Infrared and Polarized Raman Spectra of (C$_5$H$_7$N$_2$)$_6$Mo$_7$O$_{24}$·3H$_2$O

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2-Aminopyridinium heptamolybdate trihydrate, (C$_5$H$_7$N$_2$)$_6$ Mo$_7$O$_{24}$·3H$_2$O, is the first heptamolybdate with a multifunctional amine aromatic cation. An analysis of the infrared and polarized Raman spectra of the compound is reported. In the crystal, MoO$_6$ octahedra are found to have a strongly distorted structure. The coincidence of the majority of infrared and Raman bands confirms a noncentrosymmetric structure for the Mo$_7$O$_{24}^{6-}$ anion. Water bands are assigned by observing the corresponding bands in the deuterated compound. Stretching modes of water show hydrogen bonds of varying strengths. © 1994 Academic Press, Inc.

INTRODUCTION

2-Aminopyridinium heptamolybdate trihydrate is the first heptamolybdate structure containing a multifunctional amine aromatic cation (1). The crystal structure of this compound is characterized by very extensive hydrogen bonding between aminopyridinium nitrogen atoms, water oxygen atoms, and heptamolybdate oxygen atoms. The physical properties and solid state structure of amine molybdates depend on the nature of hydrogen bonding (1). Infrared and polarized Raman spectra of (C$_5$H$_7$N$_2$)$_6$Mo$_7$O$_{24}$·3H$_2$O (abbreviated as APHM) are recorded and analyzed to study the vibrational characteristics and the influence of hydrogen bonding on the structure and properties of the crystal.

EXPERIMENTAL

Single crystals of (C$_5$H$_7$N$_2$)$_6$Mo$_7$O$_{24}$·3H$_2$O were provided by P. Roman, Departamento de Quimica Inorganica, Universidad del Pais Vasco, Spain. The sample was prepared as explained in Ref. (1). A well-polished crystal (4 × 2 × 1 mm) cut with sides parallel to the crystallographic axes was used to record the Raman spectra for the orientations $a(bb)c$, $a(ba)c$, $a(cb)c$, and $a(ca)c$. Raman spectra were recorded at room temperature (300 ± 3 K) on a Spex 1401 Raman spectrometer (slitwidths 300–400 μm) equipped with a Spectra Physics Model 165 argon ion laser. The 514.5-nm line with a laser power of 40 mW

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was used, with a spectral resolution better than 3 cm^{-1}. Infrared spectra were recorded on a Perkin–Elmer 577 spectrophotometer with a KBr pellet as sample.

The compound was deuterated by dissolving the crystals in heavy water of isotopic purity 99.4%. Raman spectrum of the deuterated polycrystalline compound was recorded on a Dilor Z24 Raman spectrometer using a 514.5-nm line with a laser power of 300 mW.

FACTOR GROUP ANALYSIS

APHM crystallizes in the monoclinic system with space group $P2_1/n - C_{2h}^5$. It contains four formula units per unit cell. All the atoms occupy the general site C_1. The compound contains discrete Mo$_7$O$_{24}^{6-}$ anions, C$_5$H$_7$N$_2^+$ cations, and water molecules. The polyanions build up an infinite sequence along the b axis to form the (0 1 0) plane in such a way that the plane containing Mo(5), Mo(6), and Mo(7) atoms coincides with it. Between the layers five cations and one water molecule are inserted. The heptamolybdate anion is built up of seven very distorted molybdenum–oxygen octahedra linked together by bridging oxygen atoms. The polyanion has no center of symmetry and lies in a general position in the unit cell. Six crystallographically independent 2-aminopyridinium cations are present for each Mo$_7$O$_{24}^{6-}$ anion (1).

Factor group analysis by the correlation method (2) gives 1485 normal modes at $k = 0$ and they split into (Tables 1 and 2)

$$\Gamma_{\text{APHM}} = 372A_g + 372B_g + 371A_u + 370B_u.$$

INTERPRETATION OF SPECTRA

Vibrational assignments are carried out in terms of the characteristic vibrations of MoO$_6$ groups, aminopyridinium cations, and water molecules (Table 3).

MoO$_6$ Vibrations

The symmetric stretching mode ν_1 of the MoO$_6$ group (3), which is expected to be the most intense band in the Raman spectrum, is observed as a very strong band around 935 cm^{-1} in $a(bb)c$ and $a(ba)c$ orientations with

TABLE 1
Factor Group Modes of $(C_5H_7N_2)_6Mo_7O_{24} \cdot 3H_2O$ at $k = 0$,
Space Group $P2_1/n - C_{2h}^5$, $Z = 4$, $Z^B = 4$

	Factor group modes of C_{2h} species			
	A_g	B_g	A_u	B_u
Internal modes of				
$Mo_7O_{24}^{6-}$	87	87	87	87
H_2O	9	9	9	9
Rotational modes of				
$Mo_7O_{24}^{6-}$	3	3	3	3
H_2O	9	9	9	9
Translational modes of				
$Mo_7O_{24}^{6-}$	3	3	3	3
H_2O	9	9	9	9
C	90	90	90	90
H	126	126	126	126
N	36	36	36	36
Acoustic modes	0	0	−1	−2
	372	372	371	370

$\Gamma_{1485} = 372A_g + 372B_g + 371A_u + 370B_u$

TABLE 2
Correlation Scheme for the Internal Modes of $Mo_7O_{24}^{6-}$ and H_2O in $(C_5H_7N_2)_6Mo_7O_{24} \cdot 3H_2O$, $Z^B = 4$

Free ion symmetry C_{2v}	Site symmetry C_1	Factor group symmetry C_{2h}
$Mo_7O_{24}^{6-}$		
92 $23A_1(\alpha_{xx}, \alpha_{yy}, \alpha_{zz})$		$(\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy})\ A_g$ 87
88 $22B_1(\alpha_{xz})$	A	$(\alpha_{xz}, \alpha_{yz})\ B_g$ 87
84 $21A_2(\alpha_{xy})$		A_u 87
84 $21B_2(\alpha_{yz})$		B_u 87

Molecular symmetry C_{2v}	Site symmetry C_1	Factor group symmetry C_{2h}
H_2O		
24 $2A_1(\nu_1, \nu_2)$		A_g 9
12 $B_1(\nu_3)$	A	B_g 9
		A_u 9
		B_u 9

TABLE 3
Spectral Data (cm^{-1}) and Band Assignments of $(C_5H_7N_2)_6Mo_7O_{24} \cdot 3H_2O/D_2O$

$(C_5H_7N_2)_6Mo_7O_{24} \cdot 3H_2O$					$(C_5H_7N_2)_6Mo_7O_{24} \cdot 3D_2O$		
Raman							
(A_g) a(bb)c	(A_g) a(ba)c	(B_g) a(cb)c	(B_g) a(ca)c	IR	Raman	IR	Assignments
	3477			3480		3460	Terminal N–H stretch
3410				3410			
3368	3364					3340	
3323		3337				3300	ν_1, ν_3 H_2O
3270		3275		3280			
3178	3174	3177	3183			3160	
3137		3139		3125			N–H stretch
3097	3098	3098	3095				
3043	3043	3046		3040	3087	3060	C–H stretch
2928		2870					Combinations
2850		2850					
		2635		2640			
					2505	2510	
					2430	2440	ν_1, ν_3 D_2O
					2370	2370	
						2315	
2312							
1780		1782		1880			Combinations
1625	1620			1640		1640	
1600	1608	1613	1615	1605		1610	
1543	1545	1545	1546	1530		1570	Pyridinium ion ring stretch
						1505	

TABLE 3—*Continued*

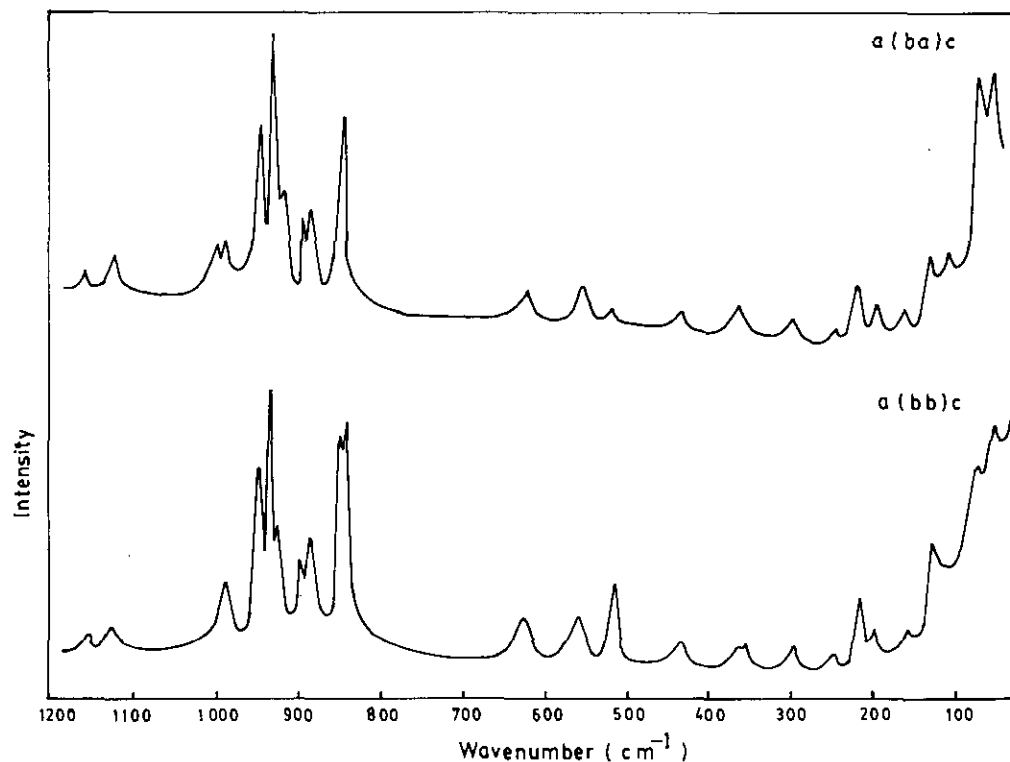| (C₅H₇N₂)₆Mo₇O₂₄ · 3H₂O					(C₅H₇N₂)₆Mo₇O₂₄ · 3D₂O		
Raman							
(A_g) a(bb)c	(A_g) a(ba)c	(B_g) a(cb)c	(B_g) a(ca)c	IR	Raman	IR	Assignments
1478	1478	1478	1473	1465		1455	
1416	1420			1405		1405	
1378	1380	1380	1383	1360	1377	1360	ν_2 H₂O/D₂O and pyridine ring stretch
1333	1330		1330				
1323	1320	1320	1318	1305	1317	1300	
1245	1246	1246	1246	1230		1230	Pyridine ring hydrogen bend
1162	1165	1168	1173	1150		1150	
1130	1130	1130	1130	1110	1121		
						1050	
	1005	1008				1010	
992	995	990	993	975	998	980	Pyridine ring breathing
948	948	945	946		962	945	
935	938	936	935	930	936	930	ν_1 MoO₆
928	928	921	920	920			
900	898	895	898	895	900	895	
887	890	888	886	880	871		ν_3 MoO₆
				865		860	
849	850	854					
845		848	848	835	850		ν_2 MoO₆
					787	790	
				760	750	750	
				705		700	C–H out-of-plane deformation
625	625	628	624	640	631	620	In-plane ring deformation
				600		610	
559	557	556	557	550	559	575	
517	520	519	519	515		540	ν_5 MoO₆
				465		465	$\nu_w{}^a$ H₂O/D₂O
435	435	433	433	410			ν_4 MoO₆
368	365	375	365	380	389	390	
355		355		350	349	355	Out-of-plane ring deformation
					323	340	
297	299	298	298			300	ν_6 MoO₆
						265	
248	248	248	245		238		
217	220	220	218	223	220	220	Metal–N vibrations
196	197	195	195	205	189		Mo–O–Mo deformation
160	164	165	163		170		
132	132	130	128		135		
	118	90	88		88		External modes
72	75	75	75		70		
56	58	58	59				

^{a} w, wagging.
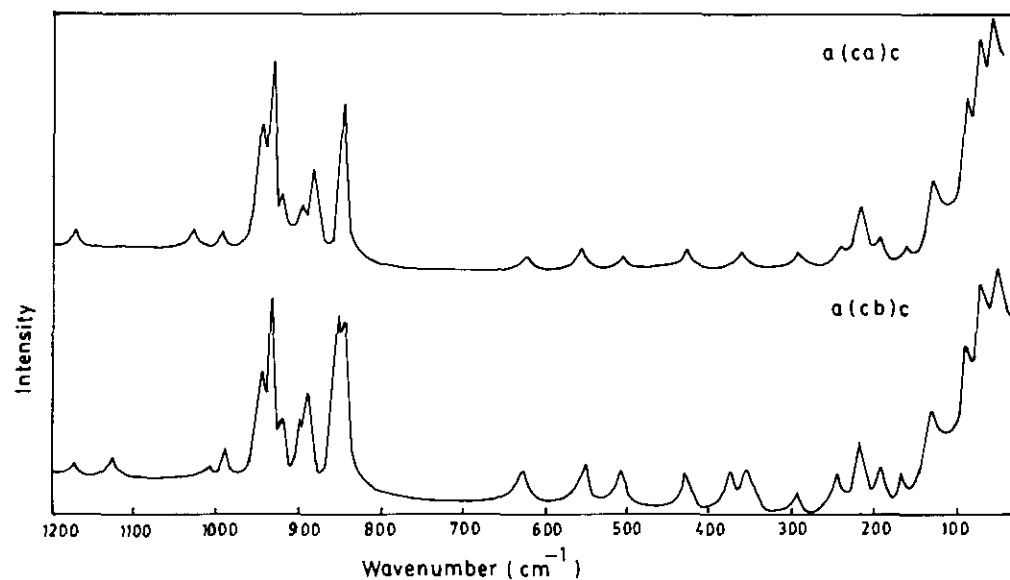
FIG. 1.   Raman spectra of $(C_5H_7N_2)_6Mo_7O_{24} \cdot 3H_2O$ in the region 50–1200 cm^{-1} for $a(bb)c$ and $a(ba)c$ orientations.

additional bands at 948 and 928 cm^{-1} (Fig. 1). In the infrared spectrum (Fig. 5) two strong bands are observed at 930 and 920 cm^{-1}. The ν_1 mode has the polarizability tensor components α_{xx}, α_{yy}, and α_{zz} (x, y, and z correspond to the a, b, and c axes), but in C_{2h} symmetry α_{xx}, α_{yy}, α_{zz}, and α_{xy} belong to A_g species (Table 2). Hence, the ν_1

mode is expected to appear in the A_g orientation without any distortions in the MoO$_6$ octahedra. From the correlation table (Table 2) it can be seen that the ν_1 mode is also active in the B_g orientation. The appearance of this mode in B_g orientation is due to the distortion of the ion, whose site is lowered from O_h to C_1, which contributes the α_{xz}

FIG. 2.   Raman spectra of $(C_5H_7N_2)_6Mo_7O_{24} \cdot 3H_2O$ in the region 50–1200 cm^{-1} for $a(cb)c$ and $a(ca)c$ orientations.
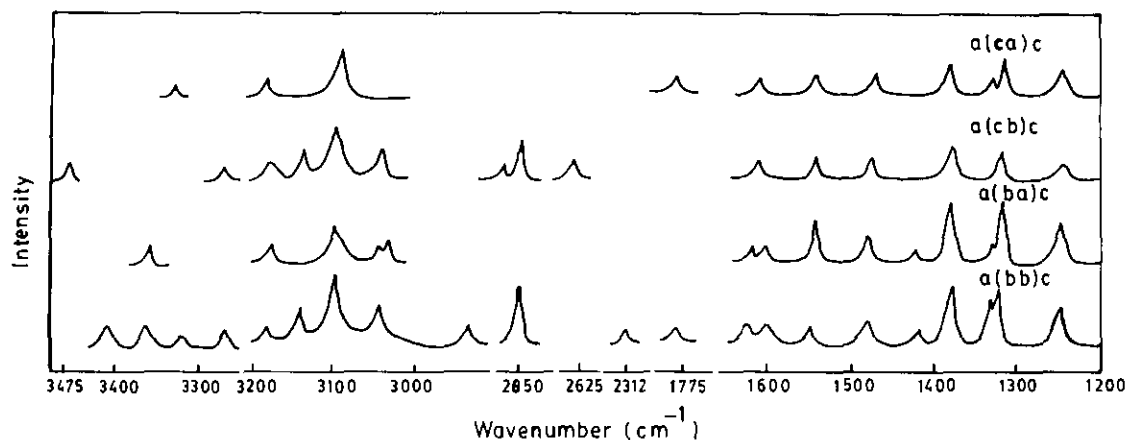
FIG. 3.   Raman spectra of $(C_5H_7N_2)_6Mo_7O_{24} \cdot 3H_2O$ in the region 1200–3600 cm^{-1}.

and α_{yz} components (4). Thus the ν_1 mode is observed with less intensity in the $a(cb)c$ and $a(ca)c$ orientations (Fig. 2). The appearance of additional bands may be due to varying Mo–O bond lengths (1.693–2.541 Å) present in the MoO$_6$ octahedra, which are classified as short, intermediate, long, and very long (1). The intensity of this mode in the IR spectrum is found to increase considerably on deuteration and the 920-cm^{-1} line becomes extinct. Similarly, in the Raman spectrum of the deuterated compound (Fig. 4), the very strong band shifts to 962 cm^{-1}. This could be due to the breaking up of hydrogen bonds on deuteration.

The lower the stretching frequency for the shortest metal–oxygen bond, the more regular the structure (5). For this compound the bands are shifted considerably to

the higher wavenumber side, showing distortions in the MoO$_6$ octahedra.

The doubly degenerate asymmetric stretching mode ν_2 is observed with complete removal of degeneracy in the $a(bb)c$ and $a(cb)c$ orientations. In the infrared spectrum two bands are observed at 835 and 760 cm^{-1}. For the deuterated compound, these bands are obtained at 790 and 750 cm^{-1}, while in the Raman spectrum three bands are obtained at 850, 787, and 750 cm^{-1}. The degeneracy is also lifted for the ν_3 mode. The intensity of IR bands supports the assignment of ν_2 and ν_3 modes. Activation of Raman and IR inactive modes is due to the lowering of symmetry of the MoO$_6$ ion. An asymmetric bending mode ν_4 is observed as a single band around 433 cm^{-1} in all the orientations and as a weak band at 410 cm^{-1} in
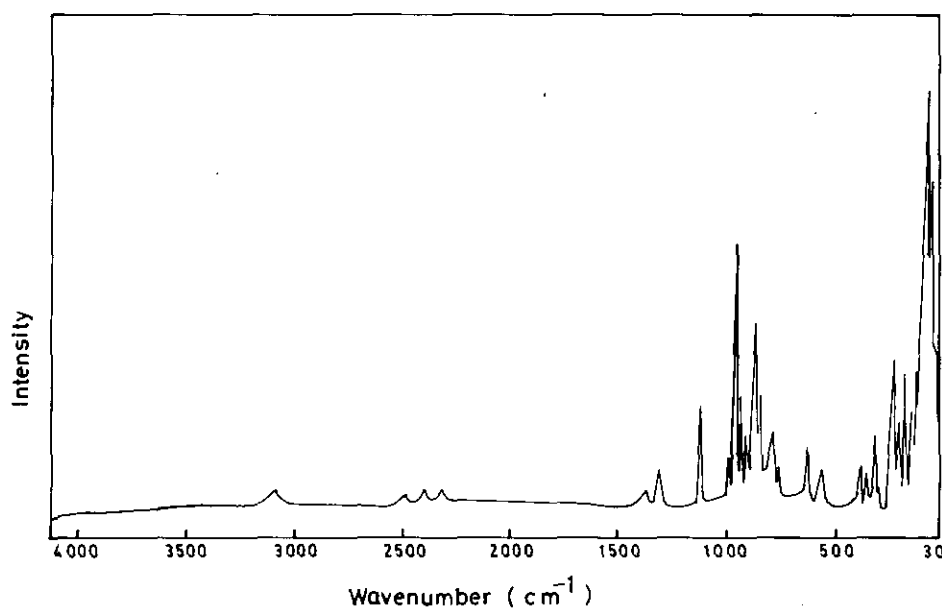

FIG. 4.   Raman spectrum of $(C_5H_7N_2)_6Mo_7O_{24} \cdot 3D_2O$ in the region 30–4000 cm^{-1}.

the infrared spectrum. Partial removal of degeneracy is observed for the symmetric bending mode ν_5 in all the orientations in Raman spectra. The ν_6 mode, which is normally inactive in the infrared and Raman spectra, is observed in three orientations around 298 cm^{-1} in the Raman spectra and at 300 cm^{-1} in the IR spectrum of the deuterated compound.

Coincidence of the majority of Raman and infrared bands confirms a noncentrosymmetric structure for the $Mo_7O_{24}^{6-}$ anion as observed from the XRD structural data. Bands observed at 920–948, ~890, 835–854, 515–559, and 197 cm^{-1} compare well with $Mo_7O_{24}^{6-}$ bands of molybdenum oxide catalysts identified by Kim et al. (3). The bending mode (ν_4) at 433 cm^{-1} is observed to be at a value higher than that in these catalysts (~350 cm^{-1}).

$C_5H_7N_2^+$ Vibrations

The vibrational modes of the pyridinium ion undergo well-characterized shifts depending upon whether the pyridine is protonated or bound through the nitrogen lone pair (1, 5). In 2-aminopyridinium cation one of the C–N bonds has a considerable degree of double-bond character (1). The pyridinium ring stretching modes (7) are obtained at 1640, 1605, 1530, and 1465 cm^{-1} in the IR spectrum. In the Raman spectra very weak bands are observed in this region. One additional band at 1505 cm^{-1} is observed in the IR spectrum of the deuterated compound. A totally symmetric pyridinium ring breathing mode (7) is observed as a medium intensity band at 992 cm^{-1} in the $a(bb)c$ orientation and as weak bands in all other orientations. The bands obtained around 620 cm^{-1} are assigned to the

in-plane ring deformation modes (7). This is observed as a very strong band in the IR spectrum centered at 640 cm^{-1}. Another band is obtained at 600 cm^{-1}. On deuteration these bands shift to 620 and 610 cm^{-1} and the intensity is considerably reduced. Out-of-plane ring deformation modes (7) are obtained as broad bands in the region 355–375 cm^{-1} in Raman spectra and at 380 and 350 cm^{-1} in the IR spectrum. For the deuterated compound three bands are obtained in both the infrared and the Raman spectra in the region 390–323 cm^{-1}. The bending vibrations of the hydrogen atoms on the pyridine ring (8) are observed in the region 1323–1130 cm^{-1} in all orientations for the Raman spectra. They are observed from 1305 to 1110 cm^{-1} in the IR spectrum. The 1110-cm^{-1} band is absent in the IR spectrum of the deuterated compound, while the 1230-cm^{-1} band appears with reduced intensity. This confirms that they are N–H stretching vibrations. In the Raman spectrum of the deuterated compound two medium intense bands are obtained at 1317 and 1121 cm^{-1}. The strong bands observed at 705 cm^{-1} in the IR spectrum of the parent compound and at 700 cm^{-1} for the deuterated compound are due to out-of-plane C–H deformation modes (7).

C–H stretching modes are observed around 3040 cm^{-1} in both Raman and IR spectra (7). The intensity of this mode is not affected by deuteration, and the corresponding bands are obtained at 3087 cm^{-1} in the Raman spectrum (Fig. 3) and at 3060 cm^{-1} in the IR spectrum. It is very difficult to unambiguously assign the N–H and O–H stretching modes. The stronger Raman bands are tentatively assigned to N–H stretching modes.

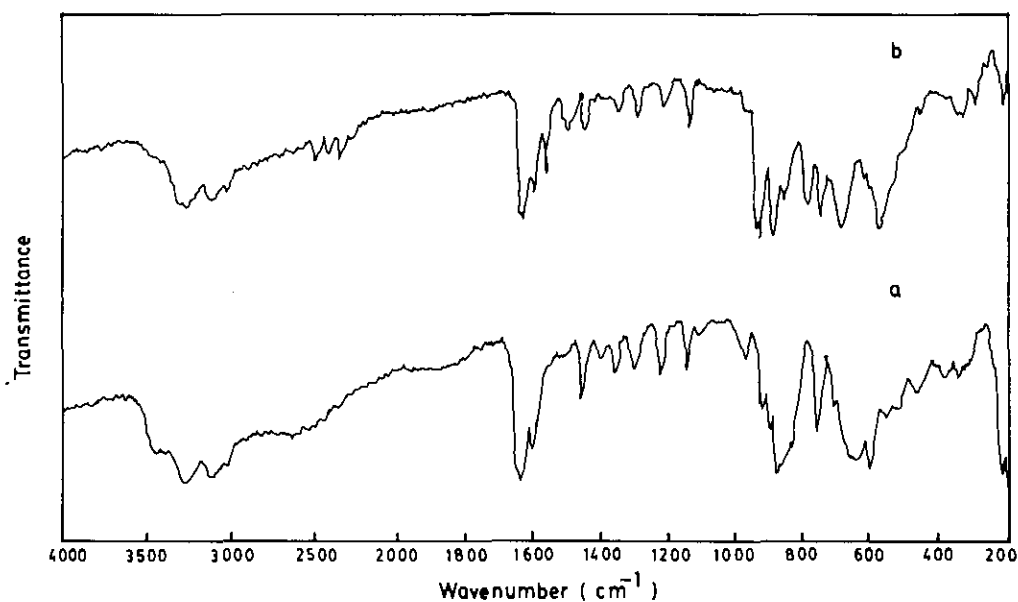The medium intensity bands observed in the IR spec-

FIG. 5. Infrared spectra of (a) $(C_5H_7N_2)_6Mo_7O_{24} \cdot 3H_2O$ and (b) $(C_5H_7N_2)_6Mo_7O_{24} \cdot 3D_2O$.

trum at 3480 and 3410 cm^{-1} are assigned to the terminal N–H stretching modes (9, 10). For the deuterated analogue only one band is obtained at 3460 cm^{-1}. On deuteration new bands appear at 2510 and 2505 cm^{-1} in the IR and Raman spectra, respectively.

H_2O/D_2O Vibrations

Stretching modes of water are observed in the region 3368–3270 cm^{-1}. For the deuterated compound D_2O bands appear around 2440 and 2370 cm^{-1} in both the Raman and the IR spectra. The bending modes of H_2O and D_2O cannot be unambiguously identified as they fall in the same region as the pyridinium ring stretching vibrations. The position of bands in the H_2O stretching region indicates the presence of hydrogen bonds of varying strengths, in agreement with X-ray diffraction studies, which predict the existence of four different types of hydrogen bonds of lengths 2.67–3.24 Å, N–H· · ·O, N–H· · ·O$_w$, O$_w$–H$_w$· · ·O, and O$_w$–H$_w$· · ·O$_w$, in the crystal.

External Modes

Bands below 265 cm^{-1} are due to the translations and rotations of MoO$_6$ groups, aminopyridinium ions, and lattice modes of water. Bands observed around 200 cm^{-1} are assigned to the Mo–O–Mo deformation mode (11, 12). The metal–nitrogen vibrations appear in the region 150–250 cm^{-1} (13).

CONCLUSIONS

MoO$_6$ octahedra, which compose the Mo$_7$O$_{24}^{6-}$ ion, are found to be strongly distorted in the crystal. The infrared and Raman inactive ν_6 mode is observed. The coincidence of the majority of infrared and Raman bands confirms the noncentrosymmetric structure of the polyanion. Bands in the stretching region of water show the presence of hydrogen bonds of varying strengths.

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