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Crystal growth, crystal structure and magnetic properties of disodium cobalt fluorophosphate†

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Crystals of Na_2CoPO_4F have been isolated and their structure determined by single crystal X-ray diffraction techniques. Na_2CoPO_4F crystallizes in the orthorhombic space group *Pbcn* (no. 60) with $a = 5.2475(9)$, $b = 13.795(2)$, $c = 11.689(2)$ Å, and $Z = 8$. Its layered structure consists of a framework formed by $[CoPO_4F]_\infty$ layers with the sodium cations located in the interlayer space, leading to infinite chains built up from bioctahedral units that share corners along the *a* axis. Magnetic measurements reveal that the predominant magnetic interactions are antiferromagnetic, but there is weak ferromagnetism at lower temperatures.

Introduction

Many compounds belonging to the fluorophosphate family exist in nature as minerals, but only a few have been synthesized.[1,2] Over the last few years, much effort has been devoted to obtaining new metal fluorophosphates with open structures because of their potential uses as molecular sieves, ionic conductors, exchangers, intercalators–deintercalators or for their interesting catalytic and magnetic properties. For example, the compounds $Na_{8-x+y-z}M_zP_2O_{9-x}F_{x+y}$ (M = Ca, Al, Ga, Fe, Ti, *etc.*) have been extensively studied because they are superionic conductors.[3–9]

At present, two fluorophosphates, Na_2MnPO_4F and Li_2NiPO_4F, are known[10,11] in the A_2MPO_4F family, where A = alkali metal, and M = transition metal, and both have a three-dimensional framework. Na_2MnPO_4F is built up from two kinds of *cis*-MnO_4F_2 octahedra sharing corners to form MnO_8F_2 chains. These chains are linked by PO_4 tetrahedra, giving rise to channels occupied by sodium cations. This structural type had been found[12,13] previously for the zirconium compounds $Na_2ZrO(SiO_4)$ and $Na_2Zr(GeO_4)$. Li_2NiPO_4F has been reported[11] more recently and is built up from infinite chains of rutile-type NiO_4F_2 octahedra which are joined together by isolated PO_4 tetrahedra sharing corners, forming channels parallel to the *b* direction where the Li^+ cations are located.

We have studied the Na–Co–P–O–F system. As a result, we have obtained the Na_2CoPO_4F compound which has a layered structure and so represents the third structural type of the A_2MPO_4F fluorophosphate family. In this paper, we present the synthesis and the crystal structure, which is compared with those of the manganese and nickel fluorophosphates, as well as the magnetic properties of $Na_2CoPO_4F_2$.

Experimental

Synthesis

Single crystals of Na_2CoPO_4F were grown by melting a mixture of $Na_2CO_3 \cdot 10H_2O$, CoF_3 and $NH_4H_2PO_4$ in the molar ratio Na : Co : P = 3 : 2 : 3. After grinding, the mixture was held in a zirconia crucible and slowly heated to 800 °C. The bath was kept at this temperature for 1 h to homogenize the melt, then cooled at 10 °C h^{-1} to 400 °C and finally quenched to room temperature. The purple crystals extracted from the resulting product corresponded to a new Co(II) fluorophosphate, Na_2CoPO_4F, whose composition was determined by single crystal X-ray diffraction.

Until now, all attempts to obtain polycrystalline powder by solid state reactions have been unsuccessful; they always led to biphasic samples. Thus, for magnetic characterization, purple crystals of Na_2CoPO_4F were picked out with the aid of tweezers and a microsope. The single crystals were ground to obtain a fine powder which was confirmed as single phase by comparison of the X-ray powder diffraction pattern of the bulk product with that calculated from the single crystal data.

Single crystal X-ray diffraction

A purple crystal of prismatic shape and dimensions 0.04 mm × 0.04 mm × 0.4 mm was coated in epoxy resin and mounted on a Siemens Smart CCD diffractometer equipped with a normal focus 2.4 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 40 kV and 30 mA. Data were collected over a hemisphere of the reciprocal space by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each 20 s exposure covered 0.3° in ω. The crystal to detector distance was 6.01 cm. Coverage of the unique set was over 99% complete to at least 23° in θ. Unit cell dimensions were determined by a least-squares fit of 50 reflections with $I > 20\sigma(I)$ and $6° < 2\theta < 46°$. The first 30 frames of data were recollected at the end of the data collection to monitor crystal decay. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Co, Na and P were taken from the *International Tables for Crystallography*.[14] The structure was solved by direct methods and refined in the orthorhombic space group *Pbcn*. Full matrix least-squares refinement was carried out by minimizing $w(F_0^2 - F_c^2)^2$. Refinement on F^2 for all reflections, weighted *R* factors (R_w) and all goodness of fit (*S*) values are based on F^2, while conventional *R* factors (*R*) are based on *F*. *R* factors based on

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Table 1 Crystal data and structure refinement for Na_2CoPO_4F

Chemical formula	Na_2CoPO_4F
Formula weight	218.88
Temperature/K	298(2)
λ(Mo-Kα)/Å	0.71073
Crystal system	Orthorhombic
Space group	*Pbcn*
a/Å	5.2475(9)
b/Å	13.795(2)
c/Å	11.689(2)
V/Å^3	846.2(3)
Z	8
μ/mm^{-1}	4.570
Density (calculated)/Mg m^{-3}	3.436
F(000)	840
Crystal dimensions/mm	$0.04 \times 0.04 \times 0.4$
θ range for data collection/°	3.43 to 23.30
Limiting indices (h, k, l), ($-h$, $-k$, $-l$)	(-5, -14, -12), (5, 8, 3)
Reflections collected	1614
Independent reflections	565 ($R_{\text{int}} = 0.0899$)
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	565/0/84
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0632$, $R_2 = 0.1824$
R indices (all data)	$R_1 = 0.1122$, $R_2 = 0.2624$
Extinction coefficient	0.030(7)
Largest diff. peak and hole/e Å^{-3}	1.684 and -1.583

F^2 are statistically about twice as large as those based on F, R factors based on all data will be even larger.

All calculations were performed using: SMART software for data collection; SAINT[15] for data reduction; SHELXTL® to resolve and refine the structure and to prepare material for publication,[16] and ATOMS[17] for molecular graphics.

CCDC reference number 1145/232. See http://www.rsc.org/suppdata/jm/b0/b003150j/ for crystallographic files in .cif format.

Magnetic measurements

Magnetic susceptibility was measured using a MPMS-XL Quantum design SQUID magnetometer operating from 300 to 1.7 K at 500 Oe.

Results and discussion

Crystal structure

A summary of the fundamental crystal data for Na_2CoPO_4F is given in Table 1. Final atomic coordinates and selected bond distances and angles are given in Tables 2 and 3, respectively.

The Na_2CoPO_4F structure consists of [$CoPO_4F$] infinite layers, which are built up from PO_4 tetrahedra and $Co_2O_7F_2$ units formed by face-sharing between two CoO_4F_2 octahedra, and the Na^+ cations located into the interlayer space (Fig. 1).

The cobalt atom occupies a general position and has octahedral coordination to four oxygen atoms and two fluorine atoms which lie in special positions. The average Co–F and Co–O bond lengths are 2.109(6) and 2.085(9) Å, respectively. These values are similar to those found[18] for the cobalt fluorophosphate Co_2PO_4F.

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for Na_2CoPO_4F

Atom	x	y	z	$U_{(\text{eq})}{}^a$
Co(1)	0.2218(4)	0.4888(2)	0.6744(1)	29(1)
P(1)	−0.2948(8)	0.6181(3)	0.5879(3)	24(1)
Na(1)	0.2446(10)	0.6237(4)	0.4169(4)	33(2)
Na(2)	0.2621(9)	0.2548(4)	0.6713(4)	35(2)
F(1)	0.5000	0.4038(7)	0.7500(0)	37(3)
F(2)	0.0000	0.3746(7)	0.7500(0)	29(3)
O(1)	−0.1499(16)	0.5362(6)	0.6527(6)	28(2)
O(2)	−0.2088(18)	0.7161(7)	0.6310(7)	38(3)
O(3)	0.4137(19)	0.6037(6)	0.6063(6)	31(2)
O(4)	0.2327(16)	0.3911(7)	0.5398(6)	34(3)

$^a U_{(\text{eq})}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected bond lengths (Å) and angles (°) for Na_2CoPO_4F

Co(1)–O(3)	2.040(9)	Co(1)–F(1)	2.070(6)
Co(1)–O(4)	2.072(9)	Co(1)–O(1)	2.073(9)
Co(1)–F(2)	2.149(7)	Co(1)–O(1^a)	2.157(8)
Co(1)–Co(1^a)	2.922(4)		
O(3)–Co(1)–F(1)	105.0(3)	O(3)–Co(1)–O(4)	101.3(3)
F(1)–Co(1)–O(4)	86.4(3)	O(3)–Co(1)–O(1)	99.9(4)
F(1)–Co(1)–O(1)	153.4(3)	O(4)–Co(1)–O(1)	97.9(3)
O(3)–Co(1)–F(2)	176.1(3)	F(1)–Co(1)–F(2)	78.0(2)
O(4)–Co(1)–F(2)	81.4(3)	O(1)–Co(1)–F(2)	76.8(3)
O(3)–Co(1)–O(1^a)	102.5(3)	F(1)–Co(1)–O(1^a)	84.0(2)
O(4)–Co(1)–O(1^a)	155.9(4)	O(1)–Co(1)–O(1^a)	81.6(3)
F(2)–Co(1)–O(1^a)	75.1(3)	Co(1^b)–F(1)–Co(1)	111.1(5)
Co(1)–F(2)–Co(1^a)	85.7(4)	Co(1)–O(1)–Co(1^a)	87.4(3)

Symmetry transformations used to generate equivalent atoms: $^a(-x, y, -z+3/2)$. $^b(-x+1, y, -z+3/2)$.

The monophosphate group shows an average P–O distance of 1.540(9) Å and the O–P–O angles range from 108.0(5) to 111.2(5)°. Theses values are similar to those usually found[10,11] in the fluorophosphates reported to date.

There are two crystallographically independent sodium atoms in general positions, with Na–O distances in the range 2.293(11) to 2.797(11) Å and Na–F distances between 2.335(5) and 2.575(10) Å.

In Fig. 2 the $[CoPO_4F]_\infty$ layers viewed along the b axis are shown. An interesting structural feature of this material is the straight metal chains formed by $Co_2O_7F_2$ bioctahedral units

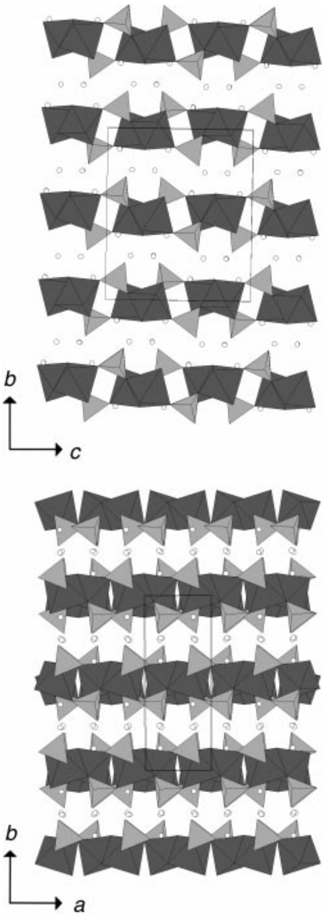

Fig. 1 View of Na_2CoPO_4F along (top) [100], (bottom) [001], showing its layered nature. The Na^+ cations are represented by open circles.

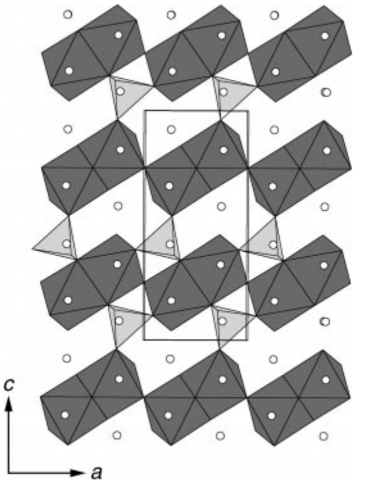

Fig. 2 View of the layer along the [010] direction.

which are connected to each other through the F(1) atoms. These chains are further joined together to form the layered framework by sharing corners with PO_4 tetrahedra through the O(1), O(3) and O(4) oxygens.

The literature reports[18–20] other fluorophosphates, such as Co_2PO_4F and $Na_3Al_2(PO_4)_2F_3$, that present bioctahedral units formed by edge- or corner-sharing. To our knowledge, Na_2CoPO_4F, is the first cobalt fluorophosphate that exhibits face-sharing between octahedra. It is also worth noting that Na_2CoPO_4F has a structure very close to that of Na_2FePO_4OH,[21,22] where the OH groups in the latter perform a similar function to the F atoms in the former.

If we compare the structure of the title compound with those of the fluorophosphates Na_2MnPO_4F and Li_2NiPO_4F, it is obvious that Na_2CoPO_4F has a very different structure. The principal difference lies in that Na_2CoPO_4F has a layered framework, which consists of cobalt bioctahedra and phosphate tetrahedra, while the other two fluorophosphates adopt tunnel structures, formed by metal octahedra and phosphate groups. On the other hand, these three compounds present isolated metallic chains that in Na_2MnPO_4F are built up from MnO_4F_2 octahedra sharing *cis*-corners in which there are only F atoms; in Li_2NiPO_4F the NiO_4F_2 octahedra are connected by (O–F) edges, resulting in rutile-like chains; and in Na_2CoPO_4F there are infinite chains of $Co_2O_7F_2$ bioctahedra sharing faces joined to each other through fluorine vertices. The alkali metals also show different coordination polyhedra, thus, in the manganese fluorophosphate, the four independent Na^+ cations form quite regular NaO_4F_2 octahedra; in the nickel compound two of three Li atoms are in distorted squared pyramids and the other lies in a strongly distorted LiO_4F_2 octahedron; and finally, in the cobalt phase, the two sodium cations are seven-coordinate.

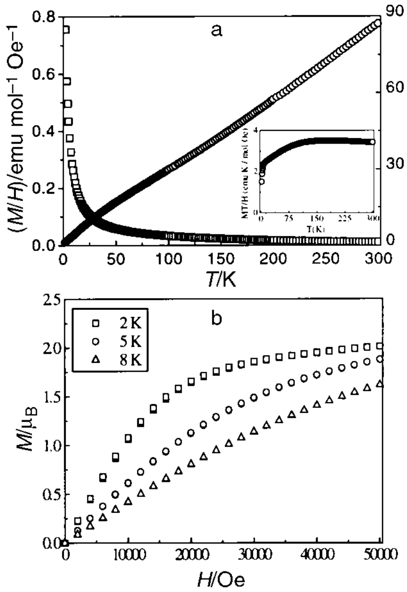

Fig. 3 (a) Magnetic susceptibility (*M*/*H*, open squares) and inverse magnetic susceptibility (*H*/*M*, open circles) plotted as a function of temperature for Na_2CoPO_4F. The inset shows the thermal evolution of the χT product. (b) *M vs. H*, at 8, 5 and 2 K, plots with the field increased and decreased.

Magnetic properties

The temperature dependence of the molar susceptibility χ and its reciprocal for Na_2CoPO_4F are shown in Fig. 3a. The reciprocal susceptibility follows the Curie–Weiss law in the range 210–300 K, it can be fitted ($r = 0.9999$) to the expression: [$\chi^{-1} = -5.0(8) + 0.3562(1)\,T$]. The values obtained for the Curie constant and Weiss temperature are 2.87 emu mol^{-1} Oe^{-1} and 13.3 K, respectively. The continuous decrease in the χT values, when the temperature decreases, indicates that the predominant magnetic interactions are antiferromagnetic (Fig. 3a). The calculated magnetic moment is 5.2 μ_B, which agrees with the experimental moment values of between 4.7–5.2 μ_B for Co(II) compounds.[23]

The field dependence of magnetization at 2, 5 and 8 K is shown in Fig. 3b. The *M vs. H* curves recorded at these lower temperatures are characteristic of a weak ferromagnetism. This behaviour could be interpreted as short-range ferromagnetic correlations between the sheets due to the two-dimensional nature of the structure. At 2 K, the value of the extrapolated moment is about 2 μ_B.

Taking into account the structural features shown by this fluorophosphate, at least three different magnetic exchange pathways could be considered in order to account for the observed magnetic behaviour. Within the metal chains built up from corner-sharing between $Co_2O_7F_2$ bioctahedra, there are two mean intermetallic exchange pathways. One could take place inside the $Co_2O_7F_2$ bioctahedra, in which the two Co(II) ions interact through the two O(1) oxygens and the shared F(2) fluorine. The intermetallic angles are very near to 90°, as is shown in Table 3, therefore the coupling could be ferromagnetic.[24] The Co–Co distance is 2.922(4) Å, thus, very weak or no direct interactions might be expected. The second magnetic exchange pathway implicates the $Co_2O_7F_2$ bioctahedra which corner-share *via* –Co–F(1)–Co– bonds. The intermetallic angle is 111.1(5)°, indicating poor d-orbital overlap, hence the coupling would be antiferromagnetic. Finally, a third exchange pathway implies interactions between two metal chains through the PO_4 groups along the [001] direction. These interactions would be preferentially antiferromagnetic, as has been observed for other transition metal phosphates.[25,26]

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