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Structure and Chelation Geometry of α,β,γ-Tridentate Triammine(dihydrogentriphosphato)cobalt(III), $[Co(NH_3)_3(H_2P_3O_{10})]$

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Abstract

$[Co(NH_3)_3(H_2P_3O_{10})]$ crystallizes in the tetragonal space group $P4_2/mbc$, with $a = b = 12{\cdot}892$ (2), $c = 13{\cdot}519$ (2) Å, $Z = 8$, $R = 0{\cdot}058$ for 1069 unique data with $F_o > 3\sigma$. The α,β,γ-tridentate complex reported here is a model for a possible chelation geometry of the biologically important MgATP complex. It contains two fused six-membered chelate rings formed by the facial coordination of one O from each of the three phosphate residues. The complex is bisected by a crystallographic mirror plane through atoms N(2)—Co—O(5)—P(2)—O(6). The triphosphate chain is in a folded conformation with torsion angles about the central phosphodiester P—O bonds of 94·8 (4) and −94·8 (4)° and a P—P—P virtual angle of 93·3 (1)°.

Introduction

Nucleoside di- and triphosphates in association with metal ions are substrates or cofactors for many enzyme-catalyzed reactions. The chelation of one, two, or three phosphate O atoms to the metal leads to a family of mono-, bi-, and tridentate coordination isomers. The specific mode of metal–phosphate coordination is of central importance in the recognition and interaction of the metal–nucleotide complex and the enzyme. In the case of the biologically common Mg^{2+} ion, the alternate coordination modes interchange rapidly in solution. The corresponding substitution-inert Co^{3+} complexes, however, are stable enough to be separated and characterized; thus they serve as useful probes of enzyme specificity (Cornelius & Cleland, 1978). To delineate the various chelation geometries we have pursued a program of X-ray crystallographic studies of polyphosphatocobalt-ammine chelation complexes, including the β,γ-bidentate (Merritt & Sundaralingam, 1980) and α,γ-bidentate (Merritt, Sundaralingam & Cornelius, 1981) coordination isomers of the chelated triphosphate chain. We present here the structure of the α,β,γ-tridentate coordination isomer; a preliminary structure was reported earlier (Merritt & Sundaralingam, 1977).

Although no enzymes are known to date which specifically require one of the four α,β,γ-tridentate diastereomers of MgATP, these forms may be intermediates in enzyme-catalyzed reactions which start with β,γ-bidentate MgATP and proceed to yield α,β-bidentate MgADP. The shift in coordination from the γ- to the α- phosphate may occur simultaneously or sequentially with chain cleavage. In the case of pyruvate kinase the cleavage is believed to occur first, followed by migration of the metal ion (Dunaway-Mariano, Benovic, Cleland, Gupta & Mildvan, 1980). If, however, the change in coordination state occurs first or simultaneously, a tridentate intermediate is possible.

Experimental

Crystals of triammine(dihydrogentriphosphato)cobalt(III), $[Co(NH_3)_3(H_2P_3O_{10})]$, were prepared as described by Cornelius, Hart & Cleland (1977). Intensity data were collected from a crystal measuring 0·07 mm × 0·15 mm × 0·17 mm on an Enraf–Nonius CAD-4 diffractometer using Ni-filtered Cu radiation ($\lambda = 1{\cdot}5418$ Å). Of 1242 unique reflections scanned in bisecting geometry, 1071 were considered observed by the criterion $F_o > 3\sigma$. Corrections for Lorentz–polarization and an overall 10% decay in intensity as measured by three standard reflections were applied during data reduction. No absorption correction was applied ($\mu = 16{\cdot}9$ mm^{-1}). The structure was solved by a combination of Patterson and difference Fourier syntheses. All H atoms were located after refining the 11 heavy atoms. Reflections with $F_o > 3\sigma$ were given weights $w = [\sigma^2 + (0{\cdot}05F_o)^2]^{-1}$. Two low-angle reflections, 201 and 210, were given zero weight due to serious secondary extinction. Full-matrix least-squares refinement of positional and thermal parameters for all atoms yielded a final R value of 0·058 for 1069 nonzero-weighted reflections. Atomic scattering factors including terms due to anomalous dispersion

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for non-H atoms were taken from *International Tables for X-ray Crystallography* (1974).*

Results and discussion

Fractional atomic coordinates, isotropic thermal parameters, bond and torsion angles are given in Tables 1 and 2. The complex is bisected by a crystallographic mirror plane through atoms N(2)—Co—O(5)—P(2)—O(6) (Fig. 1). The two fused six-membered chelate rings are thus mirror reflections, with atoms Co, O(5) and P(2) common to both rings. The conformation of the Co—O(1)—P(1)—O(4)—P(2)—O(5) ring may be described following Cremer & Pople (1975) by the amplitude of pucker Q = 0·524 (4) Å, and pseudorotational phase angles θ = 74·1 (6)°, φ = 291·8 (5)°. The average deviation of ring atoms from the least-squares plane through the ring is 0·19 Å, with O(5) and P(1) on one side of the plane and the remaining atoms on the other. The planes of the two fused six-membered rings form a right angle: 90·1 (1)°. The Co—O(5)—P(2) angle of 123·6 (4)° shared by the two rings is significantly smaller than the Co—O(1)—P(1) angle of 131·8 (3)°, and also smaller than any of the Co—O—P angles observed in other polyphosphatocobaltammine complexes (Merritt & Sundaralingam, 1980; Merritt, Sundaralingam & Cornelius, 1981). The small angle is presumably due to the constraints of tridentate chelation.

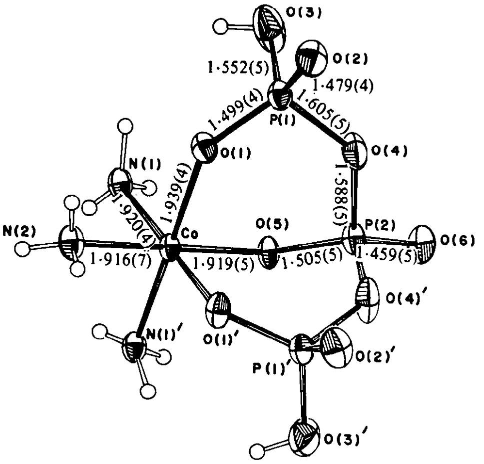

Fig. 1. The α,β,γ-tridentate [$Co(NH_3)_3(H_2P_3O_{10})$] complex with thermal ellipsoids drawn at the 50% probability level. The atoms N(2)—Co—O(5)—P(2)—O(6) lie on a crystallographic mirror plane. Bond distances are given in Å. Bond and torsion angles are given in Table 2.

Table 1. *Positional and isotropic thermal parameters*

Values for non-H atoms are given as $B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$; atoms lying on the mirror plane (z = 0) have multiplicity 0·5.

	x	y	z	B (Å^2)
Co	0·1197 (1)	0·1663 (1)	0·0000	1·17 (2)
P(1)	0·2100 (1)	0·0094 (1)	0·1558 (1)	1·62 (3)
P(2)	0·3415 (1)	0·0899 (1)	0·0000	1·43 (4)
O(1)	0·1223 (3)	0·0584 (3)	0·0999 (3)	1·80 (8)
O(2)	0·1987 (3)	−0·1025 (3)	0·1773 (3)	2·56 (10)
O(3)	0·2366 (4)	0·0714 (4)	0·2509 (4)	4·02 (13)
O(4)	0·3143 (3)	0·0175 (3)	0·0914 (4)	2·76 (11)
O(5)	0·2679 (4)	0·1805 (4)	0·0000	1·47 (11)
O(6)	0·4520 (4)	0·1145 (4)	0·0000	2·17 (13)
N(1)	0·1144 (3)	0·2717 (3)	0·1002 (3)	1·57 (9)
N(2)	−0·0282 (5)	0·1518 (5)	0·0000	1·85 (15)
H(O3)	0·190 (6)	0·113 (6)	0·261 (8)	5·5 (23)
H(1*A*)	0·108 (5)	0·234 (6)	0·163 (5)	3·9 (18)
H(1*B*)	0·174 (6)	0·307 (6)	0·104 (6)	5·1 (20)
H(1*C*)	0·083 (6)	0·301 (7)	0·076 (7)	6·6 (22)
H(2*A*)	−0·076 (9)	0·194 (8)	0·000	4·6 (27)
H(2*B*)	−0·044 (7)	0·113 (7)	0·041 (7)	10·0 (34)

Table 2. *Bond and torsion angles* (°)

N(1)—Co—N(2)	91·9 (3)	O(1)—P(1)—O(2)	115·8 (3)
N(1)—Co—O(1)	91·0 (2)	O(1)—P(1)—O(3)	111·5 (3)
N(1)—Co—O(5)	88·2 (2)	O(1)—P(1)—O(4)	109·3 (3)
N(1)—Co—N(1)'	89·8 (2)	O(2)—P(1)—O(3)	111·2 (4)
N(1)—Co—O(1)'	178·7 (2)	O(2)—P(1)—O(4)	104·6 (3)
N(2)—Co—O(1)	87·0 (3)	O(3)—P(1)—O(4)	103·3 (4)
N(2)—Co—O(5)	179·9 (4)		
O(1)—Co—O(1)'	88·3 (2)	O(4)—P(2)—O(5)	108·5 (3)
O(1)—Co—O(5)	92·9 (2)	O(4)—P(2)—O(6)	110·1 (3)
		O(4)—P(2)—O(4)'	102·2 (3)
Co—O(1)—P(1)	131·8 (3)	O(5)—P(2)—O(6)	116·5 (4)
Co—O(5)—P(2)	123·6 (4)		
P(1)—O(4)—P(2)	130·2 (3)		
Co—O(1)—P(1)—O(4)	−26·4 (4)	P(2)—O(5)—Co—O(1)	44·2 (4)
O(1)—P(1)—O(4)—P(2)	17·7 (5)	O(5)—Co—O(1)—P(1)	1·4 (3)
P(1)—O(4)—P(2)—O(5)	19·7 (4)	P(1)—O(4)—P(2)—O(4)'	−94·8 (4)
O(4)—P(2)—O(5)—Co	−55·1 (4)	P(1)—O(1)—Co—O(1)'	94·3 (4)

Molecules of the complex lie within the unit cell in planes at z = 0 and $z = \frac{1}{2}$ (Fig. 2). Within and between these planes the molecules are linked through intermolecular hydrogen bonds from the ammonia ligands to O(2), O(3) and O(6) (Table 3). O(6) is within hydrogen-bonding distance of all three ammine N atoms of a single screw-related molecule: N(1)···O(6) 3·024 (8), N(2)/N(2)'···O(6) 2·893 (6) Å. The parallel planes are additionally linked by a hydrogen bond from O(3) to O(2) of 2·574 (5) Å. Unlike the crystal structures of the α,γ-bidentate and β,γ-bidentate coordination isomers there are no interligand hydrogen bonds within the complex.

The phosphate chain of the present model compound is fairly sharply bent; the torsion angle about the phosphodiester bond P(1)—O(4)—P(2)—O(4)' is 94·8 (4)°, which yields a P—P—P angle of 93·3 (1)°. The α,β,γ-tridentate chelation mode was previously observed in the two independent molecules of Na_2ATP (Kennard *et al.*, 1972) where the phosphate chains

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36040 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

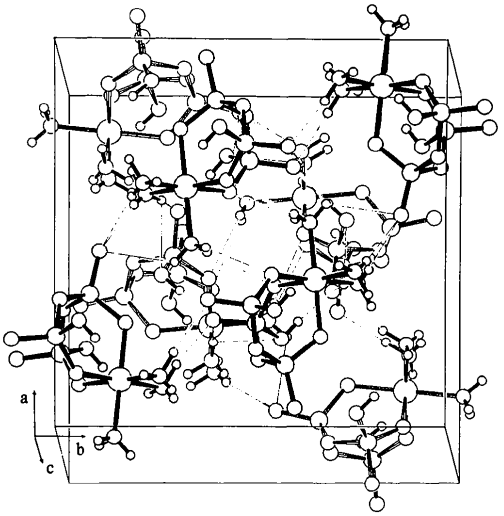

Fig. 2. A view of the crystal packing roughly along the 4_2 axis. The darker molecules are in the plane $z = 0$, while the lighter ones are in the plane $z = \frac{1}{2}$. Hydrogen bonds are shown as dotted lines.

Table 3. *Hydrogen bonding*

Hydrogen bond Donor H Acceptor	Symmetry code	$D\cdots A$ (Å)	$H\cdots A$ (Å)	$D–H\cdots A$ (°)
N(1)–H(1*A*)···O(3)	[2, 0 0 0]	3·161	2·59	117
N(1)–H(1*A*)···O(2)	[2, 0 0 0]	3·155	2·21	152
N(1)–H(1*B*)···O(2)	[4, 0 0 0]	3·086	2·24	162
N(1)–H(1*C*)···O(6)	[1, –1 0 0]	2·893	2·26	157
N(2)–H(2*A*)···O(6)	[1, –1 0 0]	3·024	2·50	123
N(2)–H(2*B*)···O(1)	[3, 0 0 0]	3·262	2·56	152
O(3)–H(O3)···O(2)	[2, 0 0 0]	2·574	1·79	162
Mean e.s.d.		0·007	0·08	8

Symmetry codes for the acceptor atoms are given as x, y and z translation preceded by the symmetry operation as follows: (1) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (2) $-y, x, \frac{1}{2} - z$; (3) $-x, -y, z$; (4) $\frac{1}{2} - x, \frac{1}{2} + y, z$.

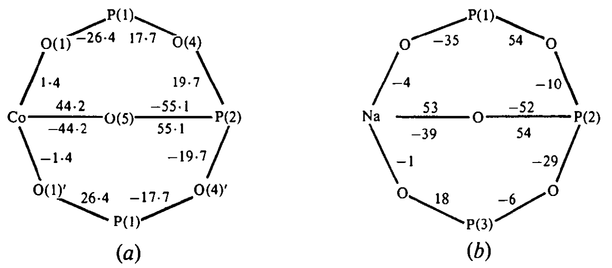

Fig. 3. Comparison of the chelate ring conformations of (*a*) $[Co(NH_3)_3(H_2P_3O_{10})]$ and (*b*) molecule *A* of Na_2ATP (Kennard *et al.*, 1972) showing ring torsion angles (°). The two lower rings in the figure (*i.e.* the β,γ-ring of Na_2ATP) are similar in conformation; however, the upper rings are dissimilar, as are both rings of molecule *B* of Na_2ATP. The e.s.d. of torsion angles in (*a*) is 0·4°; in (*b*) it is 4°.

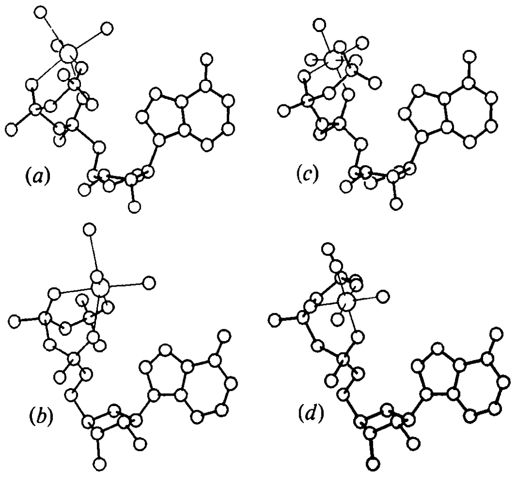

Fig. 4. Comparison of the chelate ring conformations in Na_2ATP with those of model α,β,γ-tridentate CoATP complexes generated from the metal–phosphate geometry reported in this paper. (*a*) Molecule *A* of Na_2ATP (Kennard *et al.*, 1972). (*b*) Molecule *B* of Na_2ATP. (*c*) Model of (*Δ*)*endo*-α,β,γ-tridentate CoATP corresponding in stereochemistry to (*a*). The model was generated by attaching atom C(5′) of the ribose moiety to atom O(2) of the cobaltammine complex with bond and torsion angles about this juncture equal to those in (*a*). (*d*) Model of (*Λ*)*endo*-α,β,γ-tridentate CoATP corresponding in stereochemistry to (*b*). The model was generated by attachment of the nucleoside at O(2)′, maintaining bond and torsion angles as in (*b*). Nomenclature is as defined in Merritt, Sundaralingam, Cornelius & Cleland (1978).

Table 4. *Six-membered chelate-ring pucker in α,β,γ-tridentate complexes*

	Ring	Q (Å)	θ (°)	φ (°)	Metal···OP distances (Å)		
					P_α	P_β	P_γ
$[Co(NH_3)_3(H_2P_3O_{10})]$ (this paper)							
	α,β	0·524	74	292	1·94	1·92	1·94
	α′,β	0·524	106	248			
Na_2ATP (Kennard *et al.*, 1972)							
A	α,β	0·722	79	318	2·45	2·48	2·32
	γ,β	0·470	115	113			
B	α,β	0·561	152	100	2·59	2·43	2·53
	γ,β	0·580	79	315			
$[Zn^{II}(H_2ATP)(2,2'\text{-bipyridyl})]_2.4H_2O$ (Orioli *et al.*, 1980)							
A	α,β	0·668	75	305	2·71	2·09	2·02
	γ,β	0·261	136	90			
B	α,β	0·617	103	116	2·39	2·05	1·99
	γ,β	0·341	28	256			

The amplitude of ring pucker Q and phase angles θ,φ are as defined by Cremer & Pople (1975). The six-membered chelate rings are traced starting from the metal atom and proceeding through, *e.g.*, the γ and β P atoms. *A* and *B* denote molecules *A* and *B*.

were also sharply folded, with P—P—P angles of 98 and 91°. However, the overall coordination geometry and the chelate-ring pucker of the present cobaltammine model compound are different from those in the Na_2ATP complex (Figs. 3 and 4). This is due in part to the longer metal–oxygen coordination distance in Na_2ATP (Table 4). The recently reported $[Zn^{II}(H_2ATP)(2,2'\text{-bipyridyl})]_2.4H_2O$ crystal structure also exhibits α,β,γ-tridentate coordination, although the

Table 5. *Tripolyphosphate chain conformation*

Compound	Reference	P_1-P_2 (Å)	P_2-P_3 (Å)	P_1-P_3 (Å)	∠PPP (°)	$\angle O_{12}$ (°)	$\angle P_2$ (°)	$\angle O_{23}$ (°)	τ_{12} (°)	τ_{23} (°)	Stagger about P_1-P_2 (°)	P_2-P_3 (°)
β,γ-$[Co(NH_3)_4(H_2P_3O_{10})].H_2O$	(*a*)	2·871	2·904	4·892	116	127	102	129	80	115	41	44
α,γ-$[Co(NH_3)_4(H_2P_3O_{10})].H_2O$	(*b*)	2·939	2·907	3·987	86	133	102	130	3	−106	60	60
α,β,γ-$[Co(NH_3)_3(H_2P_3O_{10})]$	(*c*)	2·896	(2·896)	4·213	93	130	102	(130)	95	(−95)	43	(43)
Na_2ATP molecule *A*	(*d*)	2·966	3·012	4·514	98	132	96	135	−128	84	38	37
molecule *B*		3·003	3·012	4·299	91	136	100	139	51	−119	22	39
$Zn_2NaP_3O_{10}.9H_2O$	(*e*)	2·912	2·906	4·392	98	130	104	129	83	64	18	29
$Zn_2(Ag/H)P_3O_{10}.9H_2O$	(*f*)	2·917	2·911	4·397	98	131	104	128	84	62	18	19
$Zn_5(P_3O_{10})_2.17H_2O$	(*g*)	2·936	2·901	4·413	98	129	104	129	−88	−60	15	29
$Al(NH_4)HP_3O_{10}$	(*h*)	2·919	(2·919)	5·240	128	132	103	(132)	−113	(−113)	1	(1)

References: (*a*) Merritt & Sundaralingam (1980); (*b*) Merritt, Sundaralingam & Cornelius (1981); (*c*) this paper; (*d*) Kennard *et al.* (1972); (*e*) Averbuch-Pouchot & Guitel (1977); (*f*) Averbuch-Pouchot & Guitel (1976); (*g*) Averbuch-Pouchot, Durif & Guitel (1975); (*h*) Averbuch-Pouchot, Durif & Guitel (1977).

Notes: The tripolyphosphate chain atoms are labeled $P_1-O_{12}-P_2-O_{23}-O_3$. τ_{12} is the torsion angle about the $O_{12}-P_2$ bond; τ_{23} is the torsion angle about the P_2-O_{23} bond. Values involving O_{23} which are given in parentheses are constrained by crystallographic symmetry to be equal to the equivalent value involving O_{12}. The stagger about the two P—P vectors given in the last two columns is calculated by projecting along the P—P vector and averaging the torsion angles of the three pairs of phosphate O atoms to generate a value between 0° (eclipsed) and 60° (staggered).

coordination of the α-phosphate is much weaker than that of the two terminal phosphates (Orioli, Cini, Donati & Mangani, 1980). Table 4 lists the chelate-ring puckering parameters for the three complexes.

Table 5 summarizes the conformations of the phosphate chain observed in the crystal structures of several tripolyphosphate chelates. The degree to which the phosphate chain is folded is seen to be dependent on the chelation mode. The chain is increasingly folded (smaller P—P—P angle) as the compounds are ordered as follows: α,β-bidentate $[Al(NH_3)(HP_3O_{10})]$, β,γ-bidentate $[Co(NH_3)_4(H_2P_3O_{10})].H_2O$, α,β,γ-tridentate Na_2ATP, α,β,γ-tridentate $[Co(NH_3)_3(H_2P_3O_{10})]$, α,γ-bidentate $[Co(NH_3)_4(H_2P_3O_{10})].H_2O$. The remaining complexes in the table are roughly isostructural and are of mixed chelation mode, with each phosphate chain coordinated to multiple metal ions.

Fig. 4 depicts models of α,β,γ-tridentate CoATP based on the $[Co(NH_3)_3(H_2P_3O_{10})]$ chelation geometry, and compares them to the observed conformations of the two independent Na_2ATP molecules. The CoATP models are constructed by taking the nucleoside conformation from the equivalent Na_2ATP molecule and replacing the metal–phosphate moiety with the cobaltammine complex reported here. The two Na_2ATP molecules have different stereochemistry: molecule *A* is (Δ)*endo*-α,β,γ-tridentate; molecule *B* is (Λ)*endo*-α,β,γ-tridentate. The first corresponds to attachment of the nucleoside at O(2) of the present complex, the second to attachment at O(2)′. In each case the bond and torsion angles about the point of attachment were taken from the equivalent Na_2ATP molecule. Thus the differences between the Na and the Co complexes shown in Fig. 4 are due solely to differences in the metal–phosphate coordination geometry. Two additional CoATP models (not shown) could be generated by attachment of the nucleoside at O(3) or O(3)′.

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A Neutron Diffraction Study of γ-$(Zn_{0.70}Ni_{0.30})_3(PO_4)_2$

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Abstract

The solid solution γ-$(Zn_{0.70}Ni_{0.30})_3(PO_4)_2$ has been studied utilizing neutron powder diffraction data. The title compound is monoclinic, $P2_1/n$, with $a = 7.505\,(1)$, $b = 8.316\,(1)$, $c = 5.056\,(1)$ Å, $\beta = 94.48\,(1)°$, $V = 314.6\,(1)$ Å^3 and $Z = 2$. The structure has been refined utilizing the Rietveld full-profile refinement technique ($R_I = 0.052$; 72 reflections), and the cation distribution between the five- and six-coordinated sites has been determined. Ni^{2+} is strongly ordered at the octahedral sites. These metal–oxygen octahedra (MO_6) are fairly regular, while the MO_5 polyhedra are distorted trigonal bipyramids.

Introduction

Pure zinc orthophosphate can exist in two forms: α-$Zn_3(PO_4)_2$ with tetrahedrally coordinated cations (Calvo, 1965), and β-$Zn_3(PO_4)_2$, stable above ~1200 K, containing five- and six-coordinated Zn ions (Stephens & Calvo, 1967). Experiments have shown that upon replacement of Zn in the α phase by Cd^{2+}, Mg^{2+} or Mn^{2+}, a solid solution may be formed known as 'γ-$Zn_3(PO_4)_2$', or preferably γ-$(Zn, M)_3(PO_4)_2$ (*e.g.* Kreidler & Hummel, 1967). Recent studies have verified that Co^{2+}, Fe^{2+}, Ni^{2+} or Cu^{2+} may also stabilize the γ phase with respect to α-$Zn_3(PO_4)_2$ (Nord & Kierkegaard, 1980).

The structure of 'γ-$Zn_3(PO_4)_2$' was determined by Calvo (1963). Two thirds of the cations occupy five-coordinated sites, henceforward called $M(1)$, while the rest reside in octahedral sites, $M(2)$. Calvo suggested that the incorporated cations should preferentially enter the $M(2)$ sites, thereby stabilizing the γ phase with respect to α-$Zn_3(PO_4)_2$. This idea has been supported by an X-ray powder diffraction study of γ-$Zn_2Mg(PO_4)_2$ by Nord (1977). Later the cation distribution in a series of γ-$(Zn,Fe)_3(PO_4)_2$ solid solutions was determined utilizing the Mössbauer effect (Annersten, Ericsson & Nord, 1980), again showing the strong ordering of Fe^{2+} at the $M(2)$ sites. These investigations were undertaken as part of a project on cation distributions in mineral and inorganic structures involving five-coordinated metal sites. In the present study neutron powder diffraction data have been used to determine the cation ordering in a γ-$(Zn,Ni)_3(PO_4)_2$ solid solution. 30 at.% Ni was used; this is close to the maximum solubility of Ni in the γ phase at about 1070 K.

Experimental

Pure orthophosphates of Zn and Ni were prepared by allowing stoichiometric amounts of $NH_4H_2PO_4$ and the respective metal oxide to react at 1200 K for two weeks. These phosphates were then mixed in the proportion 70:30 and heated to about 1070 K. The sample was quenched and ground once every week to ensure complete homogeneity as well as equilibrium. The heating continued for three months; the sample was finally quenched to room temperature.

X-ray powder data were obtained at 298 K with a Guinier–Hägg-type focusing camera (Cu $K\alpha_1$ radiation, $\lambda = 1.54050$ Å, KCl internal standard) and the photograph evaluated by a film scanner and associated programs (Malmros & Werner, 1973).

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