Crystal Structures of Neodymium Metaphosphate (NdP₃O₉) and Ultraphosphate (NdP₅O₁₄)*

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The structures of neodymium metaphosphate (NdP_3O_9) and ultraphosphate (NdP_5O_{14}) have been solved by the single-crystal X-ray heavy-atom method. NdP_3O_9 is orthorhombic, space group $C222_1$ and cell parameters $a = 11·172$ (2), $b = 8·533$ (2), $c = 7·284$ (2) Å, $Z = 4$. NdP_5O_{14} is monoclinic, space group $P2_1/c$ and cell parameters $a = 8·771$ (3), $b = 9·012$ (2), $c = 13·057$ (3) Å, $\beta = 89·58$ (2)°, $Z = 4$. A full-matrix least-squares refinement gave $R = 0·057$ and $R = 0·078$, respectively. In both structures, O atoms form a tetrahedron around each P atom and a NdO_8 polyhedron around each Nd atom. The PO_4 tetrahedra share corners to produce helical chains in the metaphosphate and cross-linked chain pairs in the ultraphosphate. The NdO_8 dodecahedra in the metaphosphate share edges in a zigzag fashion; in the ultraphosphate, the polyhedra are isolated from each other, and no O atom is common to two Nd atoms. The shortest Nd–Nd distances are 4·234 and 5·194 Å, respectively, in the metaphosphate and ultraphosphate structures.

Introduction

Three types of rare-earth phosphates have been reported: orthophosphates (RPO_4), metaphosphates (RP_3O_9) and ultraphosphates (RP_5O_{14}). Only the orthophosphates were known until Jaulmes (1969) prepared LaP_5O_{14}. Beucher (1970) obtained single crystals of ultraphosphates of all the rare earths by heating solutions of the various rare-earth oxides in excess H_3PO_4. She identified three different crystal structures, two monoclinic and one orthorhombic, and found that some compounds could exhibit two of these structures. Durif (1971) has carried out a structure refinement for the orthorhombic form of HoP_5O_{14}, the only ultraphosphate for which a refinement has been reported. Beucher (1970) also prepared metaphosphates of all the rare earths, in powder form, by solid state reaction of $R_2O_3 + 6(NH_4)_2HPO_4$ mixtures. She reported that there were two different crystal structures, but was unable to identify them. Only GdP_3O_9 exhibited both structures.

Danielmeyer & Weber (1972) have recently investigated the optical absorption and fluorescence of neodymium ultraphosphate, NdP_5O_{14}. They report that the pair interaction between Nd ions remains small in spite of the high concentration of these ions. In order to examine the crystallographic basis for the apparent isolation of the Nd ions, we have used single-crystal X-ray diffraction to refine the structure of NdP_5O_{14}. Before doing so, we used this method to refine the structure of NdP_3O_9. No crystallographic data have been reported previously for this or any other rare-earth metaphosphate. The NdP_3O_9 crystals were grown in an attempt to prepare NdP_5O_{14}, and we originally believed them to be ultraphosphate crystals.

It was only after the structure refinement had showed their composition to be NdP_3O_9 that we learned of the paper by Beucher (1970) reporting the existence of the rare-earth metaphosphates.

Experimental procedure

Small single crystals of NdP_3O_9 were obtained† when a solution containing Nd_2O_3, P_2O_5, HPO_3, and NaF was slowly cooled from 930 to 870°C. They were separated from a crystalline aggregate that formed on a platinum wire suspended in the solution to facilitate nucleation.

Small single crystals of NdP_5O_{14} were obtained by a method similar to Beucher's (1970). A mixture of H_3PO_4 (containing 15% water by weight) and Nd_2O_3, in a ratio of 30 to 1 by weight, was placed in a gold crucible and heated in air in a box furnace. The crucible was heated in steps to 600°C, held there for 5 h, then held at 650°C for 17 h, and finally removed from the furnace. When the solid obtained by this procedure was washed with a large amount of water to dissolve any excess phosphoric acid, it was found to include a considerable number of thin, rectangular platelets of NdP_5O_{14}.

For X-ray diffraction studies, a small crystal of each compound was mounted on a goniometer head. The NdP_3O_9 crystal measured $0·2 \times 0·2 \times 0·4$ mm and was mounted about the c axis, while the NdP_5O_{14} crystal measured $0·1 \times 0·1 \times 0·2$ mm and was mounted about the b axis. Oscillation and Weissenberg photographs were taken for each crystal. For both crystals, the 2θ positions of about 15 reflection peaks due to Mo $K\alpha_1$ ($\lambda = 0·70926$) radiation were measured at 25°C with a General Electric XRD diffractometer in order to deter-

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mine the cell-edge parameters. These measurements employed a 1° take-off angle and 0·02° slit.

Three-dimensional intensity data to $2\theta = 55°$ for NdP_3O_9 and to $2\theta = 45°$ for NdP_5O_{14} were collected by the stationary-crystal, stationary-counter method, with Zr-filtered Mo $K\alpha$ radiation and a 5° take-off angle. Each peak was counted for 10 s, and the background (at 2° below the 2θ value of the peak) was also counted for 10 s. The number of independent reflections measured was 451 for NdP_3O_9 and 1239 for NdP_5O_{14}. Lorentz, polarization, and φ-angle absorption corrections were applied. The linear absorption coefficient is 25 cm^{-1} for NdP_3O_9 and 19 cm^{-1} for NdP_5O_{14}. The three-dimensional absorption correction was not considered necessary. The equation

$$\sigma(F) = \tfrac{1}{2} \left[K \frac{1 + I_B/I_P}{1 - I_B/I_P} \right]^{1/2}$$

was used to estimate the variance for the structure factors, where I_B is the background count, I_P is the peak count, and K is the product of the Lorentz, polarization, absorption, α-splitting and tube-current corrections.

Structure determinations
NdP_3O_9

The oscillation and Weissenberg photographs showed diffraction symmetry mmm. The systematic absences were hkl, $h + k = 2n + 1$, and $00l$ with $l = 2n + 1$, which require the unique space group $C222_1$ (No. 20). The 2θ measurements made at 25°C were used in a least-squares refinement to obtain the orthorhombic lattice parameters.

As stated above, the true composition of the NdP_3O_9 crystals was initially unknown. Nevertheless, because Nd is much heavier than P and O, it was possible to solve the structure by using the heavy-atom method of structure analysis. In addition to the systematic absences, it was observed that, for $h0l$ reflections, the intensity is much stronger for l even than for l odd. This indicates that a heavy atom occupies the $4(b)$ site $(0, y, \tfrac{1}{4})$ and $(0, \bar{y}, \tfrac{3}{4})$.

A three-dimensional Patterson map was then generated. If a heavy atom is located at the $4(b)$ site, a strong interaction should appear on section $(0, 2y, \tfrac{1}{2})$.

Table 2. *Observed and calculated structure factors for* NdP_3O_9

This was the case, the strongest peak occurring at $(0, 0\cdot25, \tfrac{1}{2})$. This gives the position of Nd as $(0, 0\cdot125, \tfrac{1}{4})$. A structure-factor calculation based on this position gave a value of 0·31 for the difference function $R = \sum |F_o - F_c| / \sum |F_o|$, where F_o and F_c are respectively the observed and calculated structure factors. The scattering factors used for Nd^{3+}, P and O are those published (Cromer & Waber, 1965) with anomalous dispersion coefficients for Mo radiation (Cromer, 1965). With this model, a difference Fourier map revealed two independent P positions plus a number of peaks possibly due to O atoms. Introducing these two P atoms reduced the value of R to 0·20. A subsequent Fourier map clearly revealed additional oxygen peaks. From this map it was possible to locate all the O atoms by assuming a tetrahedral coordination around P. Five independent O atoms were identified. The atom parameters, scale factor and isotropic temperature factor were then refined, with a full-matrix least-squares program, to give $R = 0\cdot065$. At this stage the isotropic temperature factors were converted to anisotropic factors. Three more cycles of refinement led to a final R

Table 1. *Final atomic parameters for* NdP_3O_9*

Space group: $C222_1$; cell parameters: $a = 11\cdot172$ (2), $b = 8\cdot533$ (2), $c = 7\cdot284$ (2) Å

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nd	0	0·1265 (2)	$\tfrac{1}{4}$	0·0009 (1)	0·0017 (2)	0·0002 (2)	0	0·0001 (2)	0
P(1)	0	0·7493 (9)	$\tfrac{1}{4}$	0·0010 (5)	0·0019 (9)	0·0000 (1)	0	0·000 (1)	0
P(2)	0·3243 (5)	0·9916 (9)	0·2027 (8)	0·0016 (4)	0·0022 (7)	0·002 (1)	0·0001 (6)	0·0002 (5)	0·0008 (8)
O(1)	0·374 (2)	0	0	0·004 (2)	0·010 (4)	0·004 (4)	0	0	0·002 (4)
O(2)	0·482 (1)	0·353 (1)	0·074 (1)	0·004 (2)	0·002 (1)	0·000 (2)	0·002 (2)	0·001 (1)	0·000 (1)
O(3)	0·193 (1)	0·021 (2)	0·210 (2)	0·001 (1)	0·006 (2)	0·007 (4)	0·000 (1)	0·000 (1)	0·000 (2)
O(4)	0·123 (1)	0·345 (1)	0·210 (3)	0·004 (1)	0·000 (2)	0·025 (9)	0·000 (1)	0·006 (3)	0·000 (3)
O(5)	0·392 (1)	0·136 (2)	0·294 (2)	0·003 (1)	0·003 (2)	0·003 (5)	0·001 (1)	0·001 (2)	0·003 (3)

* Standard deviations are given in parentheses.

value of 0·057 for all reflections and a weighted $R_w =$ 0·063, where

$$R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$$

with

$$w = 1/\sigma^2.$$

A three-dimensional, electron-density difference function was calculated with this last set of parameters, and no physically significant peaks were observed. It was now evident that the compound had the chemical formula NdP_3O_9 with four molecules per unit cell and an X-ray density of 3·63 g cm^{-3}. The final atomic param-

Table 3. *Bond distances and angles in* NdP_3O_9

Tetrahedron around P(1)

P(1)–O(2)	2 × 1·571 (9) Å	O(2)–P(1)–O(2)	111·4 (8)°
P(1)–O(5)	2 × 1·579 (9)	O(2)–P(1)–O(5)	2 × 114·4 (7)
O(2)–O(5)	2·64 (2)	O(2)–P(1)–O(5)	2 × 106·1 (7)
O(2)–O(5)	2·51 (2)	O(5)–P(1)–O(5)	104·5 (9)
O(2)–O(2)	2·60 (2)		
O(5)–O(5)	2·49 (2)		

Tetrahedron around P(2)

P(2)–O(3)	1·49 (1) Å	O(3)–P(2)–O(1)	111·9 (9)°
P(2)–O(1)	1·58 (1)	O(3)–P(2)–O(4)	120·3 (9)
P(2)–O(4)	1·52 (1)	O(3)–P(2)–O(5)	108·8 (9)
P(2)–O(5)	1·59 (2)	O(1)–P(2)–O(4)	107·0 (9)
O(1)–O(3)	2·55 (2)	O(1)–P(2)–O(5)	100·8 (8)
O(1)–O(4)	2·50 (2)	O(4)–P(2)–O(5)	106·1 (8)
O(1)–O(5)	2·45 (1)		
O(3)–O(4)	2·61 (2)		
O(3)–O(5)	2·51 (2)		
O(4)–O(5)	2·49 (2)		

Inter-tetrahedral angles

P(2)–O(1)–P(2)	139 (1)°
P(1)–O(5)–P(2)	139 (1)

Dodecahedron around Nd

Nd–O(2)	2 × 2·670 (8) Å	O(2)–O(2)	2·75 (2) Å
Nd–O(2)	2 × 2·375 (7)	O(2)–O(3)	2·93 (2)
Nd–O(3)	2 × 2·35 (1)	O(2)–O(3)	2·89 (2)
Nd–O(4)	2 × 2·33 (1)	O(2)–O(4)	3·11 (2)
Nd–Nd	4·234 (5)	O(3)–O(4)	2·88 (2)
		O(3)–O(3)	3·10 (2)
		O(4)–O(4)	2·82 (2)

Table 4. *Final atomic parameters for* NdP_5O_{14}*

Space group: $P2_1/c$; cell parameters: $a = 8·771$ (3), $b = 9·012$ (2), $c = 13·057$ (3) Å, $\beta = 89·58$ (2)°

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nd	0·2774 (2)	0·1903 (2)	0·0013 (1)	0·0029 (2)	0·0013 (2)	−0·0013 (1)	0·0000 (2)	0·0002 (1)	0·0000 (1)
P(1)	−0·006 (1)	−0·002 (1)	0·1733 (7)	0·004 (1)	0·003 (1)	−0·0006 (6)	0·0006 (9)	0·0002 (6)	−0·0002 (6)
P(2)	0·493 (1)	−0·006 (1)	0·2052 (7)	0·004 (1)	0·002 (1)	−0·0008 (5)	−0·0003 (9)	0·0001 (6)	−0·0001 (6)
P(3)	0·773 (1)	0·053 (1)	0·6634 (8)	0·003 (1)	0·004 (1)	−0·0004 (6)	0·000 (1)	0·0000 (6)	0·0002 (6)
P(4)	0·683 (1)	0·255 (1)	0·5006 (7)	0·005 (1)	0·001 (1)	−0·0008 (5)	0·000 (1)	0·0002 (6)	0·0001 (6)
P(5)	0·755 (1)	0·452 (1)	0·8348 (7)	0·004 (1)	0·003 (1)	−0·0008 (6)	0·000 (1)	0·0006 (6)	0·0005 (6)
O(1)	0·533 (2)	0·190 (3)	0·506 (2)	0·002 (3)	0·009 (4)	0·000 (1)	0·000 (3)	0·000 (1)	0·000 (2)
O(2)	0·229 (2)	0·093 (3)	0·386 (2)	0·011 (4)	0·000 (3)	0·001 (1)	0·000 (3)	−0·001 (2)	−0·003 (2)
O(3)	0·080 (2)	0·116 (3)	0·120 (2)	0·002 (3)	0·005 (3)	0·002 (2)	−0·000 (2)	0·003 (2)	0·003 (2)
O(4)	0·415 (2)	0·114 (3)	0·149 (2)	0·005 (3)	0·004 (3)	0·000 (1)	0·003 (3)	−0·003 (2)	0·002 (2)
O(5)	0·075 (2)	0·377 (3)	0·388 (2)	0·002 (3)	0·005 (3)	0·000 (1)	0·002 (2)	−0·002 (2)	−0·000 (2)
O(6)	0·417 (2)	0·382 (2)	0·351 (2)	0·003 (3)	0·004 (3)	0·003 (2)	−0·002 (3)	0·003 (2)	0·002 (2)
O(7)	0·217 (3)	0·408 (3)	0·109 (2)	0·019 (5)	0·001 (3)	0·000 (2)	−0·003 (3)	0·002 (2)	−0·002 (2)
O(8)	0·784 (3)	0·308 (3)	0·898 (2)	0·012 (4)	0·003 (3)	0·000 (1)	−0·003 (3)	0·001 (1)	0·000 (2)
O(9)	0·627 (2)	0·099 (2)	0·725 (2)	0·002 (3)	0·002 (3)	0·000 (1)	0·000 (2)	0·002 (1)	−0·002 (1)
O(10)	0·907 (2)	0·085 (2)	0·739 (2)	0·008 (3)	−0·001 (2)	−0·001 (1)	−0·001 (2)	−0·002 (2)	0·001 (1)
O(11)	0·701 (3)	0·082 (3)	0·000 (2)	0·022 (5)	0·000 (3)	0·002 (2)	0·002 (3)	0·002 (3)	0·000 (2)
O(12)	0·800 (3)	0·183 (3)	0·588 (2)	0·014 (4)	0·007 (4)	−0·002 (1)	0·003 (3)	0·000 (2)	0·000 (2)
O(13)	0·595 (2)	0·427 (3)	0·793 (2)	0·002 (3)	0·009 (4)	0·000 (2)	0·003 (3)	−0·002 (2)	0·000 (2)
O(14)	0·868 (2)	0·416 (2)	0·745 (2)	0·001 (3)	0·008 (4)	0·000 (2)	0·000 (3)	0·002 (1)	0·000 (2)

* Standard deviations are given in parentheses.

eters and anisotropic temperature factors are listed in Table 1 and structure factors in Table 2. The bond distances and angles are listed in Table 3.

NdP_5O_{14}

The oscillation and Weissenberg photographs showed diffraction symmetry $2/m$. The systematic absences were $h0l$, $l=2n+1$, and $0k0$ with $k=2n+1$, which indicate the unique space group $P2_1/c$ (No. 14) in the monoclinic system. The 2θ measurements made at 25 °C were used in a least-squares refinement to obtain the monoclinic lattice parameters. They are in good agreement with the parameters reported by Beucher (1970), except that we have interchanged the a and c designations in order to be consistent with the usage of *International Tables for X-ray Crystallography.*

The heavy-atom method was also used to determine the structure of this compound. The space group $P2_1/c$ yields Harker sections at $(0,2y-\frac{1}{2},\frac{1}{2})$ and $(2x,\frac{1}{2},2z-\frac{1}{2})$ on a three-dimensional Patterson map. When such a map was generated, the strongest peaks occurred at $(0,0{\cdot}88,\frac{1}{2})$ and $(0{\cdot}56,\frac{1}{2},0{\cdot}50)$, which are consistent with the Harker sections for a Nd position of $(0{\cdot}28,0{\cdot}19,0{\cdot}00)$. A structure-factor calculation based

Table 5. *Observed and calculated structure factors for* NdP_5O_{14}

H	K	FOBS	FCAL
*** L= 0 ***			
1	0	63	66
2	0	174	250
3	0	64	66
4	0	200	235
5	0	96	93
6	0	130	116
7	0	82	75
8	0	85	69
9	0	60	63
1	1	74	82
2	1	35	33
3	1	82	94
4	1	96	103
5	1	107	123
6	1	97	98
7	1	73	67
8	1	129	127
9	1	30	16
0	2	21	19
1	2	58	61
2	2	155	186
3	2	87	91
4	2	22	13
5	2	123	128
6	2	39	28
7	2	106	101
8	2	87	81
9	2	82	77
1	3	75	94
2	3	15	14
3	3	76	89
4	3	33	34
5	3	40	39
6	3	43	38
7	3	89	82
8	3	51	46
0	4	15	7
1	4	19	21
2	4	16	7
3	4	29	29
4	4	109	118
5	4	31	31
6	4	94	105
7	4	22	17
8	4	35	35
1	5	122	166
2	5	31	38
3	5	49	52
4	5	43	52
5	5	62	65
6	5	37	33
7	5	43	37
8	5	14	12
0	6	27	24
1	6	31	10
2	6	25	24
3	6	11	10
4	6	106	119
5	6	37	45
6	6	33	25
7	6	51	65
1	7	48	49
2	7	64	77
3	7	57	67
4	7	112	136
5	7	13	16
6	7	106	116
0	8	83	100
1	8	20	8
2	8	150	208
3	8	13	12
4	8	78	93
5	8	35	47
1	9	84	122
2	9	48	54
3	9	108	142
*** L= 1 ***			
0	1	97	78
1	1	5	4
2	1	55	55
3	1	91	93
4	1	9	8
5	1	83	62
6	1	11	11
7	1	78	63
8	1	47	41
9	1	56	44
-1	1	5	5
-2	1	50	51
-3	1	100	101
-4	1	17	16
-5	1	93	84
-6	1	23	16
-7	1	95	81
-8	1	49	52
-9	1	79	61
0	2	10	11
1	2	178	179
2	2	51	47
3	2	40	51
4	2	48	51
5	2	101	109
6	2	72	76
7	2	12	11
8	2	70	69
9	2	10	11
-1	2	177	188
-2	2	26	22
-3	2	26	31
-4	2	41	45
-5	2	104	116
-6	2	58	58
-7	2	83	78
-8	2	55	52
-9	2	14	2
0	3	172	158
1	3	33	23
2	3	163	176
3	3	98	101
4	3	58	61
5	3	110	113
6	3	118	119
7	3	115	108
8	3	14	18
-1	3	8	12
-2	3	162	187
-3	3	103	106
-4	3	80	90
-5	3	119	116
-6	3	106	107
-7	3	100	89
-8	3	37	25
0	4	30	5
1	4	208	212
2	4	89	86
3	4	140	157
4	4	84	88
5	4	91	87
6	4	108	109
7	4	52	43
8	4	86	51
-1	4	182	192
-2	4	51	55
-3	4	153	157
-4	4	69	69
-5	4	97	98
-6	4	129	130
-7	4	18	24
-8	4	109	109
0	5	104	136
1	5	10	2
2	5	124	146
3	5	81	91
4	5	132	155
5	5	72	78
6	5	13	6
7	5	88	92
8	5	44	41
-1	5	23	27
-2	5	125	146
-3	5	85	85
-4	5	98	109
-5	5	87	89
-6	5	55	57
-7	5	119	115
-8	5	54	50
0	6	39	9
1	6	149	180
2	6	39	39
3	6	128	140
4	6	26	25
5	6	81	84
6	6	70	69
7	6	28	26
-1	6	148	153
-2	6	24	12
-3	6	157	172
-4	6	41	41
-5	6	91	81
-6	6	45	47
-7	6	56	48
0	7	20	14
1	7	43	26
2	7	74	87
3	7	43	53
4	7	13	6
5	7	66	75
6	7	33	37
-1	7	46	27
-2	7	63	66
-3	7	48	59
-4	7	29	30
-5	7	67	67
-6	7	14	3
0	8	13	2
1	8	20	25
2	8	13	4
3	8	13	14
4	8	14	19
5	8	14	2
-1	8	22	17
-2	8	13	17
-3	8	41	41
-4	8	14	2
-5	8	14	7
0	9	40	30
1	9	14	1
2	9	37	44
3	9	14	17
-1	9	14	15
-2	9	14	15
-3	9	14	1
*** L= 2 ***			
0	0	137	119
1	0	75	65
2	0	235	266
3	0	142	145
4	0	152	146
5	0	168	177
6	0	28	16
7	0	158	145
8	0	73	77
9	0	110	98
-1	0	71	59
-2	0	274	318
-3	0	129	138
-4	0	154	145
-5	0	153	161
-6	0	74	69
-7	0	125	114
-8	0	66	62
-9	0	91	87
0	1	9	4
1	1	178	173
2	1	10	9
3	1	130	133
4	1	77	80
5	1	95	94
6	1	69	73
7	1	100	97
8	1	102	107
9	1	33	21
-1	1	176	162
-2	1	7	5
-3	1	112	120
-4	1	93	99
-5	1	85	96
-6	1	89	92
-7	1	92	91
-8	1	118	114
-9	1	33	19
0	2	384	373
1	2	77	67
2	2	132	126
3	2	69	68
4	2	136	142
5	2	104	104
6	2	38	36
7	2	72	66
8	2	47	48
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2	3	70	73
3	3	134	136
4	3	63	61
5	3	94	100
6	3	14	10
-1	3	58	53
-2	3	91	88
-3	3	136	139
-4	3	72	80
-5	3	75	74
-6	3	48	49
0	4	40	19
1	4	222	217
2	4	45	49
3	4	192	203
4	4	86	51
5	4	148	144
6	4	93	99
-1	4	232	236
-2	4	25	15
-3	4	221	232
-4	4	84	50
-5	4	134	141
-6	4	67	70
0	5	134	142
1	5	88	81
2	5	143	152
3	5	48	54
4	5	60	67
5	5	93	98
-1	5	88	87
-2	5	149	157
-3	5	30	24
-4	5	80	82
-5	5	96	102
0	6	13	5
1	6	58	63
2	6	61	54
3	6	54	57
4	6	53	44
-1	6	60	69
-2	6	54	47
-3	6	54	62
-4	6	37	35
0	7	89	85
1	7	14	2
2	7	71	71
-1	7	26	25
-2	7	94	93
*** L= 10 ***			
0	0	209	239
1	0	85	90
2	0	139	152
3	0	89	93
4	0	154	160
5	0	161	167
6	0	14	14
-1	0	76	78
-2	0	130	138
-3	0	61	60
-4	0	101	104
-5	0	145	148
-6	0	14	14
0	1	31	21
1	1	105	111
2	1	19	10
3	1	109	112
4	1	77	93
5	1	64	73
6	1	82	92
-1	1	114	125
-2	1	15	8
-3	1	135	144
-4	1	76	92
-5	1	96	118
-6	1	74	82
0	2	166	176
1	2	12	11
2	2	180	189
3	2	97	108
4	2	70	72
5	2	45	62
6	2	55	48
-1	2	31	32
-2	2	103	108
-3	2	66	70
-4	2	90	42
-5	2	60	62
-6	2	81	77
0	3	21	17
1	3	25	27
2	3	65	71
3	3	13	14
4	3	30	28
5	3	34	32
-1	3	12	6
-2	3	56	65
-3	3	13	8
-4	3	13	3
-5	3	14	25
0	4	66	55
1	4	64	68
2	4	26	21
3	4	13	15
4	4	14	6
5	4	51	50
-1	4	56	56
-2	4	24	20
-3	4	21	11
-4	4	14	1
-5	4	49	56
0	5	13	8
1	5	11	13
2	5	49	47
3	5	14	16
4	5	74	73
-1	5	34	33
-2	5	51	57
-3	5	14	8
0	6	99	93
1	6	44	45
2	6	35	40
3	6	32	25
-2	6	32	35
-3	6	31	23

on this position gave $R = 0.39$ for the difference function. Reviewing the Patterson map for additional strong peaks revealed two P positions, and introducing these into the calculation reduced the value of R to 0.31. A difference Fourier map was then constructed on the basis of the 3 atom positions that had been established. It revealed a number of peaks, some due to P and others about half as intense due to O. Step-by-step generation of a Fourier map finally elucidated 3 more

Table 6. Bond distances and angles in NdP_5O_{14}

Tetrahedron around P(1)

P(1)—O(3)	1·48 (1) Å			
P(1)—O(5)	1·48 (1)			
P(1)—O(10)	1·62 (2)	O(3)—P(1)—O(5)	119 (1)°
P(1)—O(14)	1·64 (2)	O(3)—P(1)—O(10)	113 (1)
O(3)—O(5)	2·55 (2)	O(3)—P(1)—O(14)	106 (1)
O(3)—O(10)	2·59 (2)	O(5)—P(1)—O(10)	105 (1)
O(3)—O(14)	2·48 (2)	O(5)—P(1)—O(14)	112 (1)
O(5)—O(10)	2·47 (2)	O(10)–P(1)–O(14)	100 (1)
O(5)—O(14)	2·59 (2)		
O(10)–O(14)	2·50 (2)		

Tetrahedron around P(2)

P(2)—O(4)	1·48 (1) Å			
P(2)—O(6)	1·47 (1)			
P(2)—O(9)	1·62 (1)	O(4)–P(2)–O(6)	120 (1)°
P(2)—O(13)	1·62 (1)	O(4)–P(2)–O(9)	111 (1)
O(4)—O(6)	2·56 (2)	O(4)–P(2)–O(13)	107 (1)
O(4)—O(9)	2·55 (2)	O(6)-P(2)-O(9)	106 (1)
O(4)—O(13)	2·49 (2)	O(6)-P(2)-O(13)	111 (1)
O(6)—O(9)	2·47 (2)	O(9)-P(2)-O(13)	101 (1)
O(6)—O(13)	2·55 (2)		
O(9)—O(13)	2·50 (2)		

Tetrahedron around P(3)

P(3)—O(2)	1·46 (1) Å			
P(3)—O(9)	1·56 (1)			
P(3)—O(10)	1·57 (1)	O(2)—P(3)–O(9)	117 (1)°
P(3)—O(12)	1·55 (1)	O(2)—P(3)–O(10)	117 (1)
O(2)—O(9)	2·58 (2)	O(2)—P(3)–O(12)	114 (1)
O(2)—O(10)	2·59 (2)	O(9)—P(3)–O(10)	104 (1)
O(2)—O(12)	2·52 (2)	O(9)—P(3)–O(12)	104 (1)
O(9)—O(10)	2·47 (2)	O(10)–P(3)–O(12)	99 (1)
O(9)—O(12)	2·46 (2)		
O(10)–O(12)	2·36 (2)		

Tetrahedron around P(4)

P(4)—O(1)	1·44 (1) Å			
P(4)—O(8)	1·70 (1)			
P(4)—O(11)	1·48 (1)	O(1)—P(4)–O(8)	112 (1)°
P(4)—O(12)	1·67 (1)	O(1)—P(4)–O(11)	120 (1)
O(1)—O(8)	2·60 (2)	O(1)—P(4)–O(12)	112 (1)
O(1)—O(11)	2·53 (2)	O(8)—P(4)–O(11)	106 (1)
O(1)—O(12)	2·58 (2)	O(8)—P(4)–O(12)	95 (1)
O(8)—O(11)	2·54 (2)	O(11)–P(4)–O(12)	109 (1)
O(8)—O(12)	2·49 (2)		
O(11)–O(12)	2·56 (2)		

Tetrahedron around P(5)

P(5)—O(7)	1·48 (1) Å			
P(5)—O(8)	1·56 (1)			
P(5)—O(13)	1·53 (1)	O(7)—P(5)–O(8)	114 (1)°
P(5)—O(14)	1·56 (1)	O(7)—P(5)–O(13)	117 (1)
O(7)—O(8)	2·56 (2)	O(7)—P(5)–O(14)	116 (1)
O(7)—O(13)	2·57 (2)	O(8)—P(5)–O(13)	103 (1)
O(7)—O(14)	2·58 (2)	O(8)—P(5)–O(14)	97 (1)
O(8)—O(13)	2·41 (2)	O(13)–P(5)–O(14)	106 (1)
O(8)—O(14)	2·34 (2)		
O(13)–O(14)	2·47 (2)		

Table 6 (cont.)

Dodecahedron around Nd

Nd–O(1)	2·49 (1) Å	O(1)–O(4)	2·76 (2) Å
Nd–O(2)	2·50 (1)	O(1)–O(6)	2·85 (2)
Nd–O(3)	2·41 (1)	O(2)–O(5)	2·89 (2)
Nd–O(4)	2·38 (1)	O(2)–O(7)	2·91 (2)
Nd–O(5)	2·40 (1)	O(3)–O(4)	2·96 (2)
Nd–O(6)	2·40 (1)	O(3)–O(5)	3·02 (2)
Nd–O(7)	2·47 (1)	O(3)–O(7)	2·90 (2)
Nd–O(11)	2·46 (1)	O(3)–O(11)	3·05 (2)
Nd–Nd	6·603 (5)	O(4)–O(11)	2·82 (2)
Nd–Nd	5·194 (5)	O(6)–O(11)	2·84 (2)

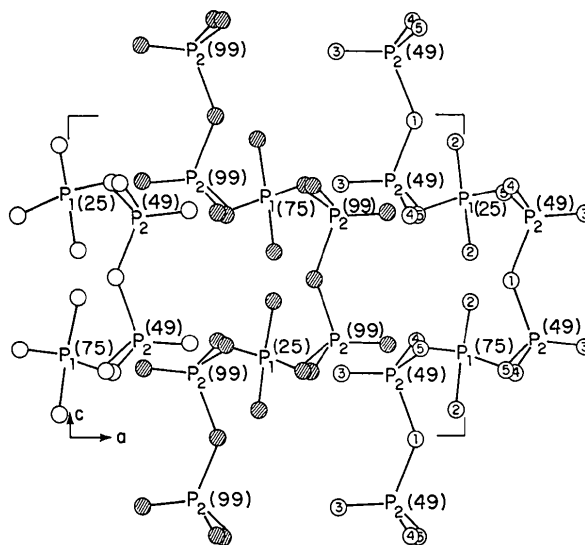|	
P(4)–O(8)—P(5)	128 (1)°
P(2)–O(9)—P(3)	133 (1)
P(1)–O(10)–P(3)	140 (1)
P(3)–O(12)–P(4)	129 (1)
P(2)–O(13)–P(5)	135 (1)
P(1)–O(14)–P(5)	138 (1)

Fig. 1. An ac projection of the arrangement of PO_4 tetrahedra in NdP_3O_9, showing the corrugated ribbons (formed by corner-sharing) that run parallel to the c axis.
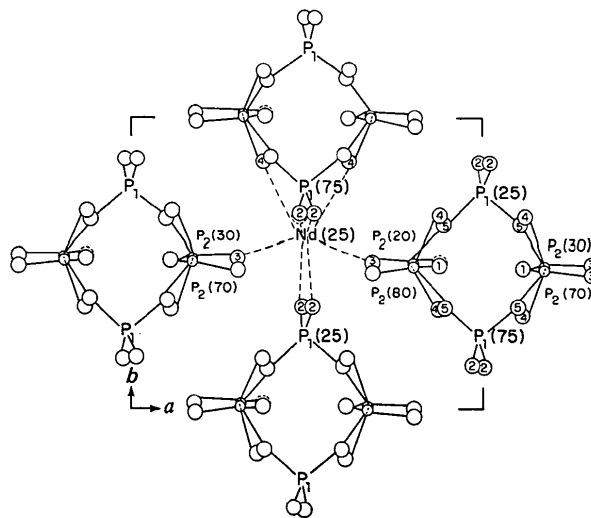

Fig. 2. An ab projection of the NdP_3O_9 structure, showing how the PO_4 tetrahedra are connected by Nd atoms.

P atoms and 14 independent O atoms. The atomic parameters and anisotropic temperature factors were then refined to the values listed in Table 4, giving an R value of 0·078 for all reflections and $R_w = 0·082$. The structure factors, based on this final parameter, are listed in Table 5. The bond distances and angles are listed in Table 6.
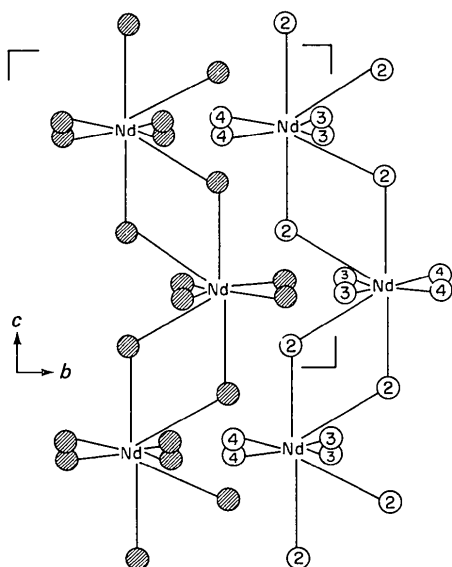

Fig. 3. A bc projection of the arrangement of NdO_8 dodecahedra in NdP_3O_9, showing the zigzag chains (formed by edge-sharing) that run parallel to the c axis.
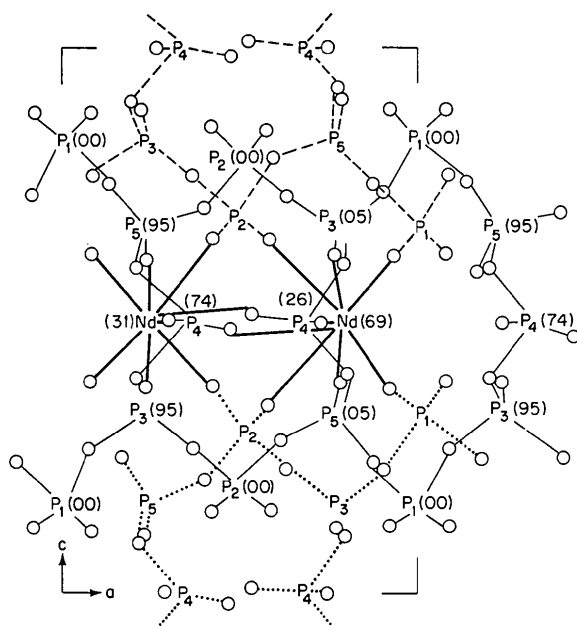
Fig. 4. An ac projection of the structure of NdP_5O_{14}, showing the planar $P_{10}O_{28}$ units and the Nd atoms linking them. The narrower solid lines connect the members of one $P_{10}O_{28}$ unit. Portions of two other units, lying in a plane displaced along the b axis, are connected by the dashed and dotted lines.

Description of the structures

In both NdP_3O_9 and NdP_5O_{14}, O atoms form a tetrahedron around each P atom and a NdO_8 polyhedron, around each Nd atom. In NdP_3O_9, the NdO_8 is a bis-disphenoid dodecahedron, while in NdP_5O_{14} it is a bicapped trigonal prism. The two compounds differ in the arrangement of the PO_4 tetrahedra and NdO_8 polyhedra.

In NdP_3O_9, the unit cell contains two independent PO_4 tetrahedra. From the bond distances and angles listed in Table 3 it is seen that the tetrahedron around P(1) is quite regular, while the one around P(2) deviates somewhat from regularity. The arrangement of the tetrahedra is shown by means of an ac projection in Fig 1. Neighboring P(2) tetrahedra form pairs by corner-sharing O(1) atoms, and these pairs are connected by P(1) tetrahedra to form helical chains running along the c axis. The P(1) and P(2) tetrahedra are connected by sharing O(5) atoms. The P(2)–O(1)–P(2) and P(1)–O(5)–P(2) angles are the same, 138·7°. Each tetrahedron shares two of its O atoms with other tetrahedra to give the O/P ratio of 3. As shown in the ab projection of Fig. 2, the chains of PO_4 tetrahedra are held together by the Nd atoms. Each NdO_8 dodecahedron contains a Nd–4O(2) plane and a Nd–2O(3)2O(4) plane, which are almost perpendicular to each other, as shown in the bc projection of Fig. 3. The dodecahedra share edges to produce zigzag chains in the direction of the c axis. Each Nd atom shares two O(2) atoms with one of the neighboring Nd atoms and shares two O(2) atoms with the other.

The atomic arrangement in NdP_5O_{14} is shown on an ac projection in Fig. 4. There are 5 non-equivalent P positions and 14 non-equivalent O positions. The PO_4 tetrahedra share corners to form pairs of one-dimensional chains cross-linked by P(4) atoms. Within a unit cell, the cross-linked chains consist of $P_{10}O_{28}$ units whose P atoms within chains lie in nearly the same ac plane. The narrower solid lines in Fig. 4 connect the members of one cross-linked pair of chains. Each inequivalent atom is represented twice in a $P_{10}O_{28}$ unit. Since 60% of the P atoms in the unit [P(1),P(2),P(4)] share 2 of their O atoms, and 40% [P(3) and P(5)] share 3 O atoms, the O/P ratio is 14 to 5. The two cross-linked chains form a band running parallel to the a axis.

Portions of two other cross-linked chains are also shown in Fig. 4. The members of one unit are connected by dashed lines, the members of the other by dotted lines. These chains also lie in the ac plane, but each is displaced by half a unit cell in the b direction from the chain connected by solid lines. They are linked to this unit and to each other by the 2 Nd atoms shown in Fig. 4, which are located between the plane of the solid unit and the plane of the dashed and dotted ones. The wider solid lines in Fig. 4 represent the Nd–O bonds. Each NdO_8 polyhedron shares all its O atoms with PO_4 tetrahedra, none with any other polyhedron.

Discussion

Every P atom in NdP_3O_9 and NdP_5O_{14} is bonded to 4 O atoms to form a PO_4 tetrahedron; every O atom is bonded to at least one P atom, and there is no direct P–Nd bonding. Therefore, the basic structures of these compounds are determined by the requirement that the O atoms must be shared in a manner that reduces the O/P ratio (R) from the value of 4 for isolated tetrahedra, as in $NdPO_4$ (Mooney, 1948), to the observed values of 3 and $\frac{14}{5}$, respectively. In NdP_3O_9 this reduction is accomplished by the formation of one-dimensional –P(2)–P(2)–P(1)– chains in which each PO_4 tetrahedron shares 2 of its O atoms with the adjacent tetrahedra leaving the other 2 unshared, to give $R = 2(\frac{1}{2}) + 2 = 3$. To decrease R to less than 3 requires cross-linking between chains.

If 2 parallel chains are completely cross-linked by sharing O atoms, each PO_4 tetrahedron shares 3 of its O atoms with the adjacent tetrahedra, leaving 1 unshared, to give $R = 3(\frac{1}{2}) + 1 = 2.5$. If only a fraction x of the tetrahedra are cross-linked, $R = 2.5x + 3(1 - x)$. In NdP_5O_{14} the P(3) and P(5) tetrahedra in the 2 chains are linked by sharing P(4) tetrahedra rather than O atoms directly, but the same formula for R can be applied if x is defined as the fraction of the tetrahedra that share 3 O atoms and $(1 - x)$ is the fraction that share only 2. Since $R = 2.8$ for NdP_5O_{14}, x must be 0.4. This value of x is obtained for the structure shown in Fig. 4, where the P(3) and P(5) tetrahedra each share 3 O atoms and the P(1), P(2), and P(4) tetrahedra each share 2 O atoms.

In NdP_5O_{14} the Nd atoms are isolated from each other by PO_4 tetrahedra, since no O atom is common to 2 Nd atoms. This isolation appears to account for the optical observations of Danielmeyer & Weber (1972) indicating that the Nd–Nd pair interaction is small in this compound. This interaction can be expected to be larger in NdP_3O_9, since each Nd atom shares 2 O atoms with one of the neighboring Nd atoms and 2 other O atoms with another. In addition, the minimum Nd–Nd distance in NdP_3O_9 is 4.234 Å, compared with 5.194 Å in NdP_5O_{14}.

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Hydrogen Bond Studies. LXXXI.* The Crystal and Molecular Structure of 2-Amino-5-chloropyridine, C5H3N(NH2)Cl

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The crystal and molecular structure of 2-amino-5-chloropyridine, $C_5H_3N(NH_2)Cl$, has been determined from four-circle X-ray diffractometer data (Mo $K\alpha$ radiation). The crystals are monoclinic, space group $P2_1/c$, with four formula units in a cell of dimensions $a = 13.4370$ (6), $b = 5.7963$ (5), $c = 7.5123$ (6) Å, $\beta = 105.512$ (6)°. The hydrogen atoms have been located and full-matrix least-squares refinement gave a final $R(F)$ value of 0.033. The molecules link via two N–H···N hydrogen bonds [3.058 (2) Å], to produce (centrosymmetric) dimers which, in turn, pack in a herring-bone formation.

Introduction

This work is part of a systematic investigation of hydrogen bonding in simple organic compounds which

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can serve as model substances for biologically important molecules. The crystal structures of 6-chloro-2-hydroxypyridine, the addition compound 6-chloro-2-hydroxypyridine–2-pyridone and 5-chloro-2-pyridone have been reported earlier by Kvick & Olovsson (1968), Almlöf, Kvick & Olovsson (1971) and Kvick & Booles