit hydrogen bonding.

the endocyclic (ring) C–N bonds. It is important to note that the longest C–N bonds in both melaminium cations are adjacent to corresponding nitrogen atoms, N_6 in ring 1 and N_{10} in ring 2. This is significant, because, as will be shown in the next section, these are the protonation sites of the melamine rings that convert them into melaminium cations. The final difference Fourier clearly shows hydrogen atoms associated with these two ring nitrogen atoms. Thus, we have confirmed the prediction of an earlier spectroscopic study of melaminium cations,⁷ namely, that the endocyclic ring nitrogen atoms are more basic than the exocyclic ones. This relates to the results of a structural determination of a cyclophosphazene hexamolybdate by Allcock et al.⁶, which showed that one of the ring nitrogen atoms was protonated. The best representation of a melaminium cation in this structure is



The atoms are numbered to correspond to melaminium cation 1 (Table IV).

Compared to the structure of the melaminium cations in $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$, melamine has a very regular undistorted D_{3h} structure. Hughes has shown that all 9 of the C–N bonds are essentially equivalent (1.33–1.36 Å), the alternating endocyclic angles are $116 \pm 1^\circ$ and $124 \pm 1^\circ$, and the exocyclic angles are very comparable ($117\text{--}120^\circ$).¹² As in the melaminium cations, melamine is a planar molecule with no displacements of individual atoms from the calculated average plane outside experimental error.¹²

Hydrogen Bonding. The stereoview of the packing arrangement viewed down the c axis (Figure 2) shows how the melaminium cations are clustered together between the

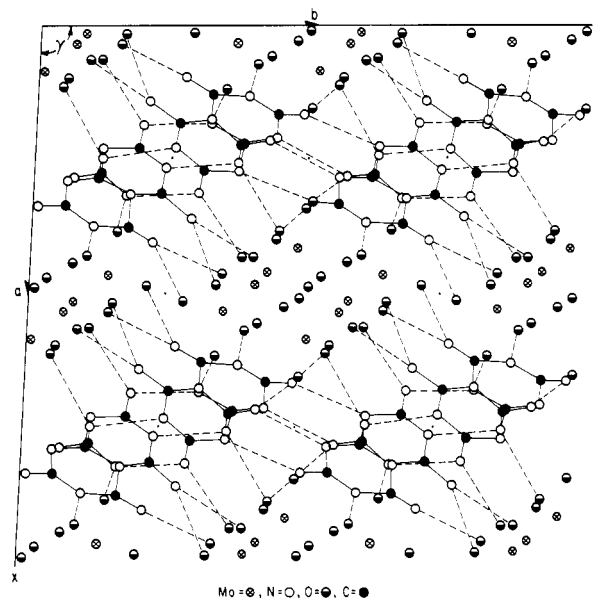


Figure 3. Projection of $(\text{Hmel})_4\text{-}\beta\text{-Mo}_8\text{O}_{26}$ parallel to the c axis and showing the hydrogen-bonding interactions.

molybdate anions. The closest approach distances that are suitably oriented to permit hydrogen bonding between melaminium nitrogen atoms on adjacent molecules and melaminium nitrogen atoms and molybdate atoms are shown as dashed lines on the c -axis projection (Figure 3). A comparison of these hydrogen-bonding closest approach distances for the two crystallographically independent melaminium cations is given in Table VI. The data in Table VI provide convincing evidence that the two crystallographically independent melaminium cations are not equivalent. For example, the closest approach distance between N_3 (ring 1) and the nonbridging O_2' is 3.284 Å, a distance too long to permit any significant hydrogen-bond formation. In contrast, the corresponding ring 2 distance, N_7 to nonbridging O_5' , is 2.910 Å. Furthermore,

(12) Hughes, E. W. *J. Am. Chem. Soc.* **1941**, *63*, 1737.

two of the short ring 1 distances ($N_5-O_{11}' = 2.895 \text{ \AA}$ and $N_5-O_7 = 2.862 \text{ \AA}$) are between the same exocyclic nitrogen atom and two nonbridging oxygen atoms. The corresponding distances of ring 2 ($N_9-O_8' = 3.121 \text{ \AA}$ and $N_9-O_{12} = 2.852 \text{ \AA}$) involve one double bridging oxygen (O_8') atom and one single bridging oxygen (O_{12}) atom. In general, the corresponding closest approach distances for hydrogen bonding from the two melaminium cations are significantly different.

The melaminium cations are extensively hydrogen bonded to the molybdate anions and to adjacent cations. This extensive hydrogen bonding acts in concert with the crystalline lattice forces to account for both the unique configuration of $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ and the nonequivalency of the crystallographically independent melaminium cations as found in $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$. It also provides an explanation for the high thermal stability (260 °C) of this species.

Hydrogen bonding also plays a role in determining the structure of $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ in $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26}\cdot 4\text{H}_2\text{O}^4$ and $(3\text{-Etpy})_4\text{Mo}_8\text{O}_{26}$.¹ In the case of the nonhydrated $(3\text{-Etpy})_4\text{Mo}_8\text{O}_{26}$, the structure is characterized by infinite chains of polyanions bridged by one of the two crystallographically independent 3-ethylpyridinium cations through hydrogen bonds

with the molybdate anions.¹ While the other cation does not contribute directly to the chain formation, it apparently does hydrogen bond to a molybdate oxygen atom.¹

The ammonium ions and the water of crystallization in $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26}\cdot 4\text{H}_2\text{O}$ are positioned to extensively hydrogen bond with each other as well as with molybdate oxygen atoms.⁴ In light of this extensive hydrogen bonding in all three of the $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ structures discussed, we believe it likely that hydrogen bonding plays an important role in determining the solid-state structures of most amine molybdates and organoammonium molybdates and influences their chemical and physical properties.

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Supplementary Material Available: Tables of anisotropic parameters and observed and calculated structure factor amplitudes and figures of the melaminium cation, the β -octamolybdate anion, and the cluster melaminium cations (13 pages). Ordering information is given on any current masthead page.

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X-ray Crystallographic, Spectral, and Molecular Orbital Studies on Molybdenum(II) Acetylene Complexes, $\text{Mo}(t\text{-BuS})_2(t\text{-BuNC})_2(\text{RC}\equiv\text{CR}')$ ($\text{R}, \text{R}' = \text{H}$ or Ph)

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Facile substitution reactions of a bis(thiolato) Mo(II) complex, $\text{cis-Mo}(t\text{-BuS})_2(t\text{-BuNC})_4$, with acetylenes ($\text{HC}\equiv\text{CH}$, $\text{PhC}\equiv\text{CH}$, and $\text{PhC}\equiv\text{CPh}$) occur to give acetylene compounds of general formula $\text{Mo}(t\text{-BuS})_2(t\text{-BuNC})_2(\text{RC}\equiv\text{CR}')$ (**1**, $\text{R} = \text{R}' = \text{H}$; **2**, $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$; **3**, $\text{R} = \text{R}' = \text{Ph}$) in substantial yields (>60%). Compound **1** crystallizes in a monoclinic cell of dimensions $a = 18.672$ (9) \AA , $b = 10.105$ (3) \AA , $c = 17.322$ (8) \AA , and $\beta = 112.58$ (7)° with $Z = 4$ in space group $P2_1/a$. Refinement by block-diagonal least-squares methods on F , employing 1685 diffractometer data, converged at $R = 0.059$. Compound **3** also crystallizes in a monoclinic space group, $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 16.982$ (9) \AA , $b = 17.378$ (8) \AA , $c = 12.013$ (6) \AA , and $\beta = 96.59$ (4)°. A total of 2694 unique intensity data were used for block-diagonal least-squares refinement on F , which converged at $R = 0.062$. The molecules **1** and **3** assume approximately trigonal-bipyramidal geometry with acetylene considered as a unidentate ligand. The triple bond lies almost parallel to the main molecular axis. The $\text{C}\equiv\text{C}$, mean $\text{Mo}-\text{C}\equiv$, and mean $\text{Mo}-\text{S}$ bond distances are respectively 1.28 (2), 2.05 (2), and 2.325 (3) \AA for **1** and 1.28 (2), 2.054 (7), and 2.338 (2) \AA for **3**. The same molecular geometry can be inferred for **2** on the basis of the spectroscopic data, inter alia the ^1H NMR spectrum. The ^1H NMR spectra of **1-3** also indicated their stereochemical rigidity in solution up to about 100 °C. Extended Hückel molecular orbital calculations were performed on the simplified molecule $\text{Mo}(\text{HS})_2(\text{HNC})_2(\text{HC}\equiv\text{CH})$ in nine possible geometrical variations to find (1) the preferred orientation of the acetylene, (2) the preferred orientation of the thiolates, and (3) the site preference of the ligands, i.e. axial vs. equatorial. The most theoretically stable molecular configuration coincides with what was established by the present X-ray analysis. The nature of the metal-acetylene bonds was elucidated from the molecular geometries, and from IR and ^1H NMR spectra, and these findings were rationalized by an EHMO analysis.

Molybdenum compounds of sulfur ligands have attracted considerable interest in recent years because of their possible implications for redox enzyme chemistry.^{2,3} In particular, the coordination of alkynes, an enzymic substrate, is the subject of a number of recent papers. As a Mo(IV) acetylene complex, only $\text{MoO}(\text{dte})_2(\text{RC}\equiv\text{CR}')$ ($\text{dte} = \text{dialkyldithiocarbamate}$) is known.⁴ While several types of Mo(II) alkyne complexes

have been reported, they are confined essentially to those carrying an $\eta\text{-C}_5\text{H}_5$ (Cp) group(s), $\text{MoX}(\text{Cp})(\text{RC}\equiv\text{CR})_2$,⁵ $\text{MoX}(\text{Cp})(\text{CO})(\text{RC}\equiv\text{CR})$,^{5,6} $\text{Mo}(\text{Cp})(\text{dpe})(\text{RC}\equiv\text{CR})$ ⁷ ($\text{dpe} = \text{diphenylphosphinoethane}$), $\text{Mo}(\text{Cp})(\text{CO})(\text{RC}\equiv\text{CR})_2$,⁸

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