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Crystal Structure of the Pentamolybdate Complex Coordinated by Adenosine-5′-monophosphoric Acid

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$Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ (where amp is adenosine-5′-monophosphate) has been crystallized by acidifying a solution containing $Na_2MoO_4\cdot 2H_2O$ and adenosine-5′-monophosphoric acid (AMP = H_2amp) to pH 3—4. A single-crystal X-ray structural analysis of a colorless crystal of $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ [space group $P3_121$, $a = 27.494(2)$, $c = 10.165(1)$ Å, $V = 6654.5(9)$ Å^3, $Z = 3$, $R = 0.086$, and $R_w = 0.073$ for 1087 independent data with $I > 3\sigma(I)$] showed that the anion is coordinated by two amp-phosphate-O atoms. $[(Hamp)_2Mo_5O_{15}]^{2-}$ is isostructural with $[(OPO_3)_2Mo_5O_{15}]^{6-}$, in which two PO_4 tetrahedra span either side of a ring of edge- and corner-linked MoO_6 octahedra. Two $[(Hamp)_2Mo_5O_{15}]^{2-}$ anions are connected with ionic bondings of the O_{anion}–Na–O_{water}–Na–O_{anion} linkage, to be oriented parallel to the *c*-axis. The adenine-base ring of the amp ligand is stacked by that of the neighboring anion at a distance of 3.4 Å along the *c*-axis. The ^{13}C and ^{31}P NMR spectra of a solution containing $Na_2MoO_4\cdot 2H_2O$ and AMP at different pH levels indicate the formation of the pentamolybdate complex at pH < 6.

The interaction of the polyoxometalates with biomolecules is a new growing area spurred by the biological activities of selected polyoxometalates. From this standpoint, it is important to investigate the structural chemistry of complexes being formed between the polyoxometalates and biomolecules. The polyoxomolybdates have a potent in vivo antitumor activity against MX-1 human breast, OAT human lung, and CO-4 human colon cancer xenografts.[1,2] We have characterized the crystal structure of γ-typed octamolybdates coordinated by chiral lysines,[3] and report here on the crystal structure of the pentamolybdate coordinating adenosine-5′-monophosphoric acid, $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ (where amp is adenosine-5′-monophophate), in which two AMP-PO_4 tetrahedra cap either side of an irregular ring of five MoO_6 octahedra linked by one corner-shared and four edge-shared contacts. This is the first example of a structural characterization of polyoxomolybdates coordinated by nucleotides to our knowledge, although the formation of stable molybdate complexes with nucleotides was reported.[4] The structure of the complex is related to that of $(RPO_3)_2Mo_5O_{15}{}^{n-}$, where R = O,[5,6] $S(C_2H_4)_2NHCH_2$,[7] and $CH_2(C_2H_4)_2NHCH_2$.[7] The ^{13}C and ^{31}P NMR spectroscopy of $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ is also described. Whether the formation of $[(Hamp)_2Mo_5O_{15}]^{2-}$ is relevant to the antitumor action of the polyoxomolybdates cannot be said at this point, but we have concentrated on strong interactions which are peculiar to the polyoxomolybdate, and which do not occur with the polyoxotungstates.

Experimental

All of the reagents required for the preparation were used without further purifications. $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ was prepared as follows. $Na_2MoO_4\cdot 2H_2O$ (2 g; 8.3 mmol) and AMP (1 g; 2.7 mmol) were dissolved with stirring in water (10 cm^3). The solution was adjusted to pH 4 with $HClO_4$, and then stirred for 30 min. The resulting white precipitate was filtered off and recrystallized from water at room temperature. After 1 d, colorless long and thin crystals were obtained. IR spectrum: 3428vs, 1647vs, 1508w, 1481m, 1423m, 1379w, 1336m, 1305m, 1253m, 1216m, 1123vs, 1079vs, 994vs, 915vs, 797s, 704vs, 636s, 561s cm^{-1}.

Data collection for an X-ray structure analysis was done on a Rigaku AFC-5S diffractometer with a graphite monochromator and Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) generated at 45 kV and 25 mA. Crystal data and the experimental conditions of the $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ are listed in Table 1. The cell dimensions were obtained from the setting angles of 25 reflections in the range of $20° < 2\theta < 25°$. No significant decay in the intensity of the three standards was observed. The positions of the Mo atom were determined by a direct method using SAPI91.[8] Na, O, P, and C atoms were located from a difference Fourier synthesis. Lorenz and polarization factors were applied and an absorption correction was made based on the isotropically refined structure, using the DIFABS program.[9] The collection factors were 0.25—1.03. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme used was $w^{-1} = \sigma^2(F_o)$. The maximum and minimum heights in the final difference synthesis were 0.6 and -0.6 e Å^3. All of the calculations were performed on a Micro VAX II computer using the TEXSAN crystallografic package.[10] Table 2 shows the atomic coordinates for $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$. The Na atom and the water O atoms of O(17) and O(19) show large thermal displacement parameters and are apparently disordered. The complete $F_o - F_c$ date are deposited as Document No. 69059 at the Office of the Editor of Bull. Chem. Soc. Jpn.

The ^{13}C and ^{31}P NMR spectra were obtained on a JEOL JNM GSX-270 FT-NMR spectrometer with a JEOL GSX-270 NMR data-processing system. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) and 85% H_3PO_4 were used as internal and external references

Table 1. Crystal Data, Structure Determination, and Refinement Data for $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$

Formula	$Mo_5O_{30}C_{20}N_{10}Na_2P_2$	Scan method	ω–2θ
M.W.	1447.9	Data collecn range	$2° \leq 2\theta \leq 60°$
Crystal system	Trigonal	Standard reflcns	Three every 100 reflcns
Space group	$P3_121$	No. of data measd	7168
a/Å	27.494(2)	No. of unique data	6792
c/Å	10.165(1)	No. of obsd data $[F > 3\sigma(F)]$	1087
V/Å^3	6654.5(9)	No. of variables	151
Z	3	Solution	SAPI91 direct method
D_c/g cm^{-3}	1.204	Refinement	Full matrix least squares
μ/cm^{-1}	7.86	R	0.089
F(000)	2076	R_w	0.075
Cryst. size/mm	$0.3 \times 0.1 \times 0.1$	GOF	2.53
Radiaion	Mo $K\alpha$	Max shift/error	0.003
λ/Å	0.71069		

Table 2. Atomic Coordinates and Isotropic Thermal Parameters for $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$

Atom	x	y	z	B_{iso}(Å^2)
Mo(1)	0.34742(26)	0.34742(26)	1/2	6.8(2)
Mo(2)	0.37464(21)	0.46252(20)	0.31957(44)	6.0(1)
Mo(3)	0.51237(20)	0.55993(21)	0.35753(46)	6.1(1)
P(1)	0.48124(59)	0.42592(57)	0.3662(12)	4.5(3)
Na(1)	0.5811(15)	0.5170(16)	0.1186(34)	21(1)
O(1)	0.3189(13)	0.3022(14)	0.3841(26)	8(1)
O(2)	0.3507(12)	0.4290(11)	0.1701(25)	6.0(8)
O(3)	0.3400(15)	0.4952(15)	0.3411(29)	8(1)
O(4)	0.5054(14)	0.6160(15)	0.4147(26)	8(1)
O(5)	0.5701(14)	0.5931(14)	0.2432(30)	8(1)
O(6)	0.3310(12)	0.4063(12)	0.4498(23)	5.5(8)
O(7)	0.4497(13)	0.5196(14)	0.2547(28)	8(1)
O(8)	0.5511(14)	0.5511(14)	1/2	6(1)
O(9)	0.4212(12)	0.4091(11)	0.3542(22)	4.3(7)
O(10)	0.4331(11)	0.5043(11)	0.4957(23)	4.3(7)
O(11)	0.5123(12)	0.4812(12)	0.2950(24)	4.6(7)
O(12)	0.4911(12)	0.3830(13)	0.3092(26)	5.9(8)
O(13)	0.5095(13)	0.2985(12)	0.1528(26)	5.3(8)
O(14)	0.5029(13)	0.2412(14)	0.4618(29)	7(1)
O(15)	0.4068(16)	0.2022(17)	0.2960(32)	11(1)
O(16)	0.5042(19)	0.5042(19)	0	10(2)
O(17)	0.6335(23)	0.5157(24)	0.2756(46)	20(2)
O(18)	0.5983(16)	0.4627(16)	-0.0413(31)	11(1)
O(19)	0.6487(41)	0.6122(43)	-0.001(12)	20(2)
N(1)	0.7222(14)	0.2868(14)	0.2323(27)	3.4(8)
N(2)	0.6214(14)	0.2456(14)	0.2384(28)	3.5(8)
N(3)	0.6717(15)	0.3877(15)	0.2496(30)	5(1)
N(4)	0.5919(18)	0.3143(17)	0.2499(33)	5(1)
N(5)	0.7886(13)	0.3880(13)	0.2415(28)	2.8(8)
C(1)	0.5361(21)	0.2778(20)	0.2378(47)	5(1)
C(2)	0.5068(23)	0.2822(22)	0.3625(48)	7(1)
C(3)	0.4487(24)	0.2644(23)	0.3203(44)	7(1)
C(4)	0.4543(19)	0.2911(19)	0.1784(40)	5(1)
C(5)	0.4581(17)	0.3449(18)	0.1890(39)	4(1)
C(6)	0.6741(20)	0.2450(19)	0.2318(37)	4(1)
C(7)	0.6328(20)	0.3002(21)	0.2419(38)	4(1)
C(8)	0.6849(19)	0.3458(19)	0.2464(38)	4(1)
C(9)	0.7382(20)	0.3471(19)	0.2364(39)	4(1)
C(10)	0.6193(18)	0.3751(18)	0.2509(34)	3(1)

for the ^{13}C and ^{31}P NMR spectra, respectively. Measurements were done at 30 °C for ^{13}C and 25 °C for ^{31}P. The parameters for measurements of the ^{13}C and ^{31}P NMR spectra are as follows: pulse width, 7.0 and 17.0 μs; acquisition time, 0.963 and 0.819 s; delay time, 4.037 and 2.037 s; sweep width, ±8500 and ±10000 Hz, respectively. The ^{13}C and ^{31}P chemical shifts are positive for higher frequencies and negative for lower frequencies.

Results and Discussion

Crystal Structure. Figure 1 shows the crystal structure of the $[(Hamp)_2Mo_5O_{15}]^{2-}$ anion. It consists of five MoO_6 octahedra forming a planar ring and two AMP-PO_4 tetrahedra capping above and below the ring. Five MoO_6 octahedra are linked by one corner-shared (by O(8) atom) and four edge-shared contacts. Since a unique crystallographic C_2-axis passing through the Mo(1) and O(8) atoms exists, the positions of three crystallographically independent Mo atoms were determined by an X-ray structure analysis. Each MoO_6 octahedron for the Mo(1) and Mo(2) sites comprises two *cis* terminal O atoms with Mo–O bond distances of 1.60(3)—1.80(3) Å, two *trans* μ-O atoms shared by two Mo atoms with Mo–O bond distances of 1.84(3)—1.98(3) Å, and two *cis* μ_3-O atoms shared by P and two Mo atoms with Mo–O bond distances of 2.25(3) —2.41(3) Å. For the Mo(3)O_6 octahedron, one of the two *cis* μ_3-O atoms is replaced by a μ-

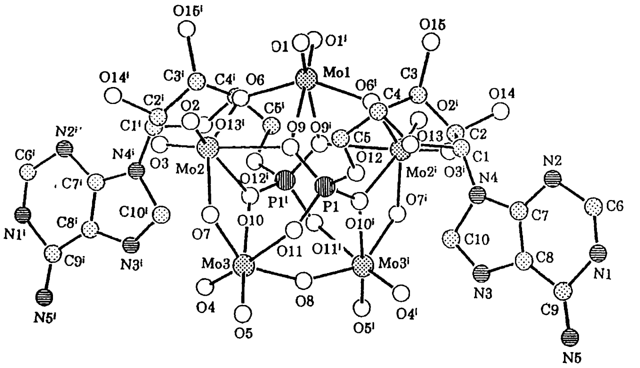

Fig. 1. Structure of $[(Hamp)_2Mo_5O_{15}]^{2-}$. ⊛, ○, ◍, ◌ and ⊜ represent the atoms of molybdenum, oxygen, phosphorus, carbon, and nitrogen, respectively.

O atom (O(11)) shared by P(1) and Mo(3) atoms. The P–O bond distances of the PO_4 tetrahedron in the amp ligand are 1.46(3)—1.51(3) Å. The O(5) and O(11) atoms in the pentamolybdate framework are coordinated by a Na(1) atom with a resultant six-fold coordination of a Na(1) atom with Na···O distances of 2.16(5)—2.59(4) Å (Fig. 2). The O(16) atom is coordinated by two Na atoms, Na(1) and Na(1^{ii}), where the latter is associated with the neighboring anion. Selected bond distances and angles are given in Table 3. As shown in Table 3, short O···O (O(5)···O(19^{ii}), O(7)···O(16), O(7)···O(18^{ii}), O(11)···O(16), and O(11)···O(17)) distances of < 3.2 Å imply a hydrogen-bonding network between these oxygen atoms of both the anion and the lattice water. Although it is expected that the Mo–O distance increases with increasing coordination number of the O atom, the Mo(3)–O(5)distance (1.80(3) Å) is long compared with other Mo–$O_{\rm terminal}$ distances (1.60(3)—1.75(3) Å). This arises from additional interactions of the O(5) atom with both the Na(1) atom at an O(5)···Na(1) distance of 2.59(4) Å and the O(19^{ii}) atom at an O(5)···O(19^{ii}) distance of 2.8(1) Å (Fig. 2). Table 4 shows selected interatomic distances. The edge- and corner-sharing MoO_6 octahedra in the pentamolybdate framework show 3.394(7)—3.402(6) Å and 3.677(9) Å for the neighboring Mo···Mo distances, respectively. There are two kinds of the Mo–O(μ_2)–Mo angles for the pentamolybdate framework, 122(2)—125(2)° and 155(2)°, which correspond to the edge- and corner-sharing MoO_6 octahedra, respectively. The Mo(1)···Mo(3), Mo(2)···Mo(2^{i}), and Mo(2)···Mo(3^{i}) distances are 5.505(9)—5.623(7) Å, and the P(1)···P(1^{i}) distance is 3.80 Å. The above structural features are the same as those for $[(RPO_3)_2Mo_5O_{15}]^{n-}$ ($R = O$,[5,6] $S(C_2H_4)_2NHCH_2$,[7] and $CH_2(C_2H_4)_2NHCH_2$).[7]

The C–C, C–O, and C–N bond distances for the amp ligand are 1.35(5)—1.59(5), 1.42(4)—1.57(4), and 1.25(4)–1.49(5) Å, respectively. The adenine-base plane is almost parallel to the *ab* plane, and make a dihedral angle of 133° with

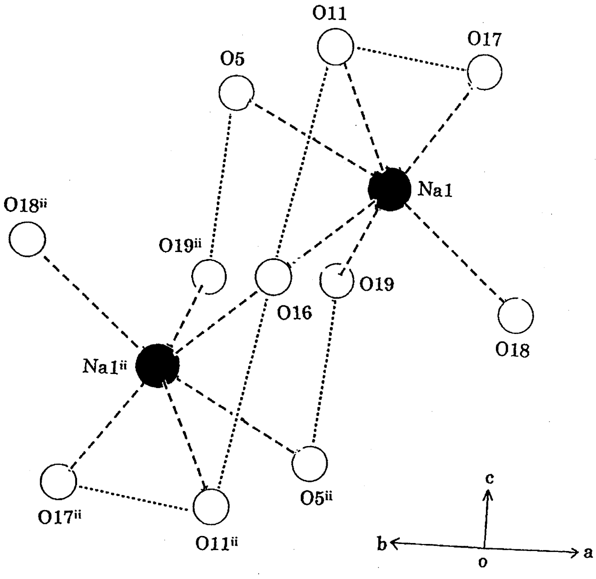

Fig. 2. Coordination sphere around Na^+ ion.

Table 3. Bond Distances and Angles for $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$

Mo(1)–O(1)	1.60(3)/Å	O(12)–C(5)	1.57(4)/Å
O(1^{i})	1.60(3)	O(13)–C(1)	1.42(4)
O(6)	1.95(3)	C(4)	1.45(5)
O(6^{i})	1.95(3)	O(14)–C(2)	1.48(5)
O(9)	2.40(3)	O(15)–C(3)	1.53(6)
O(9^{i})	2.40(3)	N(1)–C(6)	1.25(4)
Mo(2)–O(2)	1.73(3)	C(9)	1.49(5)
O(3)	1.62(3)	N(2)–C(6)	1.46(4)
O(6)	1.93(3)	C(7)	1.37(5)
O(7)	1.98(3)	N(3)–C(8)	1.37(5)
O(9)	2.41(3)	C(10)	1.30(4)
O(10)	2.29(2)	N(4)–C(1)	1.36(5)
Mo(3)–O(4)	1.75(3)	C(7)	1.36(5)
O(5)	1.80(3)	C(10)	1.45(4)
O(7)	1.84(3)	N(5)–C(9)	1.27(4)
O(8)	1.884(9)	C(1)–C(2)	1.54(6)
O(10)	2.39(3)	C(2)–C(3)	1.48(6)
O(11)	2.25(3)	C(3)–C(4)	1.59(5)
P(1)–O(9)	1.48(3)	C(4)–C(5)	1.44(5)
O(10^{i})	1.51(2)	C(7)–C(8)	1.35(5)
O(11)	1.51(3)	C(8)–C(9)	1.45(5)
O(12)	1.46(3)		
O(1)–Mo(1)–O(1^{i})	102(2)/°	O(8)–Mo(3)–O(11)	79.8(9)/°
Mo(1)–O(6)	103(1)	O(10)–Mo(3)–O(11)	89.3(9)
Mo(1)–O(6^{i})	99(1)	O(9)–P(1)–O(10^{i})	117(2)
Mo(1)–O(9)	90(1)	P(1)–O(11)	105(2)
Mo(1)–O(9^{i})	167(1)	P(1)–O(12)	110(2)
O(1^{i})–Mo(1)–O(6)	99(1)	O(10^{i})–P(1)–O(11)	109(2)
Mo(1)–O(6^{i})	103(1)	P(1)–O(12)	104(2)
Mo(1)–O(9)	167(1)	O(11)–P(1)–O(12)	113(2)
Mo(1)–O(9^{i})	90(1)		
O(6)–Mo(1)–O(6^{i})	145(2)	C(6)–N(1)–C(9)	128(4)
Mo(1)–O(9)	74(1)	C(6)–N(2)–C(7)	109(4)
Mo(1)–O(9^{i})	80(1)	C(8)–N(3)–C(10)	120(4)
O(6^{i})–Mo(1)–O(9)	80(1)	C(1)–N(4)–C(7)	125(5)
Mo(1)–O(9^{i})	74(1)	N(4)–C(10)	127(4)
O(9)–Mo(1)–O(9^{i})	78(1)	C(7)–N(4)–C(10)	108(4)
O(2)–Mo(2)–O(3)	104(1)	O(13)–C(1)–N(3)	112(4)
Mo(2)–O(6)	105(1)	N(4)–C(1)–C(2)	108(4)
Mo(2)–O(7)	96(1)	N(1)–C(6)–N(2)	126(4)
Mo(2)–O(9)	89(1)	N(2)–C(7)–N(4)	123(5)
Mo(2)–O(10)	160(1)	N(2)–C(7)–C(8)	125(5)
O(3)–Mo(2)–O(6)	93(1)	N(4)–C(7)–C(9)	112(5)
Mo(2)–O(7)	106(2)	N(3)–C(8)–C(7)	100(4)
Mo(2)–O(9)	164(1)	C(8)–C(9)	132(5)
Mo(2)–O(10)	94(1)	C(7)–C(8)–C(9)	127(5)
O(6)–Mo(2)–O(7)	148(1)	N(1)–C(9)–N(5)	125(4)
Mo(2)–O(9)	74(1)	C(9)–C(8)	104(4)
Mo(2)–O(10)	82(1)	N(5)–C(9)–C(8)	131(5)
O(7)–Mo(2)–O(9)	83(1)	N(3)–C(10)–N(4)	100(4)
Mo(2) –O(10)	71(1)		
O(9)–Mo(2)–O(10)	74.8(8)	P(1)–O(12)–C(5)	125(3)
O(4)–Mo(3)–O(5)	103(2)	C(1)–O(13)–C(4)	123(3)
Mo(3)–O(7)	104(1)	O(13)–C(1)–C(2)	94(4)
Mo(3)–O(8)	100(1)	O(14)–C(2)–C(1)	110(4)
Mo(3)–O(10)	84(1)	C(2)–C(3)	107(4)
Mo(3)–O(11)	174(1)	C(1)–C(2)–C(3)	105(4)
O(5)–Mo(3)–O(7)	105(1)	O(15)–C(3)–C(2)	120(4)
Mo(3)–O(8)	99(1)	C(3)–C(4)	102(4)
Mo(3)–O(10)	172(1)	C(2)–C(3)–C(4)	106(4)
Mo(3)–O(11)	83(1)	O(13)–C(4)–C(3)	95(3)
O(7)–Mo(3)–O(8)	141(1)	C(4)–C(5)	110(4)
Mo(3)–O(10)	71(1)	C(3)–C(4)–C(5)	110(4)
Mo(3)–O(11)	73(1)	O(12)–C(5)–C(4)	118(4)
O(8)–Mo(3)–O(10)	82(1)		

The symmetry code is the same as that given in Table 4.

Table 4. Selected Interatomic Distances (Å) for $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$

O(3)–N(5^{iii})	2.91(5)	Mo(1)–Mo(2)	3.401(6)
O(4)–N(5^{iii})	2.83(4)	Mo(2)–Mo(3)	3.394(7)
O(5)–O(19^{ii})	2.8(1)	Mo(3)–Mo(3^{i})	3.677(9)
O(7)–O(18^{ii})	2.96(5)	Mo(1)–Mo(3)	5.505(9)
O(7)–O(16)	3.12(3)	Mo(2)–Mo(2^{i})	5.57(1)
O(11)–O(16)	3.10(3)	Mo(2)–Mo(3^{i})	5.623(7)
O(11)–O(17)	2.98(6)		
O(14)–N(3^{iv})	2.90(5)	Mo(1)–P(1)	3.48(2)
O(18)–N(2^{v})	2.79(5)	Mo(2)–P(1)	3.57(2)
		Mo(2)–P(1^{i})	3.43(1)
Na(1)–O(17)	2.16(5)	Mo(3)–P(1)	3.34(1)
Na(1)–O(16)	2.30(4)	Mo(3)–P(1^{i})	3.62(1)
Na(1)–O(18)	2.41(5)		
Na(1)–O(11)	2.43(4)	P(1)–P(1^{i})	3.79(3)
Na(1)–O(5)	2.59(4)		
Na(1)–O(19)	2.6(1)		

Symmetry code: i) $x-y, -y, 5/3-z$; ii) $x-y, -y, 2/3-z$, iii) $1-x, -x+y, 4/3-z$; iv) $1-y, x-y, 1/3+z$; v) $1-x+y, 1-x, -1/3+z$.

the least-squares plane of the five MoO_6 octahedra ring. Two protonations of the anion are required for a charge in the neutrality of the molecule. The most plausible site for the protonation in the anion may be the N(1) atom in the amp ligand at pH 4 where the $[(Hamp)_2Mo_5O_{15}]^{2-}$ anion is prepared, because the calculated values (1.9, 1.9, 1.7 and 2.2) of the bond strength for the O(9), O(10), O(11), and O(12) atoms seemed to exclude the possibility of a protonation of the phosphate O atoms. This is supported by the fact that the resonance peaks (at 155.3 and 157.9 ppm) of the C(6) and C(9) atoms in the ^{13}C NMR spectra of AMP are shifted up-field into 151.1 and 154.9 ppm, probably due to a protonation of the N(1) atom[11] when the solution pH is changed from 7 to 4. It is noted that the sugar ring of the amp ligand in $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ has a different conformation from that in the AMP crystal. In $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$, the C(2) atom is positioned 0.61 Å from the least-squares plane of O(13)C(1)C(3)C(4) toward the C(5) atom (C(2)-*endo* puckering mode), while in AMP crystal the C(3) atom is located 0.66 Å apart from the least-squares plane of O(13)C(1)C(2)C(4) toward the C(5) atom (C(3)-*endo* puckering mode).[12] This conformation of the sugar ring in $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ may be associated with either the stacking of the adenine-base rings between the neighboring anions with a distance of 3.4 Å, or the hydrogen-bond between the O(14) atom (bonded to the C(2) atom) and the neighboring anion N(3^{iv}) atom an O(14)···N(3^{iv}) distance of 2.90(5) Å, as shown in Fig. 3.

Figure 4 shows the packing diagram of $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ in the unit cell, in which the adenine-base rings of the amp ligands are stacked continuously in parallel to the *c*-axis at a distance of 3.4 Å with a rotation of 120° (Fig. 3). The stacking distance (3.4 Å) is the same as that observed for the base rings of B-form DNA.[13] Each molecule is linked by the hydrogen-bonding interactions of O(3)···N(5^{iii}) (2.91(5) Å), O(4)···N(5^{iii}) (2.83(4) Å), and O(14)···N(3^{iv}) (2.90(5) Å), as shown in Table 4.

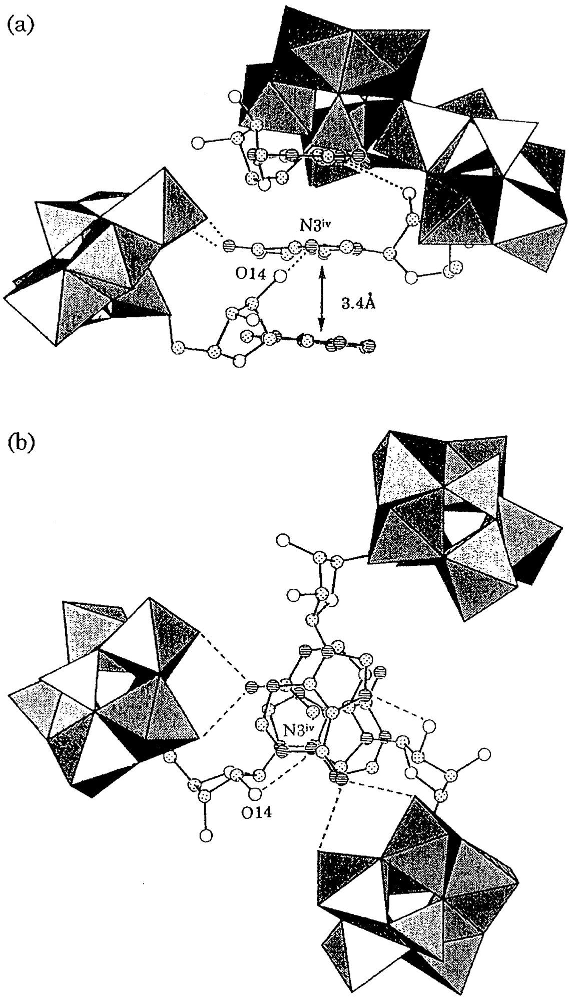

Fig. 3. Configuration among the three neighboring anions viewed in perpendicular to *c*-axis (a), and in parallel to *c*-axis (b). ○, ⊛, and ⊜ represent the atoms of oxygen, carbon, and nitrogen. Broken lines indicate hydrogen-bonding.

NMR Studies. The ^{13}C and ^{31}P NMR spectra of the aqueous solutions dissolving Na_2MoO_4 and AMP with the mole ratio of 5 : 2 at various pH levels are shown in Figs. 5 and 6, where the spectra of $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ are added for a comparison. The ^{13}C NMR spectrum at pH 7 exhibits five group of resonances, which have been assigned to the C1 (at 90.1 ppm), C4 (at 86.6 ppm), C2 (at 77.2 ppm), C3 (at 73.0 ppm), and C5 (at 66.8 ppm) atoms of AMP. The doublet peaks of the C4 atom have been attributed to the ^{31}P–^{13}C coupling.[14] The decrease in the solution pH provides resonance signals corresponding to $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$. ^{31}P NMR spectra exhibit two signals corresponding to AMP and $[(Hamp)_2Mo_5O_{15}]^{2-}$; the former due to AMP is shifted upfield and the latter due to $[(Hamp)_2Mo_5O_{15}]^{2-}$ is dominant as the pH values decreases. These spectra give the following comprehensive picture of the solute species in the Mo : AMP 5 : 2 solution; at pH 6, $[(Hamp)_2Mo_5O_{15}]^{2-}$ is formed and the acidification of the solution to pH 5 promotes the formation of the

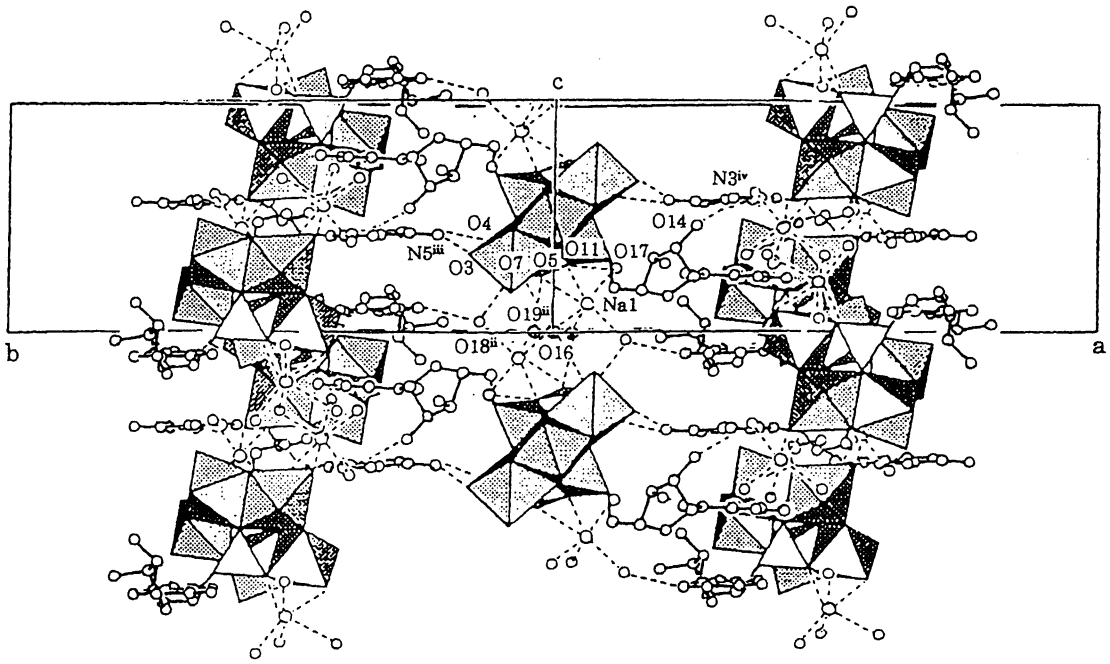

Fig. 4. Packing diagram of $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ in the unit cell. Broken lines indicate ionic-and hydrogen-bonding.

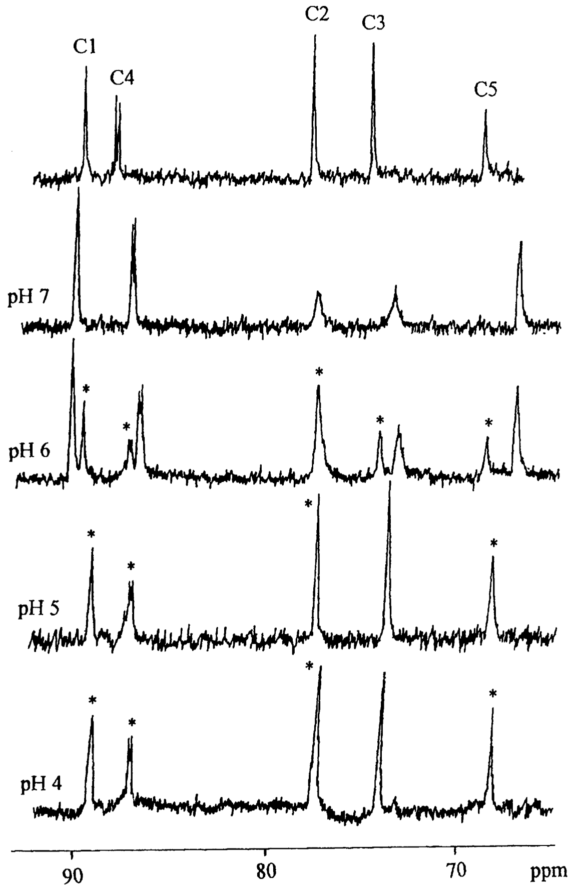

Fig. 5. ^{13}C NMR spectra of the Na_2MoO_4-AMP aqueous system (Mo : P 5 : 2) at indicated pH. The top figure is the ^{13}C NMR spectrum of $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ in the aqueous solution at pH 4.5 (natural pH level). The signals assigned to the C1—C5 atoms for the ribose moiety of $[(Hamp)_2Mo_5O_{15}]^{2-}$ are indicated by *.

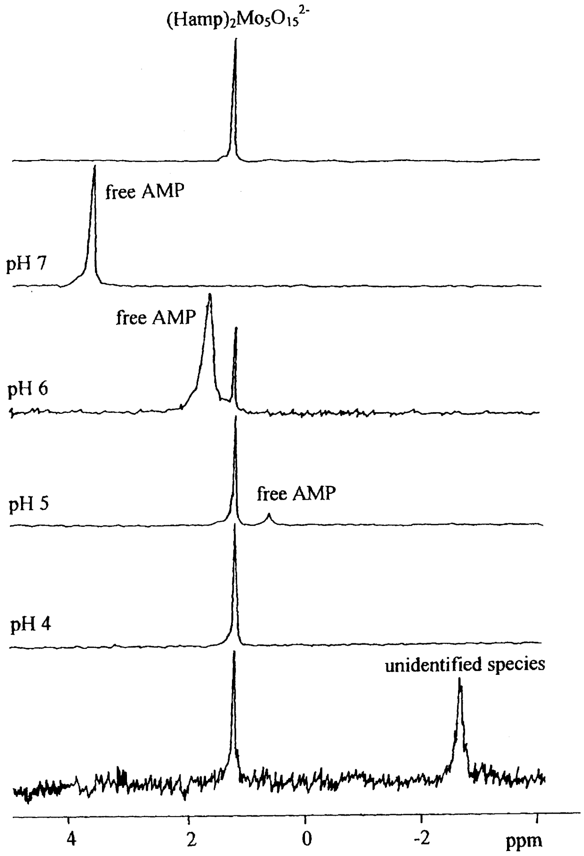

Fig. 6. ^{31}P NMR spectra of the Na_2MoO_4-AMP aqueous system (Mo : P 5 : 2) at indicated pH. The top and bottom figures are the ^{31}P NMR spectra of $Na_2[(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ in the aqueous solution at pH 4.5 (natural pH level) and the Na_2MoO_4-AMP aqueous system (Mo : P 9 : 1) at pH 4, respectively.

$[(Hamp)_2Mo_5O_{15}]^{2-}$ anion, since the ^{13}C chemical shift values (89.5, 77.2, 74.0, 87.1, and 68.4 ppm) of the C1—C5 atoms agree with those for the $[(Hamp)_2Mo_5O_{15}]^{2-}$ anion. In the region of pH 4—5, almost all of the AMP ions form a $[(Hamp)_2Mo_5O_{15}]^{2-}$ anion. Further acidification of pH ≤ 4 does not cause a serious change in the solution equilibrium. Although the high Mo : P ratio ($> 7/3$) at pH 4 increased the yield of unidentified species at -2.7 ppm in the ^{31}P NMR spectrum (Fig. 6), the ^{31}P NMR spectra of the solution indicated the formation of the $[(Hamp)_2Mo_5O_{15}]^{2-}$ anion (at 1.2 ppm).

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