Acta Chemica Scandinavica A 37 (1983) 539–543

The Crystal Structure of $Ni_2P_4O_{12}$

ANDERS G. NORD

Section of Mineralogy, Swedish Museum of Natural History, P.O. Box 50007, S-104 05 Stockholm 50, Sweden

$Ni_2P_4O_{12}$ belongs to a group of isostructural $M_2P_4O_{12}$ tetrametaphosphates with monoclinic $C2/c$ space group symmetry. The cell constants of $Ni_2P_4O_{12}$ are: a=11.642(3), b=8.239(2), c=9.850(2) Å, β=118.47(2)°, V=830.6(5) Å^3 (Z=4); D_x=3.465 g cm^{-3}. The structure has been profile-refined with neutron powder diffraction data down to R_I=0.059 on the basis of 138 independent reflections. The two distinct cation sites have fairly regular octahedral environments with average Ni-O distances of 2.06(1) and 2.07(1) Å, respectively. The $P_4O_{12}^{4-}$ ions have P-O-P angles of 133.6° and 130.2°. A comparison with other known $M_2P_4O_{12}$ structures is made, showing good correlation between metal-oxygen distances and cation radii.

$Al_4(P_4O_{12})_3$ was the first tetrametaphosphate structure to be investigated; it was determined in 1937 by Pauling and Sherman.[1] Since then about thirty inorganic tetrametaphosphate structures have been published. Some pioneer work on divalent-metal metaphosphates was done by Thilo and Grunze.[2] They showed, from X-ray powder diffraction data and paper chromatography, that many of these compounds were isomorphous with each other and probably were tetrametaphosphates of the type $M_2P_4O_{12}$. Some unit cell dimensions were later published by Beucher and Grenier,[3] indicating monoclinic symmetry. The crystal structure for this group of tetrametaphosphates was finally solved independently by means of the compounds $Cu_2P_4O_{12}$ (Patterson methods)[4] and $Mg_2P_4O_{12}$ (direct methods),[5] thus settling the space group symmetry as $C2/c$. A study of $Co_2P_4O_{12}$ has also been completed recently.[6]

The present structural study of $Ni_2P_4O_{12}$ has been undertaken for two reasons. The first is a desire to improve the general crystallographic knowledge of divalent-metal phosphates (*cf.* Ref. 7) and to try to correlate observed metal-oxygen distances and cation radii in various groups of isomorphous compounds. The second reason is that the structure will be used as a reference for future cation distribution studies of some $(Ni,M)_2P_4O_{12}$ solid solutions. Such results will then be included in a more general survey of the distribution of M^{2+} cations in solid solutions of oxosalt structures, so far restricted by the present author to orthophosphates (*e.g.* Refs. 8–11).

EXPERIMENTAL

A sample of $Ni_2P_4O_{12}$ (~10 g) was prepared by thermal decomposition and reaction of a mixture of reagent grade NiO and $NH_4H_2PO_4$("Baker's Analyzed" Chemical Reagents) in the molar proportion 1:2. The mixture was slowly (24 h) heated to 1200 K in an open platinum crucible, ground, and heated again at 1100 K for two weeks. X-ray powder diffraction data were recorded with a Guinier-Hägg type focusing camera (Cu$K\alpha_1$ radiation, λ=1.5405 Å, 295 K, KCl internal standard). The unit cell dimensions (see next section) were determined utilizing conventional least-squares techniques (programs LAZY and CELREF by A. G. Nord). Because of pronounced difficulties in preparing single crystals (*cf.* Refs. 3–5), the structural study reported here was based on neutron powder diffraction data. These were collected at room temperature at the 2 MW JEEP-2 nuclear research reactor at Kjeller (Lillestrøm, Norway), with the sample kept in a thin-walled vanadium cylinder and using a "squashed" germanium monochromator crystal (λ≈1.882 Å). The data were recorded with an OPUS-3 powder diffractometer, equipped with five ^{3}He detectors, in the

0302-4377/83 $2.50

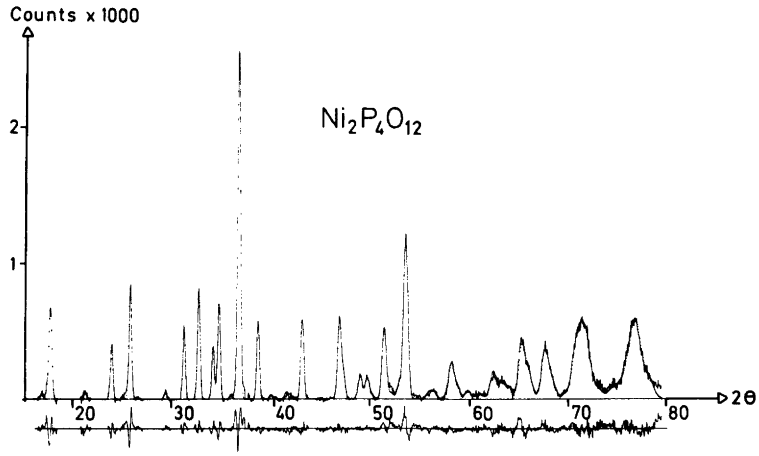

Fig. 1. The least-squares fit obtained between the observed intensities (continuous curve) and calculated intensities (points) for $Ni_2P_4O_{12}$ (neutron powder diffraction data). The discrepancy in the fit, defined as $\Delta I = I_{obs} - I_{calc}$, is plotted below to the same scale.

range $5 \leq \theta \leq 39.5°$ ($\Delta\theta = 0.025°$). The raw data from the various detectors were averaged with a NORD-10 computer at Kjeller.

STRUCTURE ANALYSIS

Crystal data. Nickel(II) tetrametaphosphate, $Ni_2P_4O_{12}$. Space group $C2/c$ (No. 15)

$a = 11.642(3)$ Å, $b = 8.239(2)$ Å,
$c = 9.850(2)$ Å, $\beta = 118.47(2)°$

$V = 830.6(5)$ Å^3, $Z = 4$, $D_x = 3.465$ g · cm^{-3}
(at 295 K); $M_w = 433.30$ *u*.

The neutron diffraction intensity profile contained 138 partly overlapping, independent Bragg reflections. After subtraction of the background, the data were processed with Rietveld's full-profile refinement procedure.[12] Some trial refinements were made to settle the wavelength, scale factor *etc.* In the final stages, the complete crystal structure was refined with 32 parameters: one scale factor, 25 atomic positional parameters (starting with those of $Mg_2P_4O_{12}$[5]), three parameters defining the Gaussian shape of the peaks as a function of θ, and three isotropic temperature factors (for nickel, phosphorus, and oxygen). The final R values (*cf.* Ref. 12) were $R_I = 0.059$, $R_p = 0.103$, and $R_{wp} = 0.111$.

Table 1. Fractional atomic coordinates and thermal parameters for $Ni_2P_4O_{12}$ (space group $C2/c$). The estimated standard deviations are given within parentheses and refer to the last digit of the respective value.

Atom	Point set	x	y	z	B (Å^2)
Ni1	4(*d*)	1/4	1/4	1/2	0.2(2)
Ni2	4(*e*)	0	0.053(1)	1/4	0.2(2)
P1	8(*f*)	0.188(2)	0.501(2)	0.194(2)	0.7(3)
P2	8(*f*)	0.010(2)	0.264(2)	–0.018(2)	0.7(3)
O1	8(*f*)	0.069(1)	0.613(2)	0.153(2)	0.4(1)
O2	8(*f*)	0.148(1)	0.362(2)	0.074(2)	0.4(1)
O3	8(*f*)	0.230(1)	0.418(2)	0.348(2)	0.4(1)
O4	8(*f*)	0.304(2)	0.575(2)	0.183(2)	0.4(1)
O5	8(*f*)	–0.050(2)	0.247(2)	0.085(2)	0.4(1)
O6	8(*f*)	0.029(1)	0.119(2)	–0.093(2)	0.4(1)

A table of observed and calculated integrated intensities is available from the author. The observed and calculated intensity profiles are shown in Fig. 1. The refined atomic parameters are listed in Table 1. Note that the labelling is *not* the same as for $Mg_2P_4O_{12}$;[5] it has been changed to accord with the labelling of the $Cu_2P_4O_{12}$ atoms[4] which better agrees with the generally adopted nomenclature used in cation distribution studies of olivines, orthopyroxenes, *etc.*

DISCUSSION

The crystal structure of $Ni_2P_4O_{12}$ is built up of two kinds each of crystallographically non-equivalent NiO_6 octahedra and PO_4 tetrahedra. The octahedra are linked by edge-sharing in $-(Ni1)O_6-(Ni2)O_6-(Ni1)O_6-(Ni2)O_6-$ chains parallel to $10\bar{1}$; the common edge O4–O5 is the shortest O–O distance within each octahedron, *viz.* 2.72(2) Å. Two PO_4 tetrahedra of each kind are linked together in a ring to form a $P_4O_{12}^{4-}$ ion with a crystallographically imposed $\bar{1}$ symmetry. The NiO_6 and PO_4 polyhedra share corners with each other, thus building up a three-dimensional framework. Illustrations of the crystal structure have been given previously (*cf.* Refs. 4,5); the tetrametaphosphate anion is shown in Fig. 2.

Some interatomic distances and angles in $Ni_2P_4O_{12}$ are given in Table 2. The PO_4 tetrahedra are distorted, with the bridging P–O distances significantly longer than the terminal ones. The two P–O–P angles are 133.6° and 130.2° respectively, so that the bridging angle at O1 is about 3° larger than at O2. The same tendency was observed in $Mg_2P_4O_{12}$ (X-ray single-crystal data)[5] and $Co_2P_4O_{12}$ (neutron powder data)[6], but for $Cu_2P_4O_{12}$ (X-ray single-crystal data)[4] both P–O–P angles are around 137°. In $Ni_2P_4O_{12}$ and $Mg_2P_4O_{12}$ (P2)O_4 is more distorted than (P1)O_4, while the converse is true for $Cu_2P_4O_{12}$ and $Co_2P_4O_{12}$.

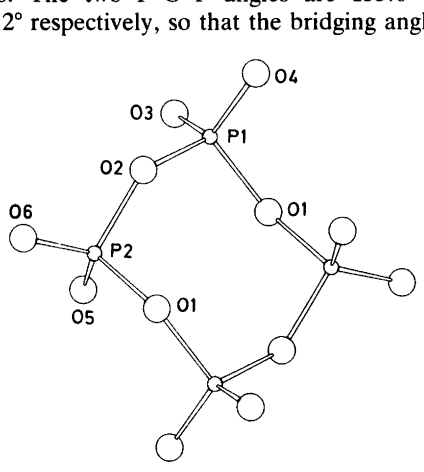

Fig. 2. The centrosymmetrical tetrametaphosphate ion.

Ni1 and Ni2 have the point symmetries $\bar{1}$ and *2*, respectively. The two NiO_6 octahedra are fairly regular (*cf.* Table 2). The metal-oxygen distance ranges and average values within each type of metal-oxygen polyhedron are compared for the four known $M_2P_4O_{12}$ tetrametaphosphate structures. This is done in Table 3. (Note that the atoms are labelled as in Ref. 4). In addition, the unit cell dimensions of these compounds are also given for comparison. It is obvious that the metal-oxygen octahedra in the nickel, magnesium, and cobalt tetrametaphosphates are fairly regular, while in $Cu_2P_4O_{12}$ the CuO_6 octahedra are very distorted, probably due to the Jahn-Teller effect. Generally, the *M*-O mean distances correspond well with what might be expected considering the values of the cation radii (see Table 3). This agreement between ionic radii and geometrical dimensions is also expressed, although less explicitly, in the unit cell dimensions. Again $Cu_2P_4O_{12}$ is a slight exception.

As mentioned in the introductory section, I have performed some cation distribution studies utilizing various orthophosphates as "base structures" for the solid solutions. In a neutron diffraction study of the olivine-related solid solution $(Ni_{0.75}Zn_{0.25})_3(PO_4)_2$,[9] with two distinct octahedral cation sites, it was shown that Ni^{2+} was partially ordered at the somewhat smaller and more regular M1 sites, with $K_D(Ni,Zn)\approx 4$. A study of isostructural $(Ni,Mg)_3(PO_4)_2$ phases[15] gave $K_D(Ni,Mg)=4.0$. The metal-oxygen octahedra in $Ni_2P_4O_{12}$ are similar in shape as well as symmetry to those of the orthophosphates mentioned, and also to the MO_6 octahedra in olivine, an important rock-forming mineral. It would therefore be interesting to use nickel tetrametaphosphate as a "base structure" for cation distribution studies of some suitable $(Ni,M)_2P_4O_{12}$ solid solutions, to see if the same cation ordering tendencies will appear here. Some investigations are already in progress; preliminary results show that in $NiZnP_4O_{12}$ there is a slight tendency for nickel to prefer the M1

Table 2. Interatomic distances (Å) and angles (°) in $Ni_2P_4O_{12}$. The standard deviations are around ±0.02 Å for the P–O distances, ±0.01 Å for the Ni-O distances, and ±0.6° or less for the angles.

P1–O1	1.56	P2–O1	1.58
P1–O2	1.56	P2–O2	1.63
P1–O3	1.51	P2–O5	1.48
P1–O4	1.53	P2–O6	1.48
Average:	1.54	Average:	1.54
O1–P1–O2	109.3	O1–P2–O2	100.1
O1–P1–O3	110.2	O1–P2–O5	111.5
O1–P1–O4	116.9	O1–P2–O6	105.3
O2–P1–O3	105.6	O2–P2–O5	109.0
O2–P1–O4	101.3	O2–P2–O6	109.3
O3–P1–O4	112.0	O5–P2–O6	119.9
Average:	109.2	Average:	109.2
P1–O1–P2	133.6	P1–O2–P2	130.2
Ni1–O3	1.97 (×2)	Ni2–O4	2.06 (×2)
Ni1–O4	2.15 (×2)	Ni2–O5	2.15 (×2)
Ni1–O5	2.07 (×2)	Ni2–O6	2.00 (×2)
Average:	2.06	Average:	2.07
O3–Ni1–O3′	180	O5–Ni2–O6	173.6 (×2)
O4–Ni1–O4′	180	O4–Ni2–O4′	170.0
O5–Ni1–O5′	180	O4–Ni2–O6	93.7 (×2)
O4–Ni1–O5	99.8 (×2)	O5–Ni2–O6	93.4 (×2)
O3–Ni1–O4	92.7 (×2)	O4–Ni2–O6′	93.4 (×2)
O3–Ni1–O5	90.1 (×2)	O4–Ni2–O5	92.0 (×2)
O3–Ni1–O5′	89.9 (×2)	O6–Ni2–O6′	89.8
O3′–Ni1–O4	87.3 (×2)	O5–Ni2–O5′	84.0
O4′–Ni1–O5	80.2 (×2)	O4′–Ni2–O5	80.6 (×2)

Table 3. Unit cell parameters and averaged metal-oxygen distances for four $M_2P_4O_{12}$ tetrametaphosphates. The standard deviation of the average distances refer to the estimated values for each separate *M*–O distance. The cited cation radii, r_M, are those for octahedrally coordinated M^{2+} ions published by Shannon and Prewitt.[13,14]

	$Ni_2P_4O_{12}$	$Mg_2P_4O_{12}$	$Cu_2P_4O_{12}$	$Co_2P_4O_{12}$
Reference	This work	Ref. 5	Ref. 4	Ref. 6
r_M (Å)	0.69	0.72	0.73	0.74
a (Å)	11.642(3)	11.756(2)	12.552(8)	11.809(2)
b (Å)	8.239(2)	8.285(1)	8.083(3)	8.297(1)
c (Å)	9.850(2)	9.917(1)	9.573(3)	9.923(2)
β (°)	118.47(2)	118.96(2)	118.66(1)	118.72(1)
V (Å^3)	830.6(5)	845.1(3)	852.3(8)	852.6(4)
M1-O mean (Å)	2.06(1)	2.065(3)	2.092(6)	2.08(2)
M2-O mean (Å)	2.07(1)	2.092(3)	2.122(6)	2.11(2)
M1-O range (Å)	1.97–2.15	2.01–2.10	1.94–2.37	2.03–2.14
M2-O range (Å)	2.00–2.15	1.99–2.16	1.91–2.47	2.03–2.16

site of the structure, and the same situation is also noted in $NiMgP_4O_{12}$.[16] Crystallographic work on some pure $M_2P_4O_{12}$ phases is also in progress.

Acknowledgements. I am very grateful to Professor Eric Welin for his kind interest in my work and for the excellent laboratory and computing facilities placed at my disposal. It is a great pleasure to thank Dr Arne F. Andresen (Kjeller, Norway) for his valuable help with the collection and processing of the neutron diffraction data. Many thanks are also due to my colleagues Dr Knut Christiansson for his helpful and inspiring discussions, and to Mr David Mills for the illustrations.

This work has in some part been financially supported by the Swedish Natural Science Research Council (NFR).

REFERENCES

1. Pauling, L. and Sherman, J. *Z. Kristallogr. 96* (1937) 481.
2. Thilo, E. and Grunze, I. *Z. Anorg. Allg. Chemie 290* (1957) 209.
3. Beucher, M. and Grenier, J. C. *Mater. Res. Bull. 3* (1968) 643.
4. Laügt, M., Guitel, J. C., Tordjman, I. and Bassi, G. *Acta Crystallogr. B28* (1974) 201.
5. Nord, A. G. and Lindberg, K. B. *Acta Chem. Scand. A29* (1975) 1.
6. Nord, A. G. *Cryst. Struct. Commun. 11* (1982) 1467.
7. Nord, A. G. and Kierkegaard, P. *Chem. Scr. 15* (1980) 27.
8. Nord, A. G. and Stefanidis, T. *Acta Crystallogr. B37* (1981) 1509.
9. Nord, A. G. *Neues Jahrb. für Mineral.*, (1982) 422.
10. Nord, A. G. and Ericsson, T. *Amer. Mineral. 67* (1982) 826.
11. Nord, A. G. *Acta Chem. Scand. A36* (1982) 95.
12. Rietveld, H. M. *J. Appl. Crystallogr. 2* (1969) 65.
13. Shannon, R. D. and Prewitt, C. T. *Acta Crystallogr. B25* (1969) 925.
14. Shannon, R. D. and Prewitt, C. T. *Acta Crystallogr. B26* (1970) 1046.
15. Nord, A. G. and Stefanidis, T. *Phys. Chem. Minerals* (1983). *In press.*
16. Nord, A. G. *To be published.*

Received November 22, 1982.