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Preparation and Crystal Structure of $(NH_4)_8Ni(HPO_4)_2(PO_4)_2Mo_{10}O_{30}\cdot 12H_2O$

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The structure of $(NH_4)_8Ni(HPO_4)_2(PO_4)_2Mo_{10}O_{30}\cdot 12H_2O$ was determined from single-crystal diffractometer data: triclinic, space group $P\bar{1}$, with $a = 15.541(1)$, $b = 10.196(5)$, $c = 9.630(1)$ Å, $\alpha = 110.46(1)$, $\beta = 97.51(1)$, $\gamma = 94.94(1)°$ and $Z = 1$. Full matrix least-squares refinements of 367 parameters gave $R = 0.028$ for 7222 reflections. The Ni^{2+} ions are on symmetry centers and are octahedrally coordinated by four water molecules and two oxygen atoms from tertiary phosphate groups. The molybdenum atoms are octahedrally coordinated. The octahedra build two rings, each containing five octahedra which share edges or apices with each other or share apices with the phosphate groups. Two phosphate groups (a tertiary and a secondary) cap each ring of molybdenum octahedra. The water molecules and the ammonium ions have from four to seven contacts within the hydrogen-bonding range (2.7–3.1 Å) to water molecules, ammonium ions or anion oxygen atoms.

The structure of many salts of heteropoly acids have been determined. A general formula for such compounds may be written as $Me_mH_nY_yX_xO_z\cdot pH_2O$, where Me is a cation (usually an alkali metal, ammonium or tetraalkylammonium), X is a non-metal (usually P, Si, B, As or S) and Y is a transition metal (usually Mo or W).

From early structure determinations[1,2] it was long believed that the ratio y/x was confined to the range $9 \leqslant y/x \leqslant 12$. In a careful study of aqueous heteropolyanion systems Petterson[3] found indications for the existence of pentamolybdodiphosphate anions, i.e. $y/x = 2.5$, and later structures of $Na_6Mo_5P_2O_{23}\cdot 13H_2O$ and $Na_4H_2Mo_5P_2O_{23}\cdot 10H_2O$ were determined.[4,5] Recently the structure determination of $Na[N(CH_3)_4]_3$-$Mo_5S_2O_{23}\cdot 4H_2O$ was published by Hori *et al.*[6] A review of the structures of heteropolyacids salts for which the ratio y/x is 2.5 is given in the paper by Hori *et al.*

In this paper we report the preparation and structure of a nickel complex with the formula $(NH_4)_8Ni(HPO_4)_2$-$(PO_4)_2Mo_{10}O_{30}\cdot 12H_2O$ (in the following called NIPMO). From X-ray powder diagrams it further appears that the analogous Co complex is isomorphous. These compounds also have $y/x = 2.5$.

Experimental

Crystals of NIPMO were grown from a solution prepared by dissolving 1.42 mol H_3PO_4, 1.94 mol $(NH_4)_2Mo_2O_7$, 1.2 mol $NiCO_3$ and 1.72 mol citric acid monohydrate in 150 mol H_2O. At room temperature green NIPMO crystals separated after some days.

Elemental analyses for Mo, Ni, N and P were performed by spectrophotometric, atomic absorption, Kjeldahl, and gravimetric methods, respectively. The water content was determined by thermogravimetry. The density of the crystals was determined by the flotation method.

The lattice constants of a single crystal of NIPMO were determined from 25 θ values measured on an Enraf-Nonius CAD-4 single-crystal diffractometer. The crystal system was determined to be triclinic. Intensity data were collected from half of the diffraction sphere ($-21 \leqslant h \leqslant 21$, $-13 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 13$). In total 7589 reflections were measured. A standard reflection was measured every 100 reflections, and no decrease in intensity was observed.

Chemical and crystallographic data and conditions for intensity data collection are recorded in Table 1.

Structure determination and refinement

The structure was determined and refined by use of programs included in the Xtal3.0 system.[7] Atomic scattering factors were calculated from coefficients for neutral atoms given by Cromer and Mann.[8] A trial structure including positions of the molybdenum, phosphorus and nickel atoms was obtained by direct methods. By structure factor and difference Fourier calculations, positions

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Table 1. Chemical and crystallographical data for $(NH_4)_8Ni[(HPO_4)_2(PO_4)_2Mo_{10}O_{30}]\cdot 12H_2O$.

Formula	$(NH_4)_8Ni[(HPO_4)_2(PO_4)_2Mo_{10}O_{30}]\cdot 12H_2O$
Formula weight	2240.47
Unit cell dimensions/Å or °	$a = 15.541(1)$
	$b = 10.196(5)$
	$c = 9.630(1)$
	$\alpha = 110.46(1)$
	$\beta = 97.51(1)$
	$\gamma = 94.94(1)$
Unit cell volume/Å^3	1403.1(1)
Space group	$P\bar{1}$
Z	1
D_m/g cm^{-3}	2.66
D_c/g cm^{-3}	2.652
% water measured	10.5
% water calculated	10.45[a]
% Mo measured	44.3
% Mo calculated	42.82
% Ni measured	2.66
% Ni calculated	2.62
% P measured	5.7
% P calculated	5.53
% N measured	5.0
% N calculated	5.00
Crystal size/mm	0.11 × 0.14 × 0.20
Temperature/°C	22
θ_{max}/°	30
Scan technique	$\omega/2\theta$
Scan angle/°	1–1.58
Max. scan time/s	600
Radiation	Graphite-monochromated discriminated MoK_α($\lambda = 0.71069$ Å)
Standard reflection	5 2 6, no decrease
No. of reflections measured	7589
Refinements	Least squares, full matrix
Function minimized	$\Sigma w(F_o - F_c)^2$
Weights, w	Unit
No. of reflections used in refinements	7222 [$I > 2.5\sigma(I)$]
μ/cm^{-1}	26.9, no correction
Corrections for	Lorentz and polarisation effects
Structure determination	Direct methods
No. of parameters refined	367
R	0.028
$(\Delta/\sigma)_{max}$	0.0005

[a] Loss of 13 H_2O per formula weight, i.e. pyrophosphate formation.

for all oxygen atoms (from anions and water molecules) and all nitrogen atoms (from ammonium ions) were found. The structure was then refined by full matrix least-squares calculations (CRYLSQ),[7f] first with individual isotropic, later with anisotropic displacement parameters. The final R index was 0.028. In a difference Fourier map calculated at this stage indications for positions of 25 hydrogen atoms were found. The inclusion of contributions from these hydrogen atoms in the least-squares calculations did not lead to a further decrease of the R index.

Atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms are reported in Table 2. Lists of structure factors, hydrogen atom positions and anisotropic displacement parameters may be obtained from the authors on request.

Structure of the $\{[Ni(PO_4)_2(H_2O)_4]Mo_{10}O_{30}(HPO_4)_2\}^{8-}$ group

The structure of the $\{[Ni(PO_4)_2(H_2O)_4]Mo_{10}O_{30}(HPO_4)_2\}^{8-}$ group is shown in Fig. 1. The group consists of two equivalent $[HPO_4, PO_4, Mo_5O_{15}]^{5-}$ groups related by the symmetry center on which the Ni^{2+} ions are placed. The five Mo(VI) ions in each unit are six-coordinated in very distorted octahedra. These octahedra are connected into five-membered rings. Of the five contacts, four are by edge-sharing, the fifth by corner-sharing [at O(12)]. In all the octahedra the lengths of the Mo–O bonds fall into three categories. The first is with two short Mo–O bonds [in the range 1.705(5)–1.727(4) Å]. The oxygen ions in these bonds are only coordinated to one molybdenum ion. They have close contacts to the

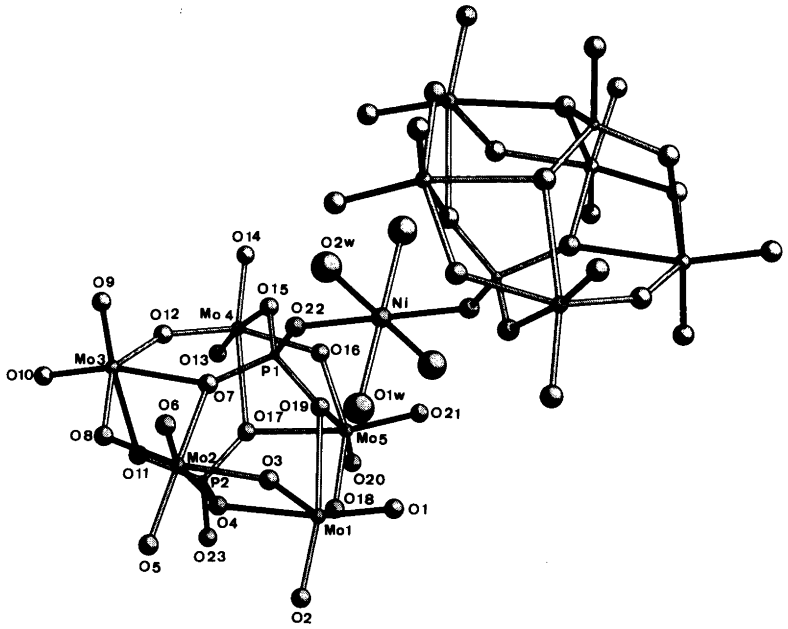

Fig. 1. Structure of the $\{[Ni(PO_4)_2(H_2O)_4]Mo_{10}O_{30}(HPO_4)_2\}^{8-}$ group.

ammonium ions [in the range 2.865(5)–3.071(6) Å]. Another category has two medium length Mo–O bonds [in the range 1.893(3)–1.947(4) Å]. In these bonds the oxygen ions are shared between two neighbouring molybdenum ions [the two shortest bonds in this category, Mo(3)–O(12) 1.893(3) Å and Mo(4)–O(12) 1.898(3) Å, are at the corner-sharing point of the five-membered ring]. The third category of Mo–O bonds contains two long bonds [in the range 2.165(3)–2.426(4) Å]. In these bonds the oxygen ions belong to the phosphate groups.

The phosphate groups are distorted. The angles around P(1) vary from 106.5 to 112.4° and around P(2) they vary from 104.5 to 112.9°. The P–O bond lengths are in reasonable agreement with the lengths found in simple secondary and tertiary phosphates. The P(2)–O(23) is the longest [1.573(4) Å] bond, and is assumed to be a P–(OH) bond. The generally accepted P–O bond length in tertiary phosphates is 1.55 Å. The P–(OH) and the P–O distances in secondary phosphates are 1.59 and 1.52 Å, respectively.

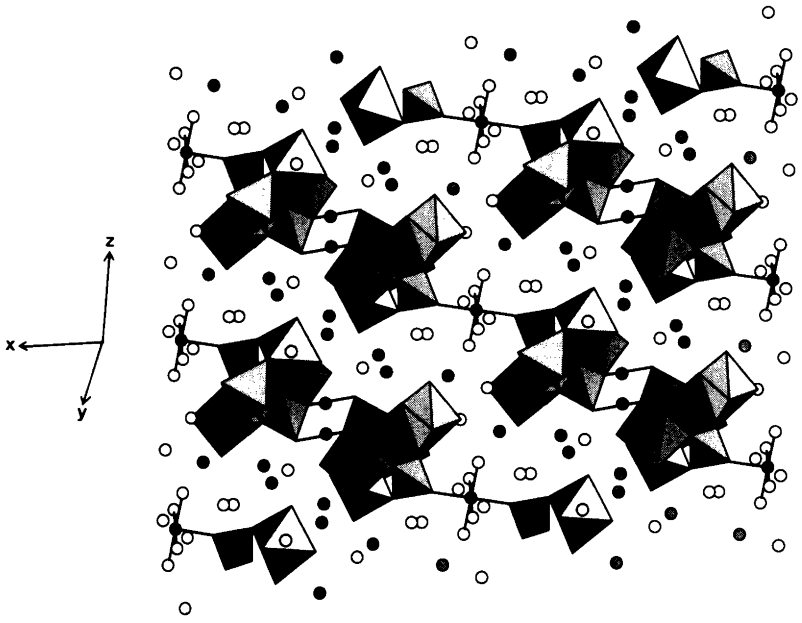

Fig. 2. Structure of $(NH_4)_8Ni(HPO_4)_2(PO_4)_2Mo_{10}O_{30}\cdot 12H_2O$ viewed perpendicular to the (010) plane. Filled circles represent NH_4 ions; open circles represent water molecules.

Table 2. Non-hydrogen positional and equivalent isotropic displacement parameters U (in Å^2) in $(NH_4)_8Ni[(HPO_4)_2(PO_4)_2Mo_{10}O_{30}]\cdot 12H_2O$.[a]

Atom	x/a	y/b	z/c	U
Mo(1)	0.14600(2)	0.95543(4)	0.45247(4)	0.0177(1)
Mo(2)	0.23542(3)	0.28010(4)	0.47793(5)	0.0208(1)
Mo(3)	0.41064(2)	0.25075(4)	0.30461(4)	0.0174(1)
Mo(4)	0.38889(2)	0.87505(4)	0.06868(4)	0.0171(1)
Mo(5)	0.24221(2)	0.71113(4)	0.20878(4)	0.0176(1)
Ni	0	0	0	0.0124(2)
P(1)	0.20656(7)	0.0188(1)	0.1388(1)	0.0095(3)
P(2)	0.36947(7)	0.0117(1)	0.4631(1)	0.0106(3)
O(1)	0.0413(2)	0.8733(4)	0.3756(4)	0.024(1)
O(2)	0.1508(2)	−0.0005(4)	0.6438(4)	0.025(1)
O(3)	0.1364(2)	0.1340(4)	0.4301(4)	0.017(1)
O(4)	0.2881(2)	0.0756(3)	0.5150(3)	0.015(1)
O(5)	0.2443(3)	0.3498(4)	0.6710(4)	0.033(1)
O(6)	0.1807(3)	0.3933(4)	0.4172(5)	0.034(2)
O(7)	0.2666(2)	0.1466(3)	0.2659(3)	0.0125(9)
O(8)	0.3545(2)	0.3470(3)	0.4741(4)	0.018(1)
O(9)	0.3782(2)	0.3319(4)	0.1812(4)	0.023(1)
O(10)	0.4846(2)	0.6653(4)	0.6181(4)	0.023(1)
O(11)	0.4403(2)	0.1247(3)	0.4646(4)	0.015(1)
O(12)	0.4252(2)	0.0726(3)	0.1663(4)	0.015(1)
O(13)	0.4801(2)	0.8111(4)	0.1276(4)	0.023(1)
O(14)	0.3947(2)	0.8447(4)	0.8846(4)	0.025(1)
O(15)	0.2625(2)	0.9557(3)	0.0204(3)	0.015(1)
O(16)	0.2993(2)	0.7182(3)	0.0459(4)	0.017(1)
O(17)	0.3489(2)	0.8948(3)	0.3062(3)	0.0138(9)
O(18)	0.2093(2)	0.7979(3)	0.4060(4)	0.017(1)
O(19)	0.1775(2)	0.9070(3)	0.2063(3)	0.0125(9)
O(20)	0.2989(3)	0.5939(4)	0.2603(4)	0.026(1)
O(21)	0.1438(2)	0.6135(4)	0.1066(4)	0.024(1)
O(22)	0.1283(2)	0.0718(3)	0.0777(4)	0.016(1)
O(23)	0.4018(2)	0.9439(4)	0.5809(4)	0.019(1)
O(1w)	0.0214(2)	0.8988(4)	0.7776(4)	0.023(1)
O(2w)	−0.0075(2)	0.1902(4)	0.9671(4)	0.022(1)
O(3w)	0.1971(3)	0.3058(5)	0.0169(5)	0.037(2)
O(4w)	0.0431(3)	0.4376(5)	0.2144(6)	0.046(2)
O(5w)	0.1637(4)	0.6756(7)	0.7796(6)	0.056(2)
O(6w)	0.3782(4)	0.4642(6)	0.9231(7)	0.060(2)
N(1)	0.2968(3)	0.6707(5)	0.5950(5)	0.028(2)
N(2)	0.3254(3)	0.1254(5)	0.8570(5)	0.028(2)
N(3)	0.5026(4)	0.4027(6)	0.7306(6)	0.037(2)
N(4)	0.0890(3)	0.3713(6)	0.8004(6)	0.034(2)

[a]The isotropic temperature expression is $t = \exp -8\pi^2 U s^2$. Standard deviations are given in parentheses.

The coordination polyhedron around the Ni^{2+} ions is a nearly regular octahedron. Of the six ligands two are oxygen atoms from tertiary phosphate groups; the remaining four are oxygen atoms in water molecules. The difference between the longest and shortest Ni–O bonds is 0.10 Å, and the maximum deviation of the O–Ni–O bond angles from 90° is 4°.

Crystal structure of $(NH_4)_8Ni[(HPO_4)_2(PO_4)_2Mo_{10}O_{30}]\cdot 12H_2O$

In the structure of NIPMO there are 43 contacts (between oxygen atoms from the anions, and ammonium ions, and water molecules) in the hydrogen bond-length range (2.760–3.118 Å). These contacts are not all hydrogen bonds. A hydrogen-bonding scheme could not be found because the hydrogen atoms were not located unambiguously. One hydrogen bond may, however, be located, viz. the bond between P(2)–O(23)–H and O(11). The

Table 3. Distances (in Å) and angles (in °) in the $\{[Ni(PO_4)_2(H_2O)_4]Mo_{10}O_{30}(HPO_4)_2\}^{8-}$ group.[a]

Mo(1)^i–O(1)^i	1.707(3)	O(1)–Mo(1)–O(2)	104.5(2)
Mo(1)^i–O(2)^{ii}	1.727(4)	O(1)–Mo(1)–O(3)	99.3(2)
Mo(1)^i–O(3)^{ii}	1.923(4)	O(1)–Mo(1)–O(4)	169.1(2)
Mo(1)^i–O(4)^{ii}	2.327(3)	O(1)–Mo(1)–O(18)	101.1(2)
Mo(1)^i–O(18)^i	1.906(4)	O(1)–Mo(1)–O(19)	89.2(2)
Mo(1)^i–O(19)^i	2.373(3)	O(2)–Mo(1)–O(3)	102.1(2)
		O(2)–Mo(1)–O(4)	85.6(2)
		O(2)–Mo(1)–O(18)	101.0(2)
		O(2)–Mo(1)–O(19)	165.9(1)
		O(3)–Mo(1)–O(4)	74.1(1)
		O(3)–Mo(1)–O(18)	144.1(2)
		O(3)–Mo(1)–O(19)	78.7(1)
		O(4)–Mo(1)–O(18)	80.7(1)
		O(4)–Mo(1)–O(19)	81.1(1)
		O(18)–Mo(1)–O(19)	72.4(1)
Mo(2)^{ii}–O(3)^{ii}	1.934(3)	O(3)–Mo(2)–O(4)	71.6(1)
Mo(2)^{ii}–O(4)^{ii}	2.426(4)	O(3)–Mo(2)–O(5)	99.5(2)
Mo(2)^{ii}–O(5)^{ii}	1.725(4)	O(3)–Mo(2)–O(6)	96.7(2)
Mo(2)^{ii}–O(6)^{ii}	1.705(5)	O(3)–Mo(2)–O(7)	84.0(1)
Mo(2)^{ii}–O(7)^{ii}	2.165(3)	O(3)–Mo(2)–O(8)	153.2(1)
Mo(2)^{ii}–O(8)^{ii}	1.925(3)	O(4)–Mo(2)–O(5)	85.5(2)
		O(4)–Mo(2)–O(6)	166.0(1)
		O(4)–Mo(2)–O(7)	72.6(1)
		O(4)–Mo(2)–O(8)	87.9(1)
		O(5)–Mo(2)–O(6)	104.5(2)
		O(5)–Mo(2)–O(7)	155.6(2)
		O(5)–Mo(2)–O(8)	95.8(2)
		O(6)–Mo(2)–O(7)	99.1(2)
		O(6)–Mo(2)–O(8)	100.7(2)
		O(7)–Mo(2)–O(8)	73.3(1)
Mo(3)^{ii}–O(7)^{ii}	2.319(3)	O(7)–Mo(3)–O(8)	69.5(1)
Mo(3)^{ii}–O(8)^{ii}	1.947(3)	O(7)–Mo(3)–O(9)	88.6(2)
Mo(3)^{ii}–O(9)^{ii}	1.718(5)	O(7)–Mo(3)–O(10)	164.8(2)
Mo(3)^{ii}–O(10)	1.713(3)	O(7)–Mo(3)–O(11)	85.5(1)
Mo(3)^{ii}–O(11)^{ii}	2.354(4)	O(7)–Mo(3)–O(12)	83.7(1)
Mo(3)^{ii}–O(12)^{ii}	1.893(3)	O(8)–Mo(3)–O(9)	101.7(2)
		O(8)–Mo(3)–O(10)	97.7(2)
		O(8)–Mo(3)–O(11)	77.4(1)
		O(8)–Mo(3)–O(12)	145.0(2)
		O(9)–Mo(3)–O(10)	102.4(2)
		O(9)–Mo(3)–O(11)	173.9(1)
		O(9)–Mo(3)–O(12)	99.7(2)
		O(10)–Mo(3)–O(11)	83.7(2)
		O(10)–Mo(3)–O(12)	104.4(2)
		O(11)–Mo(3)–O(12)	78.4(1)
Mo(4)^i–O(12)^{ii}	1.898(3)	O(12)–Mo(4)–O(13)	100.5(2)
Mo(4)^i–O(13)^i	1.722(4)	O(12)–Mo(4)–O(14)	103.8(2)
Mo(4)^i–O(14)^{iii}	1.706(4)	O(12)–Mo(4)–O(15)	80.0(1)
Mo(4)^i–O(15)^i	2.249(3)	O(12)–Mo(4)–O(16)	144.5(1)
Mo(4)^i–O(16)^i	1.958(3)	O(12)–Mo(4)–O(17)	83.2(1)
Mo(4)^i–O(17)^i	2.393(4)	O(13)–Mo(4)–O(14)	102.9(2)
		O(13)–Mo(4)–O(15)	171.8(2)
		O(13)–Mo(4)–O(16)	99.0(2)
		O(13)–Mo(4)–O(17)	85.4(2)
		O(14)–Mo(4)–O(15)	84.9(2)
		O(14)–Mo(4)–O(16)	100.4(2)
		O(14)–Mo(4)–O(17)	167.8(1)
		O(15)–Mo(4)–O(16)	76.7(1)
		O(15)–Mo(4)–O(17)	86.5(1)
		O(16)–Mo(4)–O(17)	69.1(1)
Mo(5)^i–O(16)^i	1.920(4)	O(16)–Mo(5)–O(17)	73.5(1)
Mo(5)^i–O(17)^i	2.229(3)	O(16)–Mo(5)–O(18)	152.5(1)
Mo(5)^i–O(18)^i	1.952(3)	O(16)–Mo(5)–O(19)	89.6(1)
Mo(5)^i–O(19)^i	2.318(4)	O(16)–Mo(5)–O(20)	99.5(2)
Mo(5)^i–O(20)^i	1.713(5)	O(16)–Mo(5)–O(21)	99.1(2)
Mo(5)^i–O(21)^i	1.720(3)	O(17)–Mo(5)–O(18)	81.2(1)
		O(17)–Mo(5)–O(19)	74.1(1)
		O(17)–Mo(5)–O(20)	96.5(2)
		O(17)–Mo(5)–O(21)	158.4(2)
		O(18)–Mo(5)–O(19)	72.9(1)
		O(18)–Mo(5)–O(20)	94.0(2)
		O(18)–Mo(5)–O(21)	100.6(2)

Table continued

Table 3. Continued.

		O(19)-Mo(5)-O(20)	164.7(1)
		O(19)-Mo(5)-O(21)	85.8(2)
		O(20)-Mo(5)-O(21)	104.9(2)
ψ(22)[ii]	2.012(3)	O(22)-Ni-O(1w)	92.7(1)
ψ(1w)[iv]	2.112(4)	O(22)-Ni-O(2w)	86.0(2)
ψ(2w)[v]	2.082(4)	O(22)-Ni-O(22)	180.0
ψ(22)	2.012(3)	O(22)-Ni-O(1w)	87.4(1)
ψ(1w)[iii]	2.112(4)	O(22)-Ni-O(2w)	94.0(1)
ψ(2w)[vi]	2.082(4)	O(1w)-Ni-O(2w)	91.4(2)
		O(1w)-Ni-O(22)	87.4(1)
		O(1w)-Ni-O(1w)	180.0
		O(1w)-Ni-O(2w)	88.6(2)
		O(2w)-Ni-O(22)	94.0(1)
		O(2w)-Ni-O(1w)	88.6(2)
		O(2w)-Ni-O(2w)	180.0
		O(22)-Ni-O(1w)	92.7(1)
		O(22)-Ni-O(2w)	86.0(1)
		O(1w)-Ni-O(2w)	91.4(2)
P(1)[ii]-O(7)[ii]	1.563(3)	O(7)-P(1)-O(15)	106.5(2)
P(1)[ii]-O(15)[i]	1.521(4)	O(7)-P(1)-O(19)	108.8(2)
P(1)[ii]-O(19)[i]	1.559(4)	O(7)-P(1)-O(22)	108.7(2)
P(1)[ii]-O(22)[ii]	1.505(4)	O(15)-P(1)-O(19)	109.4(2)
		O(15)-P(1)-O(22)	112.4(2)
		O(19)-P(1)-O(22)	110.9(2)
P(2)[ii]-O(4)[ii]	1.533(3)	O(4)-P(2)-P(11)	111.3(2)
P(2)[ii]-O(11)[ii]	1.518(4)	O(4)-P(2)-O(17)	112.9(2)
P(2)[ii]-O(17)[i]	1.535(3)	O(4)-P(2)-O(23)	104.5(2)
P(2)[ii]-O(23)[i]	1.573(4)	O(11)-P(2)-O(17)	109.3(2)
		O(11)-P(2)-O(23)	110.3(2)
		O(17)-P(2)-O(23)	108.5(2)

[a] The numbering of the atoms is the same as in Table 2, with roman numbers indicating atoms in symmetry-related positions. The estimated standard deviations are given in parentheses. [i] $-x, 1-y, -z$; [ii] $-x, -y, -z$; [iii] $-x, 1-y, 1-z$; [iv] $x, y-1, z-1$; [v] $x, y, z-1$; [vi] $-x, -y, 1-z$.

length of this contact is 2.659(6) Å. By bonds of this type and by the coordination of the nickel ions to an oxygen in the tertiary phosphate groups the $[HPO_4, PO_4, Mo_5O_{15}]^{5-}$ units are bonded to strings running along the [101] direction. The crystal structure is shown in Fig. 2.

All the ammonium ions have close contacts to oxygen atoms in the anions. The closest contact between two ammonium ions is 4.358(9) Å.

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