Journal of Solid State Chemistry **142,** 1–5 (1999)
Article ID jssc.1998.7908, available online at http://www.idealibrary.com on IDEAL®

Synthesis and Crystal Structure of a New Lithium Nickel Fluorophosphate $Li_2[NiF(PO_4)]$ with an Ordered Mixed Anionic Framework

M. Dutreilh, C. Chevalier, M. El-Ghozzi, and D. Avignant[1]

Laboratoire des Matériaux Inorganiques, URES A-6002 CNRS, Universite Blaise Pascal, 63177 Aubiere, France

and

J. M. Montel

Département des Sciences de la Terre, UMR 6524 CNRS 5, rue Kessler, Universite Blaise Pascal 63038 Clermont-Ferrand, France

Received January 15, 1998; in revised form May 19, 1998; accepted May 26, 1998

A new lithium nickel fluorophosphate $Li_2[NiF(PO_4)]$ has been synthesized. It crystallizes in the orthorhombic system with unit-cell parameters $a = 10.473(3)$ Å, $b = 6.2887(8)$ Å, $c = 10.846(1)$ Å, and space group *Pnma* (no. 62), $Z = 8$. Its structure has been determined from single-crystal X-ray diffraction data and refined to a conventional $R = 0.030$ ($R_\omega = 0.033$) for 647 reflections with $I > 3\sigma(I)$. The structure is built of infinite chains of a rutile type of NiO_4F_2 octahedra running along the *b* direction further joined together by isolated PO_4 tetrahedra by sharing corners. This three-dimensional framework delimits channels parallel to the *b* direction where the Li^+ ions lie. This compound is characterized by a rigorous O–F ordering. © 1999 Academic Press

INTRODUCTION

At present there is a great interest in synthesizing new phosphates or fluorophosphates with open structures because of their potential applications as molecular sieves, ionic conductors, exchangers or for their catalytic properties. In addition, the lithium compounds may be of particular interest for use as battery materials for high energy density sources. Besides these multiple potential applications certain lithium fluorophosphates turned out to be fascinating from a crystal-chemical point of view because of the particular behavior of the Li^+ ion in the presence of $(PO_4)^{3-}$ groups. During a study dealing with a new family of fluorophosphates $Li_xLn_xY_{1-x}(PO_4)_{1-x}F_{4x}$ ($Ln = Gd \rightarrow Lu$, Y) of structure closely related to the zircon (1) it has been established that Li^+ ions may be substituted for P^{5+} within PO_4 tetrahedra, whereas the charge balance may be achieved by simultaneous substitution of F^- for O^{2-} ions.

Similarly, Yakubovich *et al.* carried out work dealing with pegmatite-related phosphates and have shown that the $Na_2[MnF(PO_4)]$ fluorophosphate is built of MnO_4F_2 octahedra and PO_4 tetrahedra (2). It is therefore worth noting that the $Na_2[MnF(PO_4)]$ fluorophosphate has a structure very close to that of both zirconium compounds $Na_2[ZrO(SiO_4)]$ (3) and $Na_2[ZrO(GeO_4)]$ (4), where silicon and germanium might be considered as substituted for the phosphorus, whereas the charge balance is achieved by the substitution of O^{2-} for F^- in the octahedral environment of Zr^{4+} substituted for Mn^{2+}.

In the general frame of our investigations dealing with the study of the Li^+ ion substitution in tetrahedral MO_4 groups, we have carried out a study of the LiF–$LiNiPO_4$ system leading to the discovery of $Li_2[NiF(PO_4)]$. But in spite of the analogy of formula between this compound and the aforementioned $Na_2[MnF(PO_4)]$, these two compounds are not isotypic. Therefore, we have undertaken a structural study and this paper deals with the crystal structure determination of this compound from single-crystal X-ray diffraction data.

EXPERIMENTAL

a. Synthesis

Polycrystalline samples of the title compound were prepared in the solid state by reacting for 72 h at 870°C with stoichiometric mixtures of LiF + $LiNiPO_4$ in sealed nickel tubes. Polycrystalline $LiNiPO_4$ was prepared by solid-state reaction between lithium carbonate Li_2CO_3, nickel(II) carbonate hydroxide tetrahydrate $2NiCO_3$, $3Ni(OH)_2$, $4H_2O$,

---

[1] To whom correspondence should be addressed. E-mail: avignant@ubpcf2.univ-bpclermont.fr.

0022-4596/99 $30.00

and diammonium hydrogenophosphate $(NH_4)_2HPO_4$. Stoichiometric mixtures of the starting materials were heated for 6 h at 300°C in a nickel crucible; then the temperature was raised to 450°C for 6 h and finally brought up to 750°C and maintained during a 72-h period. Golden yellow powdered samples were identified as pure lithium nickel phosphate $LiNiPO_4$ using a SIEMENS D501 diffractometer equipped with a monochromated Cu$K\alpha$ radiation.

b. X-ray Diffraction

A preliminary study carried out using Weissenberg and precession photographs showed the symmetry to be orthorhombic with approximate unit cell parameters $a = 10.45$ Å, $b = 6.27$ Å, $c = 10.82$ Å. The systematic extinctions were compatible with *Pnma* (no. 62) and $Pn2_1a$ space groups. The intensities were recorded using a Nonius CAD4 automatic diffractometer under conditions given in Table 1. All computer programs used for data collection, reduction, and refinement were issued from the CAD4 SDP package (5).

TABLE 1
Crystallographic Data and Data Collection Parameters for $Li_2[NiF(PO_4)]$

Chemical formula	$Li_2[NiF(PO_4)]$
*F*w (g)	186.56
Symmetry	orthorhombic
Space group	*Pnma* (no. 62)
Unit cell parameters	
a (Å)	10.473(3)
b (Å)	6.2887(8)
c (Å)	10.846(1)
V (Å^3)	714.3(5)
Z	8
D. calc. (g cm^{-3})	3.469(1)
Data collection temperature (K)	293
Crystal size (mm)	$0.13 \times 0.05 \times 0.06$
Radiation	Mo$K\alpha$ ($\lambda = 0.71069$ Å) graphite monochromated
μ (Mo$K\alpha$) (mm^{-1})	5.81
Transmission factors	0.733–0.999
Scan mode	ω–2θ
Scan width	$(0.80 + 0.35 \tan\theta)°$
Scan aperture	$(2.70 + 0.40 \tan\theta)$ mm
θ range (°)	$1 \le \theta \le 35$
Index ranges	$-16 \le h \le 16$, $0 \le k \le 10$, $0 \le l \le 17$
Period of intensity control	3600 s, $\sigma = 0.02$
Number of measured reflections	3516
Number of independent reflections	1185 ($R_{int.} = 0.029$)
Observed reflections with $I > 3\sigma(I)$	647
Number of variables	90
Weighting scheme	$\omega = 1.0$ for Fo < 0.80 Fo$_{max}$ $\omega = (0.80\ Fo_{max}/Fo)^2$ for Fo ≥ 0.80 Fo$_{max}$ $\omega = 0.0$ for Fo$^2 < 3\sigma$Fo^2
Secondary extinction parameter	2.23(13) 10^{-7}
R, R_ω	0.030, 0.033
Goodness of fit	$s = 1.569$
Max. and min. electron density in final difference Fourier synthesis	0.956 e Å^{-3} close to Ni(2) 0.748 e Å^{-3}

c. Structure Determination and Refinement

Both Ni and P atomic positions were easily located using direct methods. Then, eight anionic positions with approximately the same electron density were deduced from a subsequent Fourier synthesis. As these anionic positions might be occupied either by oxygen or fluorine, which are indiscernible from the point of view of X-ray scattering, the positional parameter refinement was at first carried out using oxygen scattering factors for all these positions. Then the Li^+ ions were deduced from a difference Fourier synthesis and found to be located on three different crystallographic sites. By taking into account the multiplicities of the cationic sites and their respective charges, it has been evidenced that all of the eight anionic sites could not be occupied by oxygen ions only. So a bond-valence analysis was performed according to the Brese and O'Keeffe method (6). This analysis clearly showed that the formal charge at the anionic positions unambiguously was 1 or 2 as shown in Table 2. Therefore, the anionic sublattice is perfectly ordered and the final atomic and thermal parameters refinement was carried out with the correct O^{2-} and F^- atomic scattering factors. This refinement including a secondary extinction lead to $R = 0.030$ ($R_\omega = 0.033$) for 647 intensities with $I > 3\sigma(I)$. The atomic positional parameters are gathered in Table 3. The main interatomic distances are given in Table 4.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure of $Li_2[NiF(PO_4)]$ is built of infinite chains of rutile type of NiO_4F_2 octahedra running along the b

TABLE 2
Bond-Valence Analysis of the Crystal Structure of $Li_2[NiF(PO_4)]$

	Anionic environment	$\sum v_{ij}{}^a$	V_i expected
O(1)	Ni(1) + P(2) + Li(1) + Li(2)	1.93	2
O(2)	P(2) + 2 Li(1) + Li(3)	1.91	2
O(3)	P(1) + 2 Li(1) + Li(2)	1.76	2
O(4)	2 Ni(2) + Li(3) + P(2)	1.95	2
O(5)	2 Ni(1) + P(1) + Li(2)	1.96	2
O(6)	Ni(2) + P(1) + Li(1) + 1 Li(3)	1.96	2
F(1)	2 Ni(2) + 2 Li(1) + Li(2) + Li(3)	0.94	1
F(2)	2 Ni(1) + Li(3) + 2 Li(1) + Li(2)	0.86	1

[a] These values were calculated from the relation $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ given in Ref. (6) and using the recommended bond-valence parameters: $R_{ij} = 1.654$ Å for Ni–O and $R_{ij} = 1.599$ Å for Ni–F; $R_{ij} = 1.604$ Å for P–O; $R_{ij} = 1.466$ Å for Li–O and $R_{ij} = 1.360$ Å for Li–F.

TABLE 3
Atomic Coordinates and Thermal Parameters for $Li_2[NiF(PO_4)]$

Atoms	Wyckoff positions	*x*	*y*	*z*	B_{eq} (Å^2)
Ni(1)	4*a*	0	0	0	0.36(1)
Ni(2)	4*b*	1/2	0	0	0.38(1)
P(1)	4*c*	0.4764(2)	1/4	0.2441(2)	0.26(2)
P(2)	4*c*	0.2432(2)	3/4	0.0781(2)	0.32(3)
Li(1)	8*d*	0.260(1)	0.488(2)	0.835(1)	1.5(2)
Li(2)	4*c*	0.729(1)	1/4	0.418(1)	0.4(2)
Li(3)	4*c*	0.473(1)	1/4	0.776(1)	0.2(2)
O(1)	8*d*	0.3109(4)	0.4506(6)	0.5150(4)	0.94(6)
O(2)	4*c*	0.7816(6)	1/4	0.7833(5)	1.2(1)
O(3)	4*c*	0.3306(6)	1/4	0.2440(7)	1.23(9)
O(4)	4*c*	0.8890(6)	3/4	0.4478(6)	1.0(1)
O(5)	4*c*	0.5261(6)	1/4	0.3785(5)	0.82(9)
O(6)	8*d*	0.9680(4)	0.9483(7)	0.6805(4)	0.99(7)
F(1)	4*c*	0.6272(5)	3/4	0.0271(5)	0.61(8)
F(2)	4*c*	0.5497(5)	1/4	0.6162(5)	0.62(8)

TABLE 4
Selected Distances (Å) and Angles (°) in $Li_2\{NiF(PO_4)\}$

Ni(1) octahedron:		Ni(2) octahedron:	
Ni(1)–O(1)	2.011(4)	Ni(2)–O(6)	2.013(1)
Ni(1)–O(1)	2.011(4)	Ni(2)–O(6)	2.013(1)
Ni(1)–O(5)	2.070(4)	Ni(2)–O(4)	2.036(4)
Ni(1)–O(5)	2.070(4)	Ni(2)–O(4)	2.036(4)
Ni(1)–F(2)	2.081(3)	Ni(2)–F(1)	2.082(3)
Ni(1)–F(2)	2.081(3)	Ni(2)–F(1)	2.082(3)
$\langle$Ni(1)–X (X = O, F)$\rangle$ = 2.054(1) Å		$\langle$Ni(2)–X (X = O, F)$\rangle$ = 2.044(5) Å	
P(1) tetrahedron:		P(2) tetrahedron:	
P(1)–O(3)	1.526(6)	P(2)–O(2)	1.525(6)
P(1)–O(6)	1.540(4)	P(2)–O(2)	1.543(4)
P(1)–O(6)	1.540(4)	P(2)–O(1)	1.543(4)
P(1)–O(5)	1.547(6)	P(2)–O(4)	1.553(6)
$\langle$P(1)–O$\rangle$ = 1.538 Å		$\langle$P(2)–O$\rangle$ = 1.541 Å	
Li(1) square pyramid:		Li(2) square pyramid:	
Li(1)–O(2)	1.99(1)	Li(2)–F(1)	1.91(2)
Li(1)–O(1)	2.12(1)	Li(2)–O(1)	2.06(1)
Li(1)–O(3)	2.14(2)	Li(2)–O(1)	2.06(1)
Li(1)–O(6)	2.22(2)	Li(2)–O(3)	2.06(2)
Li(1)–F(1)	2.43(2)	Li(2)–O(5)	2.17(2)
$\langle$Li–X(X = O, F)$\rangle$ = 2.18 Å		$\langle$Li–X(X = O, F)$\rangle$ = 2.05 Å	
Li(3) octahedron:			
Li(3)–F(2)	1.91(1)	Ni(1)–Ni(1)	3.1443(0)
Li(3)–O(6)	1.96(1)	Ni(2)–Ni(2)	3.1443(0)
Li(3)–O(6)	1.96(1)	Ni(1)–Ni(2)	5.236(3)
Li(3)–O(2)	2.10(2)		
Li(3)–O(4)	2.36(1)		
Li(3)–F(1)	2.38(1)		
$\langle$Li–X(X = O, F)$\rangle$ = 2.11 Å			
Ni(2)–O(4)–Ni(2)	101.1(3)	Ni(1)–O(5)–Ni(1)	98.9(2)
Ni(2)–F(1)–Ni(2)	98.1(2)	Ni(1)–F(2)–Ni(1)	98.1(2)
O(4)–Ni(2)–O(6)	87.1(2)	O(1)–Ni(1)–O(5)	93.7(2)
O(1)–Ni(1)–O(6)	92.9(2)	O(1)–Ni(1)–O(5)	86.3(2)
O(1)–Ni(1)–F(1)	104.9(2)	O(1)–Ni(1)–F(2)	94.6(2)
O(1)–Ni(1)–F(1)	75.1(2)	O(1)–Ni(1)–F(2)	94.6(2)

direction (Fig. 1). These chains are further joined together by isolated PO_4 tetrahedra by sharing corners involving O(1), O(4), O(5), and O(6) to form the three-dimensional framework (Fig. 2). This framework delimits channels parallel to the *b* direction where the Li^+ ions lie. The Li^+ ions are coordinated by either O^{2-} or F^- anions. More accurately, the Li(1) is surrounded by four oxygens and one fluorine at the vertices of a square pyramid. The fluorine occupies the apical vertex and the corresponding Li–F distance is very long (2.43 Å). The Li(2) atom is also surrounded by four oxygens and one fluorine but the Li(2)–F distance is in this case the shortest of the Li(2)–X bond distances. The Li(3) atom is octahedrally coordinated by four oxygen and two fluorine atoms, and the fluorine ions are involved either in the shortest, or the longest bond distances within a strongly distorted polyhedron.

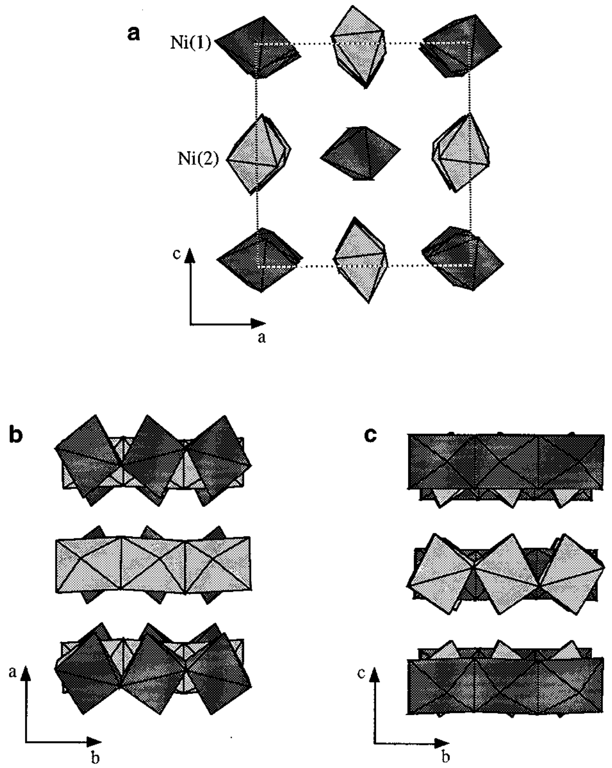

FIG. 1. Partial projection of the structure of $Li_2[NiF(PO_4)]$ showing the rutile-like chains of NiO_4F_2 octahedra (a) down [010], (b) on the xOy plane, and (c) on the yOz plane.

The phosphorous tetrahedra are quite regular with P–O mean distances of 1.538 and 1.541 Å, respectively, for P(1) and P(2).

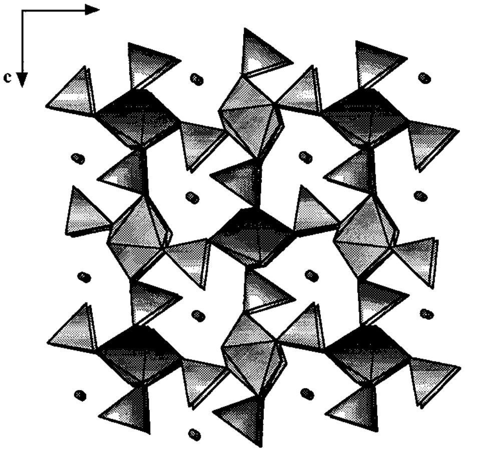

FIG. 2. Projection of the overall structure down [010].

The Ni coordination polyhedra are compressed octahedra in which the fluorine ions occupy the apical vertices and are consequently involved in the longest bond distances.

As mentioned in the Introduction, it is worth noting that the $Li_2[NiF(PO_4)]$ compound is the second representative after $Na_2[MnF(PO_4)]$ (2) of the $A_2[BF(PO_4)]$ fluorophosphates where A is an alkaline cation and B is a divalent cation of the first-row transition element. However, these two compounds exhibit significant differences in their structures. In $Na_2[MnF(PO_4)]$ there are isolated chains of MnO_4F_2 octahedra sharing *cis* corners involving only F atoms. In $Li_2[NiF(PO_4)]$ there are also isolated rutile-like chains of NiO_4F_2 octahedra sharing edges involving O–F contacts. In the former there are four types of quite regular NaF_2O_4 octahedra, whereas in the latter there are three types of Li coordination polyhedra, two having the shape of distorted square pyramids, the third being a strongly distorted octahedron LiO_4F_2 as shown by distances gathered in Table 4.

In both $Na_2[MnF(PO_4)]$ and $Li_2[NiF(PO_4)]$ fluorophosphates a perfect ordering between O and F takes place as in some other fluorophosphates such as $Mn_2(PO_4)$ F (7), $Cu_2(PO_4)F$ (8) $KA1F(PO_4)$ (9), and NH_4FePO_4F (10) or in some minerals such as the amblygonite $Li[Al(PO_4)F]$ (11) or the isokite $Ca[Mg(PO_4)F]$ (12).

In all of the aforementioned structures the F^- ions belong to the octahedra surrounding the bivalent or trivalent cations and never participate to the coordination of the phosphorus as is the case in $CoPO_3F.3H_2O$ (13), where PO_3F tetrahedra have been evidenced.

In his lead article dealing with the structural aspects of oxide and oxysalt crystals, Hawthorn (14) described several infinite chains built of octahedra and tetrahedra in $[M(TO_4)O_n$ and $[M(TO_4)_2O_n]$ structures based on finite clusters of MO_6 octahedra and TO_4 tetrahedra. Possible $[M_x(TO_4)_yO_z]$ and $[M_x(TO_3)_yO_z]$ chains can be constructed from elementary building blocks involving one or two octahedra and one, two, or four tetrahedra or triangles. Only a few representatives of these chains have been evidenced in inorganic oxysalt structures (for a general survey see Ref. 14). These chains have been classified into two types according to their occurrences, namely common and rare. The chains of $[M(TO_4)O_n]$ repeat units characterized in the title compound enter into the second group. These chains have been found in a small number of far less common minerals such as the linarite-group, the archetype of which is $Pb[Cu(SO_4)(OH)_2]$. Despite the rarity of this type of chain it is also very interesting to emphasize why this compound has been obtained with lithium. To deal with this outstanding feature it is worth recalling that the mean bond valence of a cation correlates strongly with its electronegativity (15). As regards the bond valence of a cation it may be considered as a measure of the Lewis acid strength (for a general survey see Ref. 14). Using the Hawthorn method (14) to analyze the bond-valence controls on interstitial cations we calculated the structural-unit basicity for the title compound.

In the structural unit = $[NiF(PO_4)]$ the number of bonds is $1 \times 6 + 1 \times 4 = 10$. The number of bonds needed for four-coordination of all simple anions is $4 \times 4 + 1 \times 4 = 20$. The number of additional bonds to structural units to achieve this coordination is equal to $20 - 10 = 10$. The charge on the structural unit $[NiF(PO_4)]$ is 2^-. The Lewis basicity of the structural unit = charge/bonds = $2/10 = 0.20$ v.u. This basicity matches most closely the Lewis acidity of Li at 0.22 v.u.

ACKNOWLEDGMENTS

The authors are very indebted to Mrs M. Veschambre for performing the electron microprobe analysis of the single-crystal used in X-ray data collection.

REFERENCES

1. D. Zambon, M. El-Ghozzi, D. Avignant, N. Ben Said and I. Mansouri, *J. Chim. Phys.* **88,** 1963 (1991).
2. O. V. Yakubovich, O. V. Karimova, and O. K. Mel'nikov, *Acta Crystallogr. C* **53,** 395 (1997).
3. E. N. Treushnikov, V. V. Iluhin, and N. V. Belov, *Dokl. Akad. Nauk SSSR* **190,** 334 (1970).
4. N. A. Nocirev, E. N. Treushnikov, V. V. Iluhin, and N. V. Belov, *Dokl. Akad. Nauk SSSR* **216,** 82 (1974).
5. B. A. Frenz, "Computing in Crystallography" (H. Schenk, R. Olthof-Hazekamp, H. Van Koningsveld, and G. C. Bassi, Eds.). Delft Univ. Press, Delft, The Netherlands, 1982.
6. N. E. Brese and M. O'Keeffe, *Acta Crystallogr. B* **47,** 192 (1991).
7. J. R. Rea and E. Kostiner, *Acta Crystallogr. B* **28,** 2525 (1972).
8. J. R. Rea and E. Kostiner, *Acta Crystallogr. B* **32,** 1944 (1976).

9. S. J. Kirkby, A. J. Lough, and G. A. Ozin, *Z. Kristallogr.* **210,** 956 (1995).
10. Th. Loiseau, Y. Calage, P. Lacorre, and G. Ferey, *J. Solid State Chem.* **111,** 390 (1994).
11. A. A. Moss, E. E. Fejer, and P. G. Embrey, *Mineral. Mag.* **37,** 414 (1969).
12. Deans, McConnelli, *Mineral. Mag.* **30,** 681 (1955).
13. J. Durand, L. Cot, M. Berraho, and M. Rafiq, *Acta Crystallogr. C* **43,** 611 (1987).
14. F. C. Hawthorne, *Acta Crystallogr. B* **50,** 481 (1994).
15. I. D. Brown, "Structure and Bonding in Crystals" (M. O'Keeffe and A. Navrotsky, Eds.), Vol. 2, pp. 1–30. Academic Press, New York, 1981.