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Crystal Structure and Photochemistry of Isopolymolybdates. I. The Crystal Structures of Hexakis(propylammonium)heptamolybdate(VI) Trihydrate and Hexakis(isopropylammonium)heptamolybdate(VI) Trihydrate

Yuji Ohashi,* Kazunori Yanagi, Yoshio Sasada, and Toshihiro Yamase†

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227
†Research Laboratory of Resource Utilization, Tokyo Institute of Technology,
Nagatsuta, Midori-ku, Yokohama 227

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The crystal structures of $(NH_3CH_2CH_2CH_3)_6[Mo_7O_{24}]\cdot 3H_2O$ and $(NH_3CH(CH_3)_2)_6[Mo_7O_{24}]\cdot 3H_2O$ have been determined by X-ray analysis. The crystal of the propylammonium salt is triclinic; the space group is $P\bar{1}$; $Z=2$, with $a=14.118(2)$, $b=15.977(2)$, $c=11.368(1)$ Å, $\alpha=90.23(1)$, $\beta=93.00(1)$, $\gamma=111.79(1)°$. That of the isopropylammonium salt is monoclinic; the space group is P2/n; $Z=4$, with $a=23.904(6)$, $b=10.504(1)$, $c=20.652(9)$ Å, and $\beta=115.40(2)°$. The structures were deduced by the direct method and refined by the block-diagonal least-squares technique. The final R values were 0.035 for 8084 observed reflections of the former and 0.060 for 9934 of the latter. The heptamolybdate anion of the two crystals has an approximate 2mm symmetry and its structure is similar to that observed in the crystals of the ammonium, potassium and sodium salts. The propyl- and isopropylammonium cations form some hydrogen bonds to the bridging oxygens of the heptamolybdates. Such hydrogen bonds play an important role in the UV-induced photochromism of these crystals.

Recently it has been reported that various alkylammonium polymolybdates show photochemical and photochromic properties in aqueous solution and in the solid state.[1] On exposure to UV light, they turn blue from colorless in deaerated solutions, whereas they change from colorless to red in the solid state. The photoreduced blue compound of isopropylammonium polymolybdate, $(NH_3CH(CH_3)_2)_4[Mo_{13}O_{40}]_{0.33}[H_4Mo_{12}O_{40}]_{0.67}$, was crystallized and its structure has been reported.[2] The crystal structure of the isopropylammonium salt, $(NH_3CH(CH_3)_2)_6[H_2Mo_8O_{28}]\ 2H_2O$, (IPAM2) has been analyzed by X-rays.[3] It has been proposed from the structure and the ESR measurement of the crystal that the photoreduction from Mo(VI) to Mo(V) in a MoO_6 octahedral site proceeds on irradiation with UV light, accompanying a transfer of a hydrogen-bonding proton from the isopropylammonium nitrogen to a bridging oxygen atom of the octamolybdate.[4]

In order to ascertain the mechanism, crystal structures of the propylammonium and isopropylammonium salts of the polymolybdate with somewhat different compositions have been analyzed. Hereafter the former crystal is abbreviated to PAM and the latter to IPAM.

Experimental and Structure Determination

The preparation of the two crystals was reported in the previous paper,[1] in which their chemical formulae were erroneously given owing to the low accuracy of the elemental analysis.

PAM, $(NH_3CH_2CH_2CH_3)_6[Mo_7O_{24}]\cdot 3H_2O$. Preliminary unit cell dimensions and the space group were obtained from oscillation and Weissenberg photographs. Accurate cell dimensions were determined by a least-squares technique from 19 reflections measured on a Rigaku automated four-circle diffractometer. Crystal adata re summarized in Table 1. Intensity data up to $2\theta \leq 55°$ were collected on the diffractometer with Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) monochromated by graphite. An ω-2θ scan was employed with a scan rate of 4° (2θ) min^{-1}. A total of 8084 independent reflections, ($|F_o| \geq 3\sigma(|F_o|)$), were used for the structure determination.

Table 1. Crystal data

	PAM	IPAM
Chemical formula	$(C_3H_{10}N)_6$- $[Mo_7O_{24}]\cdot 3H_2O$	$(C_3H_{10}N)_6$- $[Mo_7O_{24}]\cdot 3H_2O$
F.W.	1470.3	1470.3
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	P2/n
a/Å	14.118(2)	23.904(6)
b/Å	15.977(2)	10.504(1)
c/Å	11.368(1)	20.652(9)
α/°	90.23(1)	
β/°	93.00(1)	115.40(2)
γ/°	111.79(1)	
V/Å^3	2377.1(7)	4684(3)
Z	2	4
D_c/g cm^{-3}	2.054	2.085
μ(Mo $K\alpha$)/cm^{-1}	18.28	18.56

Although the crystal turned red on X-ray exposure, the intensities of the monitor reflections did not change significantly during the data collection. The intensities were corrected for Lorentz and polarization factors but absorption correction was not applied.

The positions of the seven Mo atoms were obtained by the direct method using program MULTAN 78.[5] The C, N, and O atoms and three water molecules appeared on the successive Fourier maps. The structure was refined by the block-diagonal least-squares method with the anisotropic temperature factors. After several cycles of refinement, six atoms of the three propylammonium ions and a water molecule, respectively, were found to be distributed over two positions. The occupancy factors of the disordered atoms were fixed at a value which was estimated from their isotropic temperature factors. All the H atoms bonded to the N atoms and to the O atoms of the ordered water molecules were located on a difference map. Some of the H atoms of the ordered propyl groups obtained from a difference map and the positions of the remaining ones were calculated geometrically. In the final refinement, the disordered atoms and the H atoms except the propyl H atoms were included with the isotropic temperature factors. The final R value became 0.035 for 8084 reflections.

TABLE 2. FINAL ATOMIC PARAMETERS OF PAM, MULTIPLIED BY 10^5 FOR Mo ATOMS, 10^4 FOR C, N, O ATOMS AND 10^3 FOR THE DISORDERED ATOMS WITH *

Atom	x	y	z	B or B_{eq}/Å^2
Mo(1)	26485(3)	9179(2)	44423(3)	2.3
Mo(2)	22464(3)	2745(3)	16807(3)	2.4
Mo(3)	49615(3)	33497(2)	35450(3)	2.3
Mo(4)	45757(3)	26910(3)	7684(3)	2.6
Mo(5)	31452(3)	29676(3)	53102(3)	2.5
Mo(6)	23451(3)	15954(3)	−4732(3)	2.8
Mo(7)	25140(3)	24267(2)	23739(3)	2.2
O(1)	1556(2)	−1(2)	4699(3)	2.8
O(2)	1208(3)	−617(2)	2067(3)	3.2
O(3)	5745(3)	4389(2)	3116(3)	3.1
O(4)	5370(3)	3766(3)	439(3)	3.9
O(5)	3566(3)	862(2)	5451(3)	2.9
O(6)	2914(3)	−191(2)	850(3)	3.1
O(7)	5645(2)	3078(2)	4670(3)	2.7
O(8)	5049(3)	1980(3)	93(3)	3.5
O(9)	3900(3)	2929(2)	6524(3)	3.0
O(10)	2728(3)	964(3)	−1406(3)	3.6
O(11)	2432(3)	3547(2)	5814(3)	3.1
O(12)	1465(3)	1902(3)	−1286(3)	3.7
O(13)	2158(2)	1752(2)	5272(3)	2.4
O(14)	1458(2)	622(2)	417(3)	2.4
O(15)	4166(2)	3879(2)	4484(3)	2.3
O(16)	3521(3)	2706(2)	−450(3)	3.0
O(17)	2134(2)	2991(2)	3440(3)	2.7
O(18)	1801(3)	2444(2)	1089(3)	3.0
O(19)	3122(2)	457(2)	3114(3)	2.1
O(20)	5144(2)	2586(2)	2325(3)	2.1
O(21)	1846(2)	1215(2)	2820(3)	2.0
O(22)	3813(2)	3284(2)	2046(3)	2.1
O(23)	3542(2)	2260(2)	3901(2)	1.8
O(24)	3175(2)	1643(2)	1193(2)	1.9
N(1)	394(3)	1459(3)	6454(4)	3.5
N(2)	3142(4)	4068(3)	−1720(4)	3.6
N(3)	4623(4)	1725(3)	−2429(4)	3.9
N(4)	6127(5)	4634(3)	6357(4)	4.8
N(5)	5177(3)	933(3)	2750(5)	3.9
N(6)	−354(3)	992(3)	967(5)	4.4
O(W2)	5484(5)	4824(3)	−1438(4)	7.3
O(W3)	4299(5)	66(4)	−925(6)	8.4
C(11)	148(4)	2276(4)	6352(5)	3.9
C(12)	−107(5)	2438(5)	5116(6)	5.3
C(13)	−257(7)	3326(6)	5009(10)	8.8
C(31)	5716(5)	2179(5)	−2610(6)	4.5
C(32)	6236(6)	1544(5)	−2654(8)	6.5
C(33)	7370(6)	1994(7)	−2939(10)	8.8
C(51)	5819(5)	960(5)	3857(7)	5.1
C(52)	6956(6)	1325(6)	3617(8)	6.9
C(53)	7338(6)	2237(7)	3213(10)	8.8
C(21)	2388(5)	4231(5)	−993(6)	5.3
C(61)	−808(8)	1657(6)	1071(9)	7.9
O(W1)	−291(4)	446(4)	3283(5)	5.2(1)[a]
C(22)	2126(9)	5015(8)	−1380(10)	7.3(2)[a]
C(23)	1678(11)	5021(10)	−2406(13)	8.9(3)[a]
C(62)	−592(9)	2231(8)	60(11)	7.7(3)[a]
C(63)	−986(12)	3027(10)	273(14)	13.6(4)
C(41)	7314(10)	4803(8)	6195(11)	6.3(3)[a]
C(42)	7705(17)	4793(15)	7603(19)	12.5(6)[a]
C(43)	8795(13)	4982(11)	7324(15)	14.8(5)
O(W1*)	−122(3)	14(2)	298(3)	6.0(8)[a]
C(22*)	141(4)	440(3)	−153(4)	9.1(10)[a]
C(23*)	133(4)	512(3)	−100(4)	8.7(10)[a]
C(41*)	698(2)	478(2)	701(2)	6.3(6)[a]
C(42*)	783(3)	444(2)	658(3)	8.5(8)[a]
C(62*)	−137(4)	198(3)	42(4)	6.8(10)[a]

a) The occupancy factors of O(W1), C(22), C(23), C(62), C(41), C(42), O(W1*), C(22*), C(23*), C(41*), C(42*), and C(62*) are 0.80, 0.80, 0.75, 0.80, 0.65, 0.65, 0.20, 0.20, 0.25, 0.35, 0.35, and 0.20, respectively.

The weighting scheme was $w=(0.00069F_o^2-0.11048|F_o|+5.42077)^{-1}$ for $3.90\leq|F_o|\leq156.14$ and $w=0.2$ for $|F_o|<3.90$ and $|F_o|>156.14$. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[6] Positional and isotropic or equivalent isotropic temperature factors are given in Table 2.

IPAM, $(NH_3CH(CH_3)_2)_6[Mo_7O_{24}]\cdot 3H_2O$. Experimental details were nearly the same as those in PAM. Refinement of the unit cell dimensions was based on 18 reflections. Crystal data are listed in Table 1. A total of 9936 independent reflections were used for the structure determination.

The positions of the seven Mo atoms were obtained by using program MULTAN 78.[5] The C, N, and O atoms and three water molecules appeared on the successive Fourier maps. The structure was refined by the block-diagonal least-squares method. After several cycles of refinement with anisotropic temperature factors, an isopropylammonium cation (N(6), C(61), C(62), and C(63)), and a water molecule (O(W3)) were found to occupy two disordered positions. The occupancy factors for the two equivalent atoms were assumed to be 0.6 and 0.4, which were estimated from the isotropic temperature factors of the atoms and were not refined in the least-squares calculation. Out of 60 H atoms, 18 were located on the difference map. The H atoms were included in the final refinement with the isotropic temperature factors. Two strong reflections, 010 and 200, were excluded because they seemed to suffer from secondary extinction. The final R value became 0.060 for 9934 reflections. The weighting scheme used in the final stages was $w=[\sigma^2(F_o)+(0.015F_o)^2]^{-1}$. Positional and equivalent isotropic temperature factors are given in Table 3.** The FACOM-HITAC system M-160 and M-170 computers were used in the calculation.

Results

The Structure of Heptamolybdate. The geometries of the heptamolybdate anions in both crystals are quite similar. Seven MoO_6 octahedra are condensed by edge sharing into a structure that has an approximate

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** Lists of the positional and isotropic temperature factors of the H atom, lists of the anistropic temperature factors of the Mo, C, N, and O atoms, tables of the bond angles and tables of the observed and calculated structure factors for both crystal structures are kept in the office of the Chemical Society of Japan (Document No. 8214).

TABLE 3. FINAL ATOMIC PARAMETERS OF IPAM, MULTIPLIED BY 10^5 FOR Mo ATOMS AND 10^4 FOR C, N, O ATOMS

Atom	x	y	z	B or B_{eq}/Å^2
Mo(1)	2614(3)	67851(6)	15724(3)	2.4
Mo(2)	−9147(3)	47911(7)	10288(3)	2.9
Mo(3)	3174(3)	67699(6)	36462(3)	2.4
Mo(4)	−8702(3)	48120(6)	30659(3)	2.9
Mo(5)	14141(3)	66003(6)	31304(3)	2.5
Mo(6)	−9734(3)	24895(7)	20165(5)	4.2
Mo(7)	3420(3)	42658(5)	26335(3)	2.1
O(1)	293(2)	6551(6)	776(3)	3.7
O(2)	−823(3)	4651(6)	250(3)	4.3
O(3)	368(3)	6493(5)	4490(3)	3.8
O(4)	−753(3)	4708(5)	3940(3)	4.1
O(5)	248(3)	8406(5)	1669(3)	3.7
O(6)	−1688(2)	5089(6)	764(3)	4.4
O(7)	301(3)	8385(5)	3557(3)	3.8
O(8)	−1644(2)	5088(6)	2602(3)	4.4
O(9)	1539(2)	8191(5)	3175(3)	3.9
O(10)	−1771(3)	2496(7)	1623(5)	7.7
O(11)	2148(2)	5932(5)	3476(3)	3.7
O(12)	−763(3)	900(5)	2114(4)	6.3
O(13)	1153(2)	6415(5)	2127(3)	2.8
O(14)	−863(2)	2939(5)	1187(3)	3.8
O(15)	1196(2)	6413(5)	3916(2)	2.8
O(16)	−830(2)	2961(5)	2953(3)	3.9
O(17)	1147(2)	4323(5)	3011(3)	3.1
O(18)	166(2)	2659(4)	2544(3)	3.9
O(19)	−613(2)	6525(4)	1294(2)	2.5
O(20)	−569(2)	6528(4)	3079(2)	2.6
O(21)	145(2)	4688(4)	1679(2)	2.6
O(22)	182(2)	4682(4)	3417(2)	2.4
O(23)	419(2)	6410(4)	2661(2)	2.0
O(24)	−700(2)	4498(4)	2127(3)	2.6
N(1)	−1037(3)	8284(6)	1972(3)	3.0
C(11)	−1714(4)	8145(9)	1617(5)	4.4
C(12)	−1956(5)	8802(14)	891(5)	7.3
C(13)	−1977(5)	8725(15)	2082(7)	8.6
N(2)	1609(3)	6721(6)	1064(3)	3.1
C(21)	1559(4)	8141(8)	885(4)	4.0
C(22)	1864(4)	8402(9)	383(4)	4.9
C(23)	1877(5)	8824(9)	1588(5)	5.2
N(3)	458(4)	3318(9)	729(4)	6.8
C(31)	1039(7)	2848(16)	935(7)	10.1
C(32)	1117(6)	1915(12)	440(6)	7.5
C(33)	1493(10)	2995(36)	1734(10)	27.9
N(4)	479(4)	3541(7)	4796(4)	5.6
C(41)	602(9)	2215(13)	4861(7)	11.2
C(42)	1021(6)	1889(12)	5682(6)	8.3
C(43)	233(11)	1405(15)	4369(10)	16.2
N(5)	679(3)	234(6)	2849(4)	4.0
C(51)	1331(12)	1145(23)	3403(13)	21.6
C(52)	1797(7)	1791(15)	3444(10)	13.0
C(53)	1735(12)	510(25)	4136(11)	21.4
N(6)	−2133(6)	3772(13)	3722(7)	5.5
C(61)	−1731(7)	2570(16)	3990(10)	6.1
C(62)	−1914(9)	1825(22)	3340(11)	7.6
C(63)	−1886(10)	1963(21)	4583(9)	7.8
N(6′)	1861(15)	6648(18)	5489(11)	8.5
C(61′)	1644(14)	8006(28)	5569(11)	6.6
C(62′)	1802(14)	8777(25)	5231(12)	6.2
C(63′)	1741(12)	8412(27)	6382(15)	6.2
O(W1)	2492(5)	3778(9)	4445(5)	10.9
O(W2)	−145(5)	897(10)	943(6)	11.0
O(W3)	1688(5)	4652(12)	4980(6)	6.0
O(W3′)	−2793(9)	5478(23)	1419(10)	8.0

TABLE 4. BOND DISTANCES (l/Å) OF $[Mo_7O_{24}]^{6-}$ IN PAM AND IPAM

Bond	Distance PAM	Distance IPAM	Type
Mo(1)–O(1)	1.729(3)	1.696(6)	a
Mo(1)–O(5)	1.713(4)	1.717(6)	a
Mo(1)–O(13)	1.973(3)	1.977(5)	b
Mo(1)–O(19)	1.931(3)	1.935(5)	b
Mo(1)–O(21)	2.258(3)	2.243(5)	c
Mo(1)–O(23)	2.156(3)	2.151(5)	c
Mo(2)–O(2)	1.702(4)	1.719(6)	a
Mo(2)–O(6)	1.715(4)	1.717(6)	a
Mo(2)–O(14)	1.978(3)	1.968(6)	b
Mo(2)–O(19)	1.946(3)	1.949(5)	b
Mo(2)–O(21)	2.224(3)	2.306(5)	c
Mo(2)–O(24)	2.183(3)	2.123(5)	c
Mo(3)–O(3)	1.708(4)	1.720(6)	a
Mo(3)–O(7)	1.715(4)	1.705(6)	a
Mo(3)–O(15)	1.984(3)	1.965(5)	b
Mo(3)–O(20)	1.932(3)	1.949(5)	b
Mo(3)–O(22)	2.264(3)	2.238(5)	c
Mo(3)–O(23)	2.171(3)	2.183(5)	c
Mo(4)–O(4)	1.722(4)	1.708(6)	a
Mo(4)–O(8)	1.713(4)	1.704(7)	a
Mo(4)–O(16)	1.986(4)	1.965(6)	b
Mo(4)–O(20)	1.938(3)	1.937(5)	b
Mo(4)–O(22)	2.253(3)	2.303(5)	c
Mo(4)–O(24)	2.144(3)	2.169(5)	c
Mo(5)–O(9)	1.714(4)	1.693(6)	a
Mo(5)–O(11)	1.717(4)	1.733(6)	a
Mo(5)–O(13)	1.923(3)	1.900(5)	b
Mo(5)–O(15)	1.917(3)	1.914(5)	b
Mo(5)–O(17)	2.506(3)	2.461(6)	d
Mo(5)–O(23)	2.171(3)	2.158(5)	c
Mo(6)–O(10)	1.700(4)	1.723(10)	a
Mo(6)–O(12)	1.723(4)	1.731(9)	a
Mo(6)–O(14)	1.926(3)	1.901(6)	b
Mo(6)–O(16)	1.927(4)	1.881(7)	b
Mo(6)–O(18)	2.546(4)	2.469(7)	d
Mo(6)–O(24)	2.160(3)	2.192(5)	c
Mo(7)–O(17)	1.729(3)	1.739(6)	a
Mo(7)–O(18)	1.736(4)	1.730(7)	a
Mo(7)–O(21)	1.897(3)	1.873(5)	b
Mo(7)–O(22)	1.895(3)	1.868(5)	b
Mo(7)–O(23)	2.285(3)	2.259(5)	c
Mo(7)–O(24)	2.285(3)	2.264(5)	c

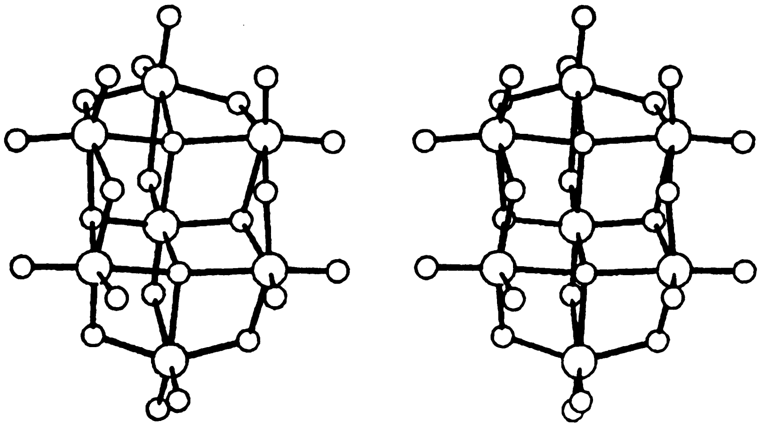


Fig. 1. Stereoscopic drawing of the heptamolybdate anion in PAM.

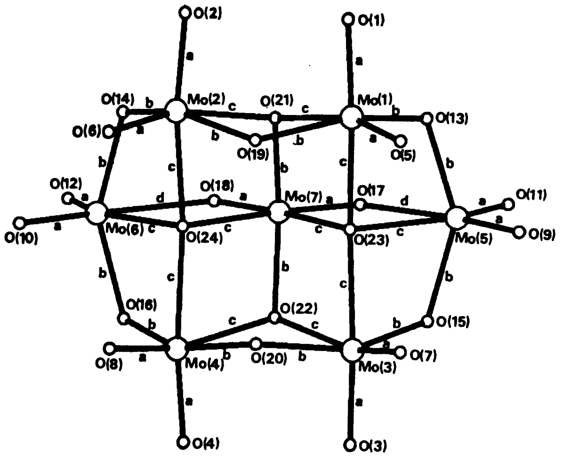


Fig. 2. The numbering of the atoms and the bond types in the heptamolybdate anion.

point symmetry 2mm(C_{2v}). Figure 1 shows the stereoscopic drawing of the heptamolybdate ion in PAM. Such a structure of $[Mo_7O_{24}]^{6-}$ is also found in the crystal of the ammonium,[7] potassium,[7] and sodium[8] salts.

Bond distances of the heptamolybdate ions in PAM and IPAM are listed in Table 4. The corresponding values are in fair agreement, although some distances and angles relevant to O(16), O(21), O(22), and O(24) are significantly different between the two crystals. The discrepancy is probably due to the different hydrogen bonding scheme.

The Mo–O bonds can be classified into four types by their bond distances; *a*(1.69—1.73 Å), *b*(1.90—1.97 Å), *c*(2.16—2.30 Å), and *d*(2.46—2.55 Å). Figure 2 shows the numbering of the atoms and the types of the bonds. The seven MoO_6 octahedra are divided into two classes; five octahedra of Mo(1), Mo(2), Mo(3), Mo(4), and Mo(7) have three types of Mo–O bonds, whereas two octahedra of Mo(5) and Mo(6) have four types of the bonds. The electronic state of Mo(5) and Mo(6) may be different from that of the other Mo atoms. The seven MoO_6 octahedra in the ammonium salt are also divided into two classes.

TABLE 5. BOND DISTANCES (l/Å) OF PROPYL- AND ISOPROPYLAMMONIUM IONS

Propylammonium ion		Isopropylammonium ion	
N(1)-C(11)	1.47(1)	N(1)-C(11)	1.47(1)
C(11)-C(12)	1.48(1)	C(11)-C(12)	1.52(2)
C(12)-C(13)	1.51(1)	C(11)-C(13)	1.49(2)
N(2)-C(21)	1.48(1)	N(2)-C(21)	1.53(1)
C(21)-C(22)	1.49(1)	C(21)-C(22)	1.53(1)
C(22)-C(23)	1.30(2)	C(21)-C(23)	1.50(1)
N(3)-C(31)	1.47(1)	N(3)-C(31)	1.36(2)
C(31)-C(32)	1.46(1)	C(31)-C(32)	1.48(2)
C(32)-C(33)	1.55(2)	C(31)-C(33)	1.55(4)
N(4)-C(41)	1.62(2)	N(4)-C(41)	1.42(2)
C(41)-C(42)	1.67(3)	C(41)-C(42)	1.59(3)
C(42)-C(43)	1.51(3)	C(41)-C(43)	1.33(3)
N(5)-C(51)	1.50(1)	N(5)-C(51)	1.77(3)
C(51)-C(52)	1.53(1)	C(51)-C(52)	1.27(4)
C(52)-C(53)	1.44(2)	C(51)-C(53)	1.55(4)
N(6)-C(61)	1.44(1)	N(6)-C(61)	1.54(3)
C(61)-C(62)	1.45(2)	C(61)-C(62)	1.45(3)
C(62)-C(63)	1.59(2)	C(61)-C(63)	1.56(3)
C(21)-C(22*)	1.59(4)	N(6′)-C(61′)	1.55(5)
C(22*)-C(23*)	1.33(4)	C(61′)-C(62′)	1.23(5)
N(4)-C(41*)	1.33(4)	C(61′)-C(63′)	1.65(5)
C(41*)-C(42*)	1.60(4)		
C(42*)-C(43*)	1.52(4)		
C(61)-C(62*)	1.30(4)		
C(62*)-C(63)	1.56(4)		

TABLE 6. TORSION ANGLES (ϕ/°) OF THE CENTRAL N-C-C-C BONDS OF THE PROPYLAMMONIUM CATIONS

N(1)-C(11)-C(12)-C(13)	174.4
N(2)-C(21)-C(22)-C(23)	63.8
N(3)-C(31)-C(32)-C(33)	175.6
N(4)-C(41)-C(42)-C(43)	178.3
N(5)-C(51)-C(52)-C(53)	62.0
N(6)-C(61)-C(62)-C(63)	173.3
N(2)-C(21)-C(22*)-C(23*)	135.7
N(4)-C(41*)-C(42*)-C(43)	163.4
N(6)-C(61)-C(62*)-C(63)	126.7

The Structure of Propylammonium and Isopropylammonium Cations. Bond distances of the propyl- and isopropylammonium ions are listed in Table 5. The rather large deviations from the normal values may be brought

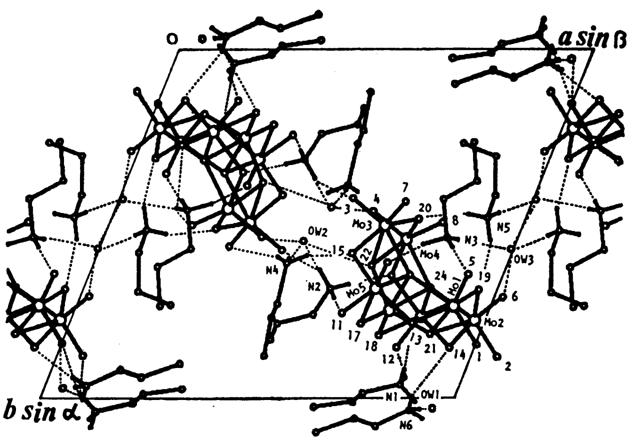


Fig. 3. Crystal structure of PAM viewed along the c axis. The hydrogen bonds are drawn with dotted lines. The hydrogen atoms of the propyl group and the minor portions of the disordered atoms are omitted for clarity.

about by the disordered structures of these ions. Table 6 shows the torsion angles of the central C–C bond in the propylammonium ions. The conformation of the ions may be easily changed in the crystal.

Crystal Structure and Hydrogen Bonding Scheme. The crystal structure of PAM viewed along the c axis is shown in Fig. 3. The hydrophobic groups of the propylammonium ions are brought together around the $(1/2,0,z)$ region. All the N–H groups of the propylammonium ions and O–H groups of the water molecules make hydrogen bonds with the heptamolybdate anion or the water molecules. The hydrogen bonds construct a three-dimensional network. The distances of X···O, X–H, and H···O and the angles of X–H···O are listed in Table 7, where X means the N or O atoms. The N(1)–H(N13) and N(2)–H(N32) groups make trifurcate hydrogen bonds with O(1), O(2), and O(W1), and O(8), O(10), and O(W3), respectively. However, the distances of H. .O and the angles of N–H···O indicate that N(1)–H(N13). .O(2), N(1)–H(N13)···O(W1), N(3)–H(N32)···O(8), and N(3)–H(N32)···O(10) may

TABLE 7. HYDROGEN BOND DISTANCES (l/Å) AND ANGLES (ϕ/°) IN PAM

X means N or O atoms and unit number indicates the equivalent position as follows:

(i) (x,y,z) (ii) $(-x,-y,-z)$ (iii) $(1-x,-y,-z)$
(iv) $(1-x,1-y,-z)$ (v) $(x,y,1+z)$ (vi) $(-x,-y,1-z)$
(vii) $(1-x,1-y,1-z)$ (viii) $(x,y,-1+z)$.

X–H···O	Unit	X···O	X–H	H···O	X–H···O
N(1)–H(N11)···O(13)	i	2.776(6)	0.75(5)	2.04(5)	172(5)
N(1)–N(N12)···O(12)	v	2.859(7)	0.78(6)	2.14(6)	152(6)
N(1)–H(N13)···O(1)	vi	3.092(6)	0.92(8)	2.22(8)	158(7)
N(1)–H(N13)···O(2)	vi	2.812(6)	0.92(8)	2.51(8)	100(6)
N(1)–H(N13)···O(W1)	vi	3.010(8)	0.92(8)	2.52(8)	114(6)
N(2)–H(N21)···O(16)	i	2.814(6)	0.83(6)	1.99(6)	176(6)
N(2)–H(N22)···O(11)	viii	2.937(6)	0.81(7)	2.14(7)	169(7)
N(2)–H(N23)···O(3)	iv	2.912(6)	0.82(8)	2.29(8)	133(7)
N(2)–H(N23)···O(W2)	i	3.068(9)	0.82(8)	2.41(8)	138(7)
N(3)–H(N31)···O(5)	viii	2.829(6)	0.71(8)	2.12(8)	177(8)
N(3)–H(N32)···O(8)	i	2.894(7)	0.71(7)	2.43(7)	124(6)
N(3)–H(N32)···O(10)	i	2.812(7)	0.71(7)	2.53(7)	106(6)
N(3)–H(N32)···O(W3)	i	3.062(9)	0.71(7)	2.40(7)	157(7)
N(3)–H(N33)···O(9)	viii	2.740(7)	0.96(7)	1.88(7)	147(6)
N(4)–H(N41)···O(7)	i	2.982(7)	0.57(5)	2.44(5)	162(6)
N(4)–H(N42)···O(W2)	v	2.763(10)	0.70(7)	2.07(7)	171(7)
N(4)–H(N43)···O(15)	vii	2.727(7)	0.90(6)	1.85(6)	163(5)
N(5)–H(N51)···O(20)	i	2.704(6)	0.77(5)	1.95(5)	163(5)
N(5)–H(N52)···O(W3)	iii	2.900(9)	0.67(5)	2.23(5)	176(6)
N(5)–H(N53)···O(19)	i	2.767(6)	0.84(5)	1.97(5)	158(5)
N(6)–H(N61)···O(14)	ii	2.878(6)	0.73(6)	2.15(6)	174(7)
N(6)–H(N62)···O(14)	i	2.927(6)	0.55(7)	2.44(7)	151(8)
N(6)–H(N62)···O(18)	i	3.061(7)	0.55(7)	2.65(7)	135(8)
N(6)–H(N63)···O(W1)	i	2.785(8)	1.15(8)	1.64(8)	176(7)
N(6)–H(N63)···O(W1*)	i	2.771(5)	1.15(8)	1.82(8)	137(6)
O(W2)–H(W21)···O(4)	i	2.702(8)	0.87(7)	1.88(7)	158(7)
O(W2)–H(W22)···O(22)	iv	2.909(8)	0.80(8)	2.22(7)	144(7)
O(W3)–H(W31)···O(6)	i	2.809(8)	0.83(9)	1.98(9)	177(8)
O(W3)–H(W32)···O(W3)	iii	2.874(13)	1.07(6)	2.62(6)	93(3)
O(W1)···O(1)	vi	2.908(7)			
O(W1*)···O(1)	vi	2.697(3)			

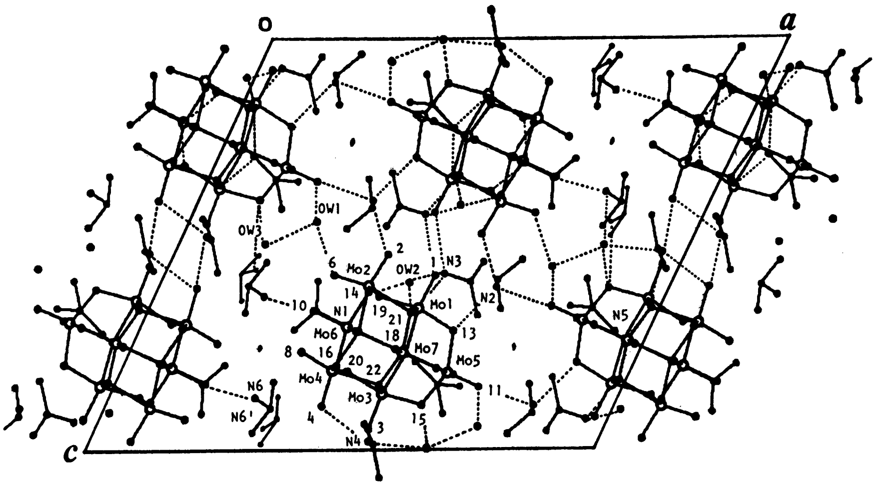


Fig. 4. Crystal structure of IPAM viewed along the b axis. The hydrogen bonds are drawn with dotted lines. The hydrogen atoms of the isopropylammonium cation and the minor portions of the disordered water molecule, O(W3′), are omitted for clarity.

TABLE 8. HYDROGEN BOND DISTANCES (l/Å) IN IPAM
The unit number indicates the equivalent position as fllows:

(i) (x,y,z) (ii) $(1/2-x,y,1/2-z)$
(iii) $(-1/2-x,y,1/2-z)$ (iv) $(x,1+y,z)$
(v) $(-x,1-y,-z)$ (vi) $(1/2+x,1-y,1/2+z)$
(vii) $(x,-1+y,z)$ (viii) $(-x,1-y,1-z)$.

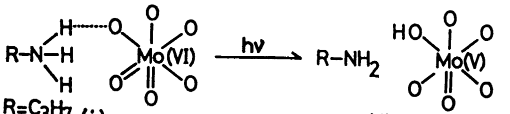
Hydrogen bond	Unit	l/Å
N(1)···O(19)	i	2.76(1)
N(1)···O(12)	iv	2.81(1)
N(1)···O(20)	i	2.77(1)
N(2)···O(2)	v	2.93(1)
N(2)···O(11)	ii	2.83(1)
N(2)···O(13)	i	2.86(1)
N(3)···O(1)	v	2.85(1)
N(3)···O(21)	i	2.78(1)
N(3)···O(W2)	i	3.05(2)
N(4)···O(4)	i	2.97(1)
N(4)···O(4)	viii	3.03(1)
N(4)···O(3)	viii	2.97(1)
N(4)···O(22)	i	2.88(1)
N(4)···O(W3)	i	2.99(2)
N(5)···O(5)	vii	2.92(1)
N(5)···O(7)	vii	2.80(1)
N(5)···O(9)	vii	2.85(1)
N(5)···O(18)	i	2.78(1)
N(6)···O(10)	iii	2.75(2)
N(6)···O(W3)	viii	2.93(2)
N(6′)···O(15)	i	2.95(4)
N(6′)···O(W3′)	vi	2.83(4)
O(W1)···O(6)	vi	2.85(1)
O(W1)···O(11)	i	2.90(1)
O(W1)···O(W3)	i	2.75(2)
O(W2)···O(5)	vii	2.96(1)
O(W2)···O(14)	i	2.92(1)
O(W3)···O(15)	i	2.72(1)
O(W3′)···O(8)	i	2.82(3)
O(W3′)···O(8)	iii	2.90(3)

not be those of hydrogen bonds, although the N···O distances of these bonds are rather shorter than those of N(1)–H(N13)···O(1) and N(3)–H(N32)···O(W3).

The crystal structure of IPAM viewed along the b axis is shown in Fig. 4. The isopropylammonium cations occupy the space between the heptamolybdate anions. Interatomic distances of the possible hydrogen bonds are listed in Table 8.

Discussion

It has been proposed from the X-ray analysis[3] and ESR measurement[4] of the IPAM2 crystal that the photoreduction of Mo(VI) to Mo(V) proceeds *via* UV-induced charge transfer in the terminal Mo=O bond of a MoO_6 site, followed by a transfer of a hydrogen-bonding proton from an isopropylammonium nitrogen to a bridging oxygen of the MoO_6 site as follows.



(1)

Figure 5 shows the geometry in the environment of the photoreducible MoO_6 site found in the IPAM2 crystal.

In the heptamolybdate anion of the present PAM and IPAM crystals, the photoreducible Mo atom is considered to be Mo(5) or Mo(6), because each of them has a long Mo–O bond, as is observed in the photoreducible site of the IPAM2 crystal. Figure 6(a) and (b) show the geometries of the hydrogen bonding scheme at the Mo(5) and Mo(6), respectively, in the PAM crystal. There are five hydrogen bonds between the N–H groups of the propylammonium cations and the bridging oxygen atoms of the Mo(5) and Mo(6) sites. One of the hydrogen bonds may be responsible for the proton transfer from the cation to the anion. In the crystal of IPAM, only the Mo(5) site has such a hydrogen bonding scheme, which is shown in Fig. 7. One of the two hydrogen bonds may bring about the

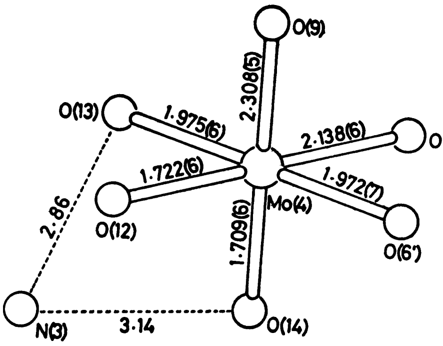


Fig. 5. Bond distances (l/Å) and interatomic distances (l/Å) between the non-bonded atoms in the environment of the photoreducible MoO_6 site in IPAM2. These values are taken from the reference 3. Positions of H atoms are omitted for clarity.

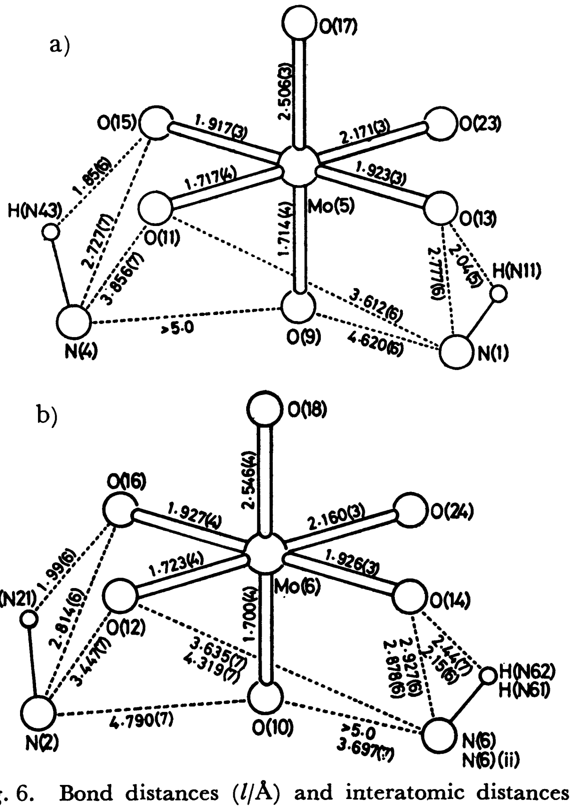


Fig. 6. Bond distances (l/Å) and interatomic distances (l/Å), (less than 5 Å), between non-bonded atoms in the environment of the (a) Mo(5) and (b) Mo(6) sites in PAM. In the Mo(6) site, O(14) makes two hydrogen bonds with N(6)-H(N62) and N(6)-H(N61) in the unit of (ii), ($-x$, $-y$, $-z$). The upper and lower values correspond to the former and latter hydrogen bonds, respectively.

proton transfer.

It should be noted that the crystal of the ammonium heptamolybdate does not exhibit photoreduction on irradiation with UV light,[1] although it has a similar hydrogen bonding scheme.[7] This indicates that some additional factors should be taken into account for the photoreduction. If the positively charged terminal oxygen atom forms a charge transfer complex with the negatively charged alkylamine nitrogen atom in the complex (ii), the Mo(V) species formed by the UV irradiation would be stabilized. Since the propyl- and isopropylammonium cations have considerably loose contacts with the neighboring molecules in the crystal, such a charge transfer complex would be easily formed in the solid state. When the crystal is allowed to stand in the dark after irradiation, the charge transfer complex returns to the initial hydrogen bonding complex (i) and its color is bleached.[1] On the other hand, the ammonium cation has more than four hydrogen bonds with the neighboring heptamolybdates and water molecules. Moreover, it is closely packed in the crystal. The formation of the charge transfer complex may be inhibited and the coloration cannot be observed even if the crystal is exposed to UV light.

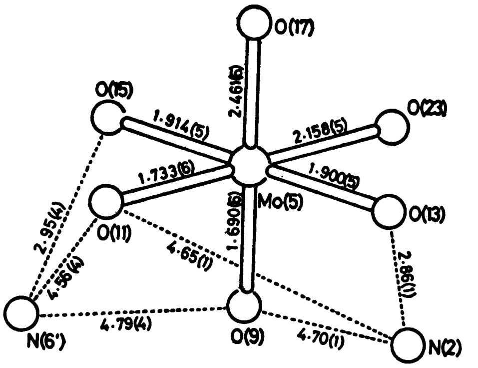
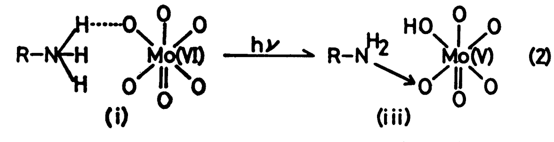


Fig. 7. Bond distances (l/Å) and interatomic distances (l/Å), (less than 5 Å), between the non-bonded atoms in the environment of the Mo(5) site in IPAM. Positions of H atoms are omitted for clarity.

It is concluded that the photochromism of alkylammonium isopolymolybdates is brought about by the following reaction process (2) instead of (1) in the crystal. The mechanism of the change in color when the photoreduced crystal is dissolved in water has been discussed elsewhere.[9]



(2)

References

1) T. Yamase and T. Ikawa, *Bull. Chem. Soc. Jpn.*, **50**, 746 (1977).

2) T. Yamase, T. Ikawa, Y. Ohashi, and Y. Sasada, *J. Chem. Soc., Chem. Commun.*, **1979**, 697.

3) M. Isobe, F. Marumo, T. Yamase, and T. Ikawa, *Acta Crystallogr., Sect. B*, **34**, 2728 (1978).

4) T. Yamase, *J. Chem. Soc., Dalton Trans.*, **1978**, 283.

5) P. Main, "MULTAN 78, A System of Computer Programms for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," University of York, York (1978).

6) "International Tables for X-Ray Crystallography," Vol. IV, The Kynoch Press, Birmingham (1974), p. 72.

7) H. T. Evans, B. M. Gatehouse, and P. Leverett, *J. Chem. Soc., Dalton Trans.*, **1975**, 505.

8) K. Sjöbom and B. Hedman, *Acta Chem. Scand.*, **27**, 3673 (1973).

9) T. Yamase, R. Sasaki, and T. Ikawa, *J. Chem. Soc., Dalton Trans.*, **1981**, 628.