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Preparation and Crystal Data of Isomorphous Octamolybdates. Crystal Structure Analysis of (3-MepyH)$_2$(3-EtpyH)$_2$[Mo$_8$O$_{26}$]

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The preparation of a series of isomorphous β-octamolybdates of 3-methylpyridinium and 3-ethylpyridinium is reported along with their chemical characterization and crystal data. The compounds can be represented as $(3\text{-MepyH})_x(3\text{-EtpyH})_{4-x}[\text{Mo}_8\text{O}_{26}]$*, where* $0 < x \leqslant 4$*, their crystal structure consisting of* $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ *polyanions and* $(3\text{-MepyH})^+$ *and* $(3\text{-EtpyH})^+$ *cations linked through N–H···O bonds. The compound with* $x = 2$ *crystallizes in the monoclinic system, space group* $P2_1/n$*, with two molecules in a cell of dimensions* $a = 13.858(4)$, $b = 11.018(3)$, $c = 14.005(8)$ *Å*, $\beta = 91.35(5)°$, $V = 2138(1)$ *Å*^{3}, $D_o = 2.46$, $D_x = 2.47$ *Mg m*$^{-3}$, $\mu(\text{MoK}\alpha) = 23.07$ *cm*$^{-1}$, $R = 0.064$ *and* $wR = 0.068$ *for 5090 observed reflexions.*

Introduction

The first X-ray structure determination of ammonium octamolybdate pentahydrate was reported as early as 1950 by Lindqvist [1], and only molybdenum and oxygen atoms were located. The structure of the octamolybdate anion, $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$, consists of eight distorted edge-sharing MoO$_6$ octahedra. Further X-ray studies [2] have completed the structural information on $(\text{NH}_4)_4[\text{Mo}_8\text{O}_{26}]\cdot5\text{H}_2\text{O}$ by locating all the oxygen atoms in the polyanion, although N and water O-atoms were less sharply resolved than the anionic O-atoms. Crystal structure determination of a correlated compound, the ammonium octamolybdate tetrahydrate, $(\text{NH}_4)_4[\text{Mo}_8\text{O}_{26}]\cdot4\text{H}_2\text{O}$, has been carried out between 1972 and 1977 by different authors [3–5], with very good agreement between their results. Atovmyan and Krasochka have found Mo–O distances for the $[\text{Mo}_8\text{O}_{26}]^{4-}$ polyanion. Gatehouse and Vivier *et al.* have solved more precisely this structure and found the same results for the polyanion, and showed only slight differences in N and O atoms for the rest of the compound.

A polymeric octamolybdate anion, $[\text{Mo}_8\text{O}_{27}]^{6-}$, has been determined in $(\text{NH}_4)_6[\text{Mo}_8\text{O}_{27}]\cdot4\text{H}_2\text{O}$ [6, 7]. The structure consists of octamolybdate units which polymerize to infinite chains through one common edge and corner. The octameric units correspond in structure to that in the salts $\text{M}_2[\text{Mo}_4\text{O}_{13}]$ (M = K, Rb) crystallized from melts [8–10]. Polymeric tetramolybdate anions show differences in the way of sharing the octahedra. The units in the $\text{M}_2[\text{Mo}_4\text{O}_{13}]$ are linked by shared edges, where the units in $(\text{NH}_4)_6[\text{Mo}_8\text{O}_{27}]\cdot4\text{H}_2\text{O}$ share octahedral corners.

Fuchs and Hartl [11] have solved the second isomer of $[\text{Mo}_8\text{O}_{26}]^{4-}$ ion in $[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{Mo}_8\text{O}_{26}]$. This polyanion [12], $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$, consists of six MoO$_6$ octahedra and two MoO$_4$ tetrahedra.

A different discrete polyanion, the dihydrogenoctamolybdate, $[\text{H}_2\text{Mo}_8\text{O}_{26}]^{6-}$, has been described [13]. This isopolyanion is composed of MoO$_6$ distorted octahedra sharing edges with two hydrogen atoms bounded at two oxygen atoms.

Recently, three ethylpyridinium β-octamolybdates have been characterized [14–16], and the crystal structure of disodiumbistetramethylammonium octamolybdate dihydrate has been analyzed [17]. All of these octamolybdates contain the β-isomer. The octamolybdate anion has the same structure as that found in the ammonium salts cited previously.

There has recently been published a novel discrete polyanion in $\text{Na}_4[\text{Mo}_8\text{O}_{24}(\text{OCH}_3)_4]\cdot8\text{MeOH}$, which decomposes with the loss of formaldehyde [18]. The crystal structure consists of $[\text{Mo}_8\text{O}_{24}(\text{OCH}_3)_4]^{4-}$ anions and two crystallographically independent $[\text{Na}_2(\text{CH}_3\text{OH})_4]^{2+}$ cations. The framework of the anions is very similar to those found for a number of substituted octamolybdates [7, 13].

Crystal structures of $[(\text{CH}_3)_2\text{NH}_2]_4[\text{Mo}_8\text{O}_{26}]\cdot2\text{DMF}$ [19] and $(3\text{-MepyH})_4[\text{Mo}_8\text{O}_{26}]$ [20] will be published elsewhere.

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TABLE I. Crystal Data for Isomorphous Octamolybdates.

Compound	I [14]	II	III	IV [20]
MW	1616.16	1616.16–1560.04	1616.16–1560.04	1560.04
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	13.822(3)	13.825(3)	13.754(3)	13.652(2)
b	10.998(3)	10.993(3)	10.950(4)	10.887(1)
c	14.346(3)	13.964(4)	13.840(4)	13.759(1)
β, °	91.53(3)	91.39(4)	90.96(4)	90.87(1)
V, Å^3	2180.0(6)	2121.6(7)	2084.1(7)	2044.7(4)
Z	2	2	2	2
D_x, Mg m^{-3}	2.46	2.46–2.53	2.46–2.53	2.53
D_o	2.45	2.48	2.51	2.53
μ(MoKα), cm^{-1}	22.8	22.8–24.1	22.8–24.1	24.1
F(000)	1560	1560–1496	1560–1496	1496
R	0.02	–	–	0.03
wR	0.03	–	–	0.04

When trying to prepare crystalline 2, 3 and 4-methylpyridinium octamolybdates from aqueous solutions of 3-ethylpyridinium cations, we observed that three isostructural polymolybdates with these organic cations were formed. These compounds can be formulated as $(C_6H_8N)_x(C_7H_{10}N)_{4-x}$ $[Mo_8O_{26}]$ [21].

The aim of this paper is to describe the preparation, chemical characterization and crystal data of a family of isostructural β-octamolybdates of 3-ethylpyridinium and 3-methylpyridinium cations, as well as to report the crystal structure of one of them. Until now only four members of the series have been found. It seems that it is possible to prepare more compounds under controlled experimental conditions.

Experimental

A suspension of MoO_3 (5.0 g) and distilled water was stirred and heated, and 3-Ethylpyridine (5.0 ml) was added. After evaporating the resulting solution was cooled and filtered, and crystals of 3-ethylpyridinium octamolybdate (**I**) appeared in the solution. Washed with water, ethanol and ether, the greenish prismatic crystals were dried in air. They were found to be stable to air, light and X-ray exposure.

A solution of $(3\text{-EtpyH})_4[Mo_8O_{26}]$ (3.0 g) in water (800 ml) was heated and stirred and when dissolved, 3-methylpyridine was added in acidic media ($pH < 5$). Several concentrations of this organic base (from defect to excess) yielded, after evaporating, compounds **II**, **III** and **IV**, respectively, which can be represented as $(C_6H_8N)_x(C_7H_{10}N)_{4-x}[Mo_8O_{26}]$, where $0 < x \leqslant 4$. Crystals were similar in colour and properties to **I**.

Analyses of Compounds I–IV

Compound **I** (found, Mo 47.24, C 20.91, H 2.52, N 3.54, weight loss at 520 °C 28.90%, calculated for $(C_7H_{10}N)_4[Mo_8O_{26}]$, 47.49, 20.79, 2.47, 3.46, 28.75%).

Compound **II** (found, Mo 48.32, C 20.00, H 2.29, N 3.87, weight loss at 520 °C 27.50%).

Compound **III** (found, Mo 48.84, C 19.11, H 2.13, N 4.04, weight loss at 520 °C 26.72%).

Compound **IV** (found, Mo 49.37, C 18.69, H 2.11, N 3.63, weight loss at 520 °C 26.10%, calculated for $(C_6H_8N)_4[Mo_8O_{26}]$, 49.20, 18.48, 2.08, 3.59, 26.19%).

IR Spectra

Compounds **I**–**IV** showed very similar spectra. All the bands for **I** were present in **II**, **III** and **IV**, except for the ν(CC) vibration at 1308 cm^{-1} in compound **IV**. ν(NH) appeared between 3600 and 2600 cm^{-1} and also at 3060 cm^{-1}.

The $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion was characterized between 1000 and 300 cm^{-1} by the following bands: 945 vs, 895 vs, 850 vs, 830 vs, 745 s, 720 vs, 695 vs, 550 vs, 515 s, 455 s, 395 s and 350 s (vs = very strong, s = strong).

IR spectra could not distinguish $(3\text{-EtpyH})^+$ and $(3\text{-MepyH})^+$ cations in compounds **II** and **III**.

^1H NMR Spectra

Octamolybdates were recorded in deuterated DMSO. Compounds **II** and **III** exhibited δ signals corresponding to protons from CH_3 and C_2H_5 groups, but they did not integrate for an integer of protons. Compounds **I** and **IV** only showed δ signals for the CH_3 and C_2H_5 groups.

TG Studies

Decomposition curves of the octamolybdates were determined by a Perkin-Elmer TGS-1 thermo-

TABLE II. Atomic Parameters for $(C_6H_8N)_4(C_7H_{10}N)_4[Mo_8O_{26}]$. Thermal parameters as $U_{eq} = (1/3)\Sigma(U_{ij}a_i^*a_j^*a_ia_j\cos(a_i, a_j)) \times 10^4$ for non-H atoms, $\exp(-8\pi^2 U \sin(\theta/\lambda)^2) \times 10^3$ for H-atoms.

Atom	x/a	y/b	z/c	U_{eq}/U
Mo1	0.08553(6)	0.27509(7)	0.05936(6)	493(3)
Mo2	−0.10293(6)	0.31100(8)	−0.10119(6)	505(3)
Mo3	−0.25680(6)	0.52427(8)	−0.05461(7)	518(3)
Mo4	−0.06578(6)	0.48733(7)	0.10976(6)	465(3)
O1	0.03880(43)	0.34020(57)	−0.09412(46)	498(20)
O2	0.21178(45)	0.31697(62)	0.02003(48)	546(22)
O3	0.07648(50)	0.13085(63)	0.01826(52)	595(24)
O4	0.10399(52)	0.26007(68)	0.17805(54)	650(26)
O5	−0.08093(44)	0.51418(57)	−0.06190(45)	498(20)
O6	−0.22492(47)	0.35565(64)	−0.05502(53)	593(24)
O7	−0.10559(52)	0.15709(65)	−0.08728(55)	641(26)
O8	−0.05302(43)	0.32245(57)	0.06196(44)	483(20)
O9	−0.19134(46)	0.49680(63)	0.09612(48)	555(22)
O10	−0.04536(51)	0.46687(66)	0.22769(51)	617(25)
O11	−0.11875(53)	0.33490(72)	−0.21795(57)	696(28)
O12	−0.37134(49)	0.52466(73)	−0.01524(56)	670(27)
O13	−0.26832(51)	0.54634(69)	−0.17359(56)	666(27)
N11	0.33137(74)	0.92185(106)	0.15182(70)	735(37)
C12	0.38385(85)	0.84388(113)	0.10514(93)	699(42)
C13	0.40744(76)	0.86493(106)	0.01365(87)	639(38)
C14	0.37605(81)	0.96733(105)	−0.03020(81)	636(37)
C15	0.31964(94)	1.04694(114)	0.01767(92)	744(45)
C16	0.29552(88)	1.02189(133)	0.11177(95)	775(47)
C17	0.46367(102)	0.77261(134)	−0.04301(126)	1005(64)
N21	0.53767(71)	0.50464(84)	0.33957(68)	657(32)
C22	0.61507(79)	0.57471(101)	0.35458(77)	606(35)
C23	0.65551(74)	0.63465(97)	0.28083(77)	579(33)
C24	0.61240(80)	0.62099(109)	0.19309(80)	644(38)
C25	0.53182(82)	0.54805(114)	0.17964(84)	677(40)
C26	0.49417(78)	0.49188(111)	0.25499(92)	679(40)
C27	0.74507(91)	0.70840(124)	0.29741(91)	760(45)
C28	0.76360(107)	0.80512(147)	0.22832(105)	935(59)
H11	0.316	0.906	0.221	80
H12	0.410	0.768	0.140	60
H14	0.396	0.987	−0.097	70
H15	0.296	1.124	−0.014	70
H16	0.250	1.078	0.148	70
H171	0.423	0.692	−0.040	100
H172	0.525	0.753	−0.005	100
H173	0.479	0.782	−0.109	100
H21	0.513	0.458	0.396	60
H22	0.640	0.582	0.423	60
H24	0.637	0.667	0.136	60
H25	0.504	0.534	0.113	60
H26	0.433	0.441	0.248	70
H271	0.803	0.656	0.309	70
H272	0.744	0.748	0.365	70
H281	0.708	0.860	0.224	80
H282	0.771	0.762	0.164	80
H283	0.824	0.853	0.239	80

balance. They showed three steps. The final product of thermal decomposition was MoO_3, as detected by its powder diffraction pattern. The formation of MoO_3 corresponds to the weight loss given in the analyses.

Crystal Data

Cell dimensions were obtained from Weissenberg and precession photographs. These data were confirmed and refined in a four-circle diffractometer with graphite monochromated

TABLE III. Intermolecular Contacts.

X–H···Y	X···Y	X–H	H···Y	<X–H···Y
Hydrogen bonds				
N11–H11···O4(i)	3.09(1) Å	1.01 Å	2.39 Å	126°
*N21–H21···O7(ii)	2.87(1)	1.01	2.09	133
*N21–H21···O3(ii)	2.95(1)	1.01	2.15	136
Other contacts				
C15–H15···O2(iii)	3.33(1)	1.01	2.48	142
C22–H22···O7(i)	3.39(1)	1.01	2.51	146
C25–H25···O12(iv)	3.26(1)	1.01	2.36	149
C26–H26···O13(iv)	3.33(1)	1.01	2.49	140

Symmetry codes

(i) $0.5 - x, 0.5 + y, 0.5 - z$ (ii) $0.5 + x, 0.5 - y, 0.5 + z$

(iii) $x, 1 + y, z$ (iv) $-x, 1 - y, -z$

*Bifurcated hydrogen bond.

MoKα radiation. Crystal data are listed in Table I.

A single crystal belonging to crystal type **II** (Table I) was selected for X-ray analysis. Its crystal data are given in the abstract and differ slightly from those given in Table I. Intensity data for 6455 reflexions up to $\theta = 30$ degrees were collected on a four-circle diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71069$ Å). Scattering factors for neutral atoms and anomalous dispersion corrections for Mo were taken from [22]. A Patterson synthesis gave the positions of the Mo atoms. The remaining atoms of the structure were located on successive Fourier syntheses. Refinement was carried out by full-matrix anisotropic least squares (H-atoms as isotropic fixed contributors). A convenient weighting scheme was used to prevent bias on $\langle w\Delta^2F\rangle$ *vs.* $\langle F_o\rangle$ and *vs.* $\langle \sin\theta/\lambda\rangle$. Final disagreement indices were $R = 0.064$ and $wR = 0.068$ for 5090 observed reflexions ($I > 3\sigma(I)$).

Table II lists the final atomic parameters. Tables of observed and calculated structure factors and anisotropic thermal parameters for non-H atoms are included as supplementary material.

Most calculations were performed using the XRAY-76 System [23] running on a VAX 11/750 computer.

Results and Discussion

All the compounds of the series are roughly isomorphous. They show $P2_1/n$ symmetry, and their cell parameters have very close values, $Z = 2$. The major differences are in the cell volumes.

The determination of % values of Mo, C, H and N from chemical analysis is not an accurate method for establishing the degree of substitution of one cation by the other.

IR and ^{1}H NMR spectra are not able to determine the correct x value for compounds **II** and **III**. These techniques have only demonstrated the presence of the two protonated bases.

Thermogravimetric studies show three decomposition steps. The initial decomposition temperature was 170 °C for compound **I** and 170–175 °C for compounds **II**, **III** and **IV**.

The compound whose crystal structure determination is reported in the experimental section corresponds exactly to a value of x = 2. It contains discrete $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ centrosymmetric polyanions linked to the $(3\text{-MepyH})^+$ and $(3\text{-EtpyH})^+$ cations through hydrogen bonds of type N–H···O (mono- and bifurcated), and other contacts of type C–H···O (Table III).

The geometrical features within the polyanion are shown in Table IV, where, as commonly occurs, three families of Mo–O distances are found. The distortion of the MoO_6 octahedra has been evaluated in terms of $\Delta = \Sigma|d_i - \bar{d}|/12$, where d_i represents the individual O–O distances within the octahedra. The Δ values are 0.09, 0.09, 0.09 and 0.07 for Mo(1), Mo(2), Mo(3) and Mo(4), respectively. A schematic view of this unit can be seen in Fig. 1 of [14].

Figure 1 shows a schematic drawing of the cations with the atomic labelling. There are two independent cations in the cell, one of $(3\text{-MepyH})^+$ type and the other of $(3\text{-EtpyH})^+$ type. Table V lists the distances and angles within these units. The rings are planar, C17, C27 and C28 being 0.11(1), 0.05(1) and −0.46(2) Å, respectively, out of the planes defined

TABLE IV. Mo–O Distances within the Polyanion (Å). For symmetry codes see Table IV.

Mo1–O4	1.684(8)	Mo2–O11	1.666(8)
Mo1–O3	1.694(7)	Mo2–O7	1.707(7)
Mo1–O2	1.903(7)	Mo2–O6	1.889(7)
Mo1–O8	1.991(6)	Mo2–O1	1.990(6)
Mo1–O5(iv)	2.323(6)	Mo2–O5	2.324(6)
Mo1–O1	2.343(7)	Mo2–O8	2.375(6)
Mo3–O13	1.688(8)	Mo4–O10	1.684(7)
Mo3–O12	1.693(7)	Mo4–O9	1.749(6)
Mo3–O6	1.910(7)	Mo4–O8	1.946(6)
Mo3–O2(iv)	1.916(7)	Mo4–O1(iv)	1.950(6)
Mo3–O9	2.298(7)	Mo4–O5(iv)	2.156(6)
Mo3–O5	2.444(6)	Mo4–O5	2.426(7)

Three families of Mo–O distances:

Short	1.70(2)
Medium	1.94(4)
Long	2.34(9)

TABLE V. Bond Lengths (Å) and Angles (°) within the Cations.

N11–C12	1.31(2)	C12–N11–C16	123(1)
N11–C26	1.33(2)	N11–C12–C13	121(1)
C12–C13	1.35(2)	C12–C13–C14	119(1)
C13–C14	1.35(2)	C12–C13–C17	121(1)
C13–C17	1.52(2)	C14–C13–C17	119(1)
C14–C15	1.36(2)	C13–C14–C15	120(1)
C15–C16	1.39(2)	C14–C15–C16	119(1)
		N11–C16–C15	118(1)
N21–C22	1.33(1)	C22–N21–C26	123(1)
N21–C26	1.32(2)	N21–C22–C23	120(1)
C22–C23	1.36(2)	C22–C23–C24	117(1)
C23–C24	1.36(2)	C22–C23–C27	120(1)
C23–C27	1.50(2)	C24–C23–C27	123(1)
C24–C25	1.39(2)	C23–C24–C25	121(1)
C25–C26	1.34(2)	C24–C25–C26	119(1)
C27–C28	1.47(2)	N21–C26–C25	119(1)
		C23–C27–C28	117(1)

by the corresponding atoms within the rings. The conformation of the ethyl substituent is defined by the torsional angles C22–C23–C27–C28 of −157(1)° and C24–C23–C27–C28 of 25(2)°.

We are attempting to prepare a more complete series of compounds between **I** and **IV** in order to verify if the x value can be a fraction. In this case, a disordered distribution of the cations must be expected over the two crystallographic sites.

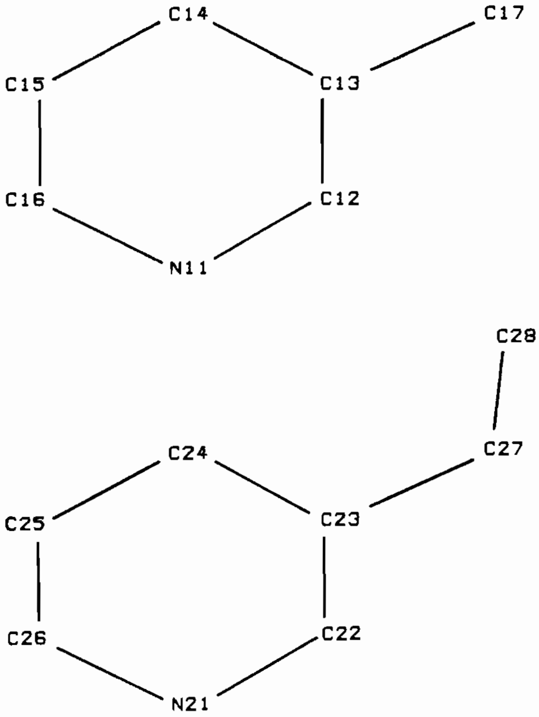

Fig. 1. Schematic drawing of the cations with their atom labelling.

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