A Two-Dimensional Mixed-Metal Phosphate Templated by Ethylene Diamine, [enH$_2$][CoIn(PO$_4$)$_2$H(OH$_2$)$_2$F$_2$]

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A fluorinated mixed-metal phosphate containing indium and cobalt in 1 : 1 ratio, [enH$_2$][CoIn(PO$_4$)$_2$H(OH$_2$)$_2$F$_2$], **1,** has been synthesized by hydrothermal methods from a gel-composition of 1.0 Co(OAc)$_2$: 1.0 In(OAc)$_3$: 2.0 H$_3$PO$_4$: 2.0 en: 2.0 HF: 240 H$_2$O. Large pale pink-purple single crystals (200 μm) were formed in 70% yield based on cobalt, with only minor amorphous impurity phases. Compound **1** is triclinic, space group $P\bar{1}$, a = 5.217(1), b = 7.596(2), c = 8.904(2) Å, α = 109.11(1), β = 97.46(1), γ = 109.95(1)°, V = 301.6(1) Å^3. The magnetic moment is 5.02 BM, indicating a d^7 high-spin Co^{2+} center. Fluoride is crucial to formation of the mixed-metal phase since the In and Co metals are connected to each other by bent F$^-$ bridges, as well as hydrogen phosphate groups, which connect the (Co–F–In) chains into a 2-D sheet structure. © 1999 Academic Press

INTRODUCTION

The search for microporous materials with new architectures, compositions, and pore chemistry is highly active, and the organic templating of open framework metal phosphates has been much studied in this regard. One particular goal is the incorporation of active metals into known microporous phases to modify their catalytic behavior. The transition-metal substituted aluminophosphates CoAPO-18 (1) and CrAPO-5 (2) are successful examples of this approach.

In similarly directed work, Chippindale *et al.* have synthesized the mixed cobalt-gallophosphates, [pyH][CoGa$_2$(PO$_4$)$_3$] (3) and [C$_4$H$_{10}$N][CoGa(PO$_4$)$_2$] (4). In both these cases the cobalt substituted to different degrees at the same chemical sites as the gallium, and the metals are tetrahedrally coordinated. To date however, relatively few examples of stoichiometric mixed-metal phosphates in which the metal sites are chemically distinct (5, 6) have been prepared.[2]

Recently we have studied indium phosphate phases templated by organoamines. By contrast to the Al and Ga analogues, the larger indium centers in these compounds are invariably octahedral; moreover, in addition to phosphate groups, fluoride or hydroxide bridges were commonly seen (7, 8). We were interested to see whether introduction of transition-metals to this system would lead to their substitution into existing structures, or produce new phase types.

Herein we report the hydrothermal synthesis of an organically templated mixed cobalt-indium phosphate [enH$_2$][CoIn(PO$_4$)$_2$H(OH$_2$)$_2$F$_2$], **1,** which forms 200 μm crystals in good (70%) yield. This is a two-dimensional sheet material in which the Co and In metal atoms have octahedral coordination environments which are chemically different.

EXPERIMENTAL

A gel of composition 1.0 Co(OAc)$_2$: 1.0 In(OAc)$_3$: 2.0 H$_3$PO$_4$: 2.0 en: 2.0 HF: 240 H$_2$O was heated for 6 days and afforded large (200 μm) single crystals of the title compound **1,** as pale purple-pink prisms (Fig. 1). The yield was about 70% based on cobalt, and the solid product contained a minor amount (10% by mass) of amorphous metal phosphate contaminants. Stoichiometries using excess In or Co resulted in the formation of **1** along with greater quantities of the impurity phases, but no other crystalline mixed-metal phases could be identified.

Elemental analysis from combustion of **1** gave C = 4.94 (4.79)%, H = 2.75 (2.99)%, N = 5.29 (5.59)%. The numbers in parentheses indicate the ideal calculated. Some error might originate from the inorganic phosphate impurities, which could not be entirely eliminated by sieving through 40 mesh grids, and which should reduce the % values for C and N.

X-ray energy dispersive analysis (EDAX) on individual crystals of **1** gave excellent agreement for the metal-phosphate ratios In : Co : P 1 : 1 : 2. Typical values gave In = 6.2, Co = 5.9, P = 11.6 atomic %. Fluoride was also confirmed to be present in stoichiometric amounts (5.1 atomic %), though quantification cannot be determined accurately by this technique.

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[2] *Note added in proof*: A 3-D mixed-metal phosphate with distinct MnO$_5$ and GaO$_4$ sites, [MnGa(PO$_3$OH)$_2$(PO$_4$)][C$_6$N$_2$H$_{14}$] has been reported [A. M. Chippindale, A. D. Bond, A. R. Cowley, and A. V. Powell, *Chem. Mater.* **9,** 2830 (1997)].
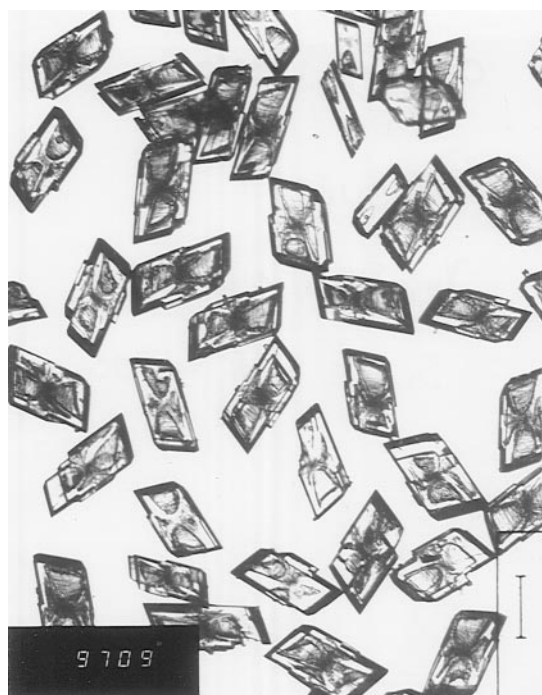
FIG. 1. Optical micrograph of crystals of **1**. Scale bar = 200 μm.

TABLE 1
Structure Determination Summary for 1

Empirical formula	$C_2H_{15}CoF_2InN_2O_{10}P_2$
Color, habit	Pale purple prism
Crystal size (mm)	$0.2 \times 0.15 \times 0.08$
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 5.217(1)$ Å
	$b = 7.596(2)$ Å
	$c = 8.904(2)$ Å
	$\alpha = 109.11(1)°$
	$\beta = 97.46(1)°$
	$\gamma = 109.95(1)°$
Volume	$301.62(14)$ Å^3
Z	1
Formula weight	500.9
Density (calc.)	2.75 mg/m^3
Absorption coefficient	3.62 mm^{-1}
F(000)	245
Temperature (K)	298
Scan type and range	$2\theta–\theta, 3.0° < 2\theta < 55.0°$
Index ranges	$0 < h < 6; -8 < k < 8; -11 < l < 11$
Reflections collected	1497
Independent reflections	1348 ($R_{int} = 2.20\%$)
Observed reflections	1276 ($F > 4.0\sigma(F)$)
Absorption correction	Semi-empirical, min/max (0.75/0.88)
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.00001F^2$
Number of parameters refined	96
Final R indices (obs. data)	$R = 2.33\%$, $wR = 3.11\%$
R indices (all data)	$R = 2.58\%$, $wR = 3.80\%$
Goodness-of-fit	1.78
Largest and mean Δ/σ	0.001, 0.000
Data-to-parameter ratio	13.3 : 1
Largest difference peak	1.07 eÅ^{-3}
Largest difference hole	-0.44 eÅ^{-3}

A specimen of **1** of approximate dimensions $200 \times 150 \times 80$ μm was chosen for single crystal structure determination. Intensity data were collected on a Siemens P4-RA diffractometer, and structure solution and refinement were carried out using the SHELXTL package of programs. (G. M. Sheldrick, Siemens Analytical Instruments, 1993). The structure was solved from the Patterson function, since direct methods were confused by the location of two different types of metal atoms at two different inversion centers of the unit cell.

All atoms were located. The major issue of the identity of the bridges as fluoride rather than hydroxide is supported by i) the EDAX analysis showing stoichiometric F, ii) the refinement of these atoms as nonpositive definite as oxygens with substantially higher R values, and iii) the lack of any chemically sensible associated electron density peaks that might represent hydrogens in the vicinity of the bridging atom.

Refinement, including a correction for absorption, was successful and gave final discrepancy indices of $R = 0.023$ and $wR = 0.031$ with a data : parameter ratio of 13 : 1. The largest difference peak was about 1.0 eÅ^{-3} in the vicinity of the cobalt atom; all other residual difference peaks and holes were of less than 0.5 eÅ^{-3}. Peaks were located for all hydrogen atoms, which were refined using a riding model and common isotropic thermal parameter. Details of the structure determination are given in Table 1. Bond lengths, angles, and nonbonded contacts are listed in Tables 2–4, respectively. Atomic positional parameters are given in Table 5.

Thermal gravimetric analysis of **1** gave the following weight loss figures: 220–250°C, $\Delta m = -11.9\%$; and 300–600°C, $\Delta m = -23.1\%$. This approximately corresponded to the loss of 3 H_2O for the first weight loss (10.8%) and 1 mol. eq. of ethylene diamine and 2 HF for the second (20.0%). The third molecule of water might be evolved by a condensative loss from the (P–OH– –O=P), which is also hydrogen bonded to the NH_3 end groups of the diamine. A partial occupancy of hydroxide (OH) for the bridging site between the metals might also explain this and cannot be ruled out entirely.

Magnetic susceptibility measurements on **1** (Sherwood Scientific Magnetic Susceptibility Balance Mark II) gave a molar susceptibility, $\chi_M = 0.01068$ erg G^{-2} mol^{-1}. Diamagnetic correction gave a susceptibility for the Co ion $\chi_{Co} = 0.01077$ erg G^{-2} mol^{-1} and $\mu_{eff} = \{2.828(\chi_{Co}T)^{1/2}\} = 5.02$ BM for T = 293 K.

RESULTS AND DISCUSSION

Description of the Structure

Although the crystal habit was not plate-like in nature, a single crystal X-ray structure determination showed **1** to

TABLE 2
Bond Lengths (Å) for 1

In(1)–F(1)	2.100 (2)	In(1)–O(1)	2.119 (3)
In(1)–O(2)	2.124 (3)	Co(1)–F(1)	2.043 (2)
Co(1)–O(3)	2.054 (3)	Co(1)–O(5)	2.180 (3)
P(1)–O(1)	1.537 (3)	P(1)–O(4)	1.567 (2)
P(1)–O(2)a	1.527 (3)	P(1)–O(3)b	1.522 (3)
N(1)–C(2)	1.479 (5)	C(2)–C(2)c	1.519 (7)

be a two-dimensional sheet material, $[enH_2][CoIn(PO_4)_2$ $H(OH_2)_2F_2]$, with a Co : In ratio of 1 : 1. As with all mixed inorganic : organic phases, the structure meets the requirements of reasonable geometric arrangement for the individual components, along with optimization of both packing efficiency and hydrogen bonding between them.

The inorganic sheets make close contact to neighboring sheets through [P–O–H––O=P] hydrogen bond bridges between phosphate groups and are also interlayered by ethylene diammonium ions, for which all N–H groups form hydrogen bonds to oxygen atoms of the sheet.

The structure of the sheet is shown in Fig. 2, along with the atom labeling scheme. The metals are linked together in alternating fashion by bent fluoride bridges; In(1)–F(1) = 2.100(2), Co(1)–F(1) = 2.043(2) Å and In(1)–F(1)–Co(1) = 133.8(1)°. A phosphate group bridges the same indium and cobalt atoms as the fluoride, forming a (In–O–P–O–Co) linkage. One of the two remaining oxygens on the phosphate is also coordinated to an indium of a parallel strand of metals, thus forming the sheet structure. Topologically the sheet can be seen as being made up of six-membered

TABLE 3
Bond Angles (°) for 1

F(1)–In(1)–O(1)	90.2(1)	F(1)–In(1)–O(2)	94.7(1)
O(1)–In(1)–O(2)	91.4(1)	F(1)–In(1)–F(1)d	180.0(1)
O(1)–In(1)–F(1)d	89.8(1)	O(2)–In(1)–F(1)d	85.3(1)
F(1)–In(1)–O(1)d	89.8(1)	O(1)–In(1)–O(1)d	180.0(1)
O(2)–In(1)–O(1)d	88.6(1)	F(1)d–In(1)–O(1)d	90.2(1)
F(1)–In(1)–O(2)d	85.3(1)	O(1)–In(1)–O(2)d	88.6(1)
O(2)–In(1)–O(2)d	180.0(1)	F(1)d–In(1)–O(2)d	94.7(1)
O(1)d–In(1)–O(2)d	91.4(1)	F(1)–Co(1)–O(5)	90.5(1)
F(1)–Co(1)–O(3)	87.2(1)	O(5)–Co(1)–O(3)	90.7(1)
F(1)–Co(1)–F(1)e	180.0(1)	O(5)–Co(1)–F(1)e	89.5(1)
O(3)–Co(1)–F(1)e	92.8(1)	F(1)–Co(1)–O(5)e	89.5(1)
O(5)–Co(1)–O(5)e	180.0(1)	O(3)–Co(1)–O(5)e	89.3(1)
F(1)e–Co(1)–O(5)e	90.5(1)	F(1)–Co(1)–O(3)e	92.8(1)
O(5)–Co(1)–O(3)e	89.3(1)	O(3)–Co(1)–O(3)e	180.0(1)
F(1)e–Co(1)–O(3)e	87.2(1)	O(5)e–Co(1)–O(3)e	90.7(1)
O(1)–P(1)–O(4)	105.0(1)	O(1)–P(1)–O(2)a	112.2(2)
O(4)–P(1)–O(2)a	107.0(1)	O(1)–P(1)–O(3)b	110.4(2)
O(4)–P(1)–O(3)b	107.4(2)	O(2)a–P(1)–O(3)b	114.2(2)
In(1)–F(1)–Co(1)	133.8(1)	In(1)–O(1)–P(1)	136.9(2)
In(1)–O(2)–P(1)a	135.2(2)	Co(1)–O(3)–P(1)f	141.9(2)
N(1)–C(2)–C(2)c	109.2(4)		

TABLE 4
Nonbonded Contacts for 1

O(4)–––O(4)g	2.476	O(4)–H(4)––O(4)g	167.6
N(1)–––O(3)c	2.951	N(1)–H(1A)––O(3)c	172.8
N(1)–––O(1)	2.956	N(1)–H(1B)––O(1)	167.3
N(1)––O(4)h	2.735	N(1)–H(1C)––O(4)h	158.5
O(5)–––F(1)i	2.927	O(5)–H(5A)––F(1)i	123.3
O(5)––O(3)i	3.048	O(5)–H(5B)––O(3)i	154.3

Symmetry generated atoms

(a) $1-x, -y, -z$	(b) $x, y-1, z$	(c) $1-x, 1-y, 1-z$
(d) $-x, -y, -z$	(e) $1-x, 1-y, -z$	(f) $x, y+1, z$
(g) $1-x, -y, 1-z$	(h) $x-1, y, z$	(i) $-x, 1-y, -z$

$[In_2Co_2P_2]$, four-membered $[In_2P_2]$, and three-membered [InCoP] rings.

The final oxygen of the phosphate group, O(4), is terminal and projects alternately above and below the sheet. It forms a close contact with a symmetry-related O(4) of an adjacent sheet O(4)–––O(4) = 2.476 Å, indicating these are hydrogen-bonded together. A proton for this O–––O vector was found as an electron density peak about 0.9 Å from O(4) directed toward its symmetry-related neighbor. This was treated as a hydrogen atom with a 50% occupancy, H(4), which lies disordered about the inversion center at (1/2, 0, 1/2). Hence one proton is associated with two phosphate groups per formula unit. The P(1)–O(4) distance is 1.567(2) Å and is thus consistent with the (O–H–––O) disorder, in that it is shorter than expected for a normal terminal P–OH functionality (about 1.59 Å) but still longer

TABLE 5
Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å²) for 1

	x	y	z	U(eq)[1]
In(1)	0.0000	0.0000	0.0000	0.009(1)
Co(1)	0.5000	0.5000	0.0000	0.007(1)
P(1)	0.5370(2)	−0.0357(1)	0.2325(1)	0.009(1)
F(1)	0.2425(4)	0.3155(3)	0.0908(2)	0.022(1)
O(1)	0.2534(5)	−0.0176(4)	0.1959(3)	0.022(1)
O(2)	0.2498(5)	−0.0781(3)	−0.1585(3)	0.016(1)
O(3)	0.4886(6)	0.7419(3)	0.1846(3)	0.024(1)
O(4)	0.6587(5)	0.0744(3)	0.4247(3)	0.015(1)
H(4)	0.5485	0.0090	0.4644	0.060
O(5)	0.1322(6)	0.4765(5)	−0.1653(3)	0.028(1)
H(5A)	0.1386	0.5955	−0.1445	0.060
H(5B)	−0.0159	0.4089	−0.1449	0.060
N(1)	0.2357(6)	0.2675(4)	0.5092(3)	0.017(1)
H(1A)	0.3332	0.2740	0.6033	0.050
H(1B)	0.2573	0.1755	0.4237	0.050
H(1C)	0.0512	0.2290	0.5059	0.050
C(2)	0.3460(7)	0.4698(5)	0.5008(4)	0.018(1)
H(2A)	0.3289	0.5690	0.5940	0.046
H(2B)	0.2381	0.4640	0.4022	0.046

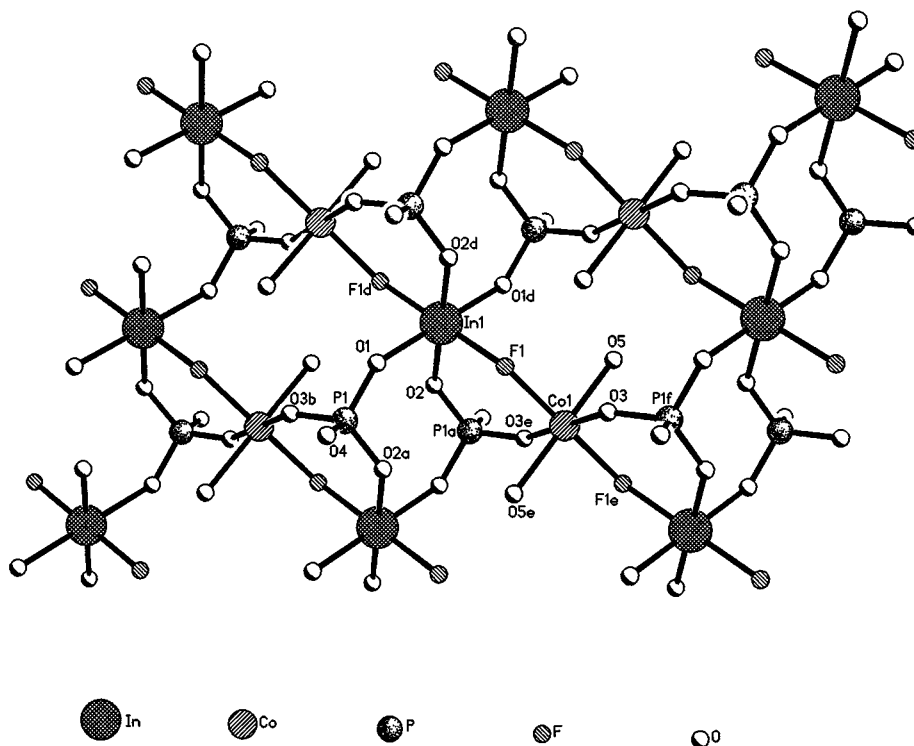[1] U(eq) is one-third of the orthogonalized Uij tensor.

FIG. 2. Crystal structure of **1** viewed along the c-axis, with atomic labeling scheme.

than terminal P–O$^-$ (about 1.50 Å), which has P=O character.

The coordination of the indium and cobalt atoms is octahedral, with only minor deviation from orthogonality, and both sit on crystallographic inversion sites. However the chemical environments of the two metals are slightly different. While both have two bonds to the fluoride bridges, the other four bonds from indium are to phosphate oxygens, In(1)–O(1) = 2.119(3), In(1)–O(2) = 2.124(3) Å; whereas the cobalt has only two bonds to phosphate, Co(1)–O(3) = 2.054(3), with the remaining two sites occupied by terminal aqua ligands. These have a much longer associated bond length, Co(1)–O(5) = 2.180(3) Å, which also rules out their assignment as terminal fluorides. Electron density peaks for the hydrogen atoms of the aqua ligand could also be located. The aqua groups project out over the [In$_2$Co$_2$P$_2$] six-membered rings of the sheet and may participate in weak, incipient hydrogen bonding to the O(3) and F(1) atoms on the opposite side of the ring.

The templating, or structure-directing, effect of the ethylene diammonium ions can be seen in part from the structural arrangement shown in Fig. 3. Each NH$_3$ end group forms three well-directed hydrogen bonds to the projecting phosphates, as indicated by the nonbonded contacts N(1)–O(1), O(3), and O(4) of 2.956, 2.951, and 2.735 Å, respectively. The [enH$_2$] also fits snugly into the cavity created by the phosphate groups of adjacent sheets, hydro-

gen-bonding to each other as already described. Interestingly, we have recently discovered two other lamellar metal-phosphates, 0.5[enH$_2$][M(PO$_4$)$_2$H], M = Ti, (9) and Zr (10), which though not isostructural to each other, also possess intersheet [P–O–H– –O=P] hydrogen bonds in addition to hydrogen bonds to [enH$_2$] counterions, as is the case for **1**.
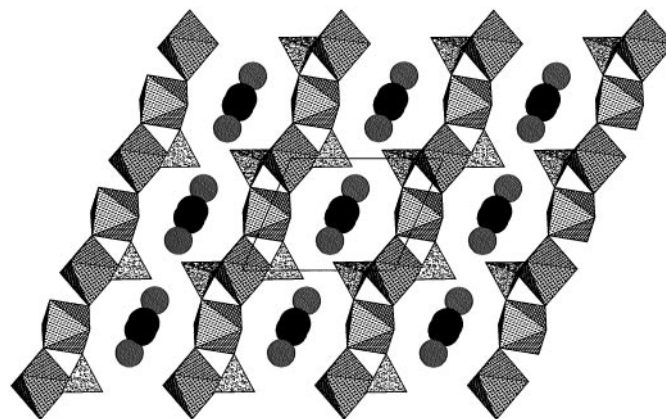

FIG. 3. Polyhedral representation of **1** viewed along the *a*-axis showing the packing of the [enH$_2$] cations between the anionic layers. (Octahedra: In, uniformly darker; Co, dashes on top face).

The degree of protonation, together with the identification of the bridging atom between In and Co as fluorine leads to an oxidation state of Co(II) for charge balance in the structure. Support of this assignment comes from magnetic studies of the compound, which show the magnetic moment to be 5.02 BM, consistent with a Co^{2+} d^7 high-spin state.

Comparison to Previous Studies

While mixed-metal phosphate phases of the substitutional-type mentioned earlier (1–4) are now well established, few examples of mixed-metal phosphates with distinct coordination sites for the different metals have been structurally characterized.

Notably, Meyer and Haushalter have determined the crystal structure of an unusual mixed-metal phosphate $K[Ni(H_2O)_2Al_2(PO_4)_3]$, which has tetrahedral (P), trigonal-bipyramidal (Al), and octahedral (Ni) framework sites (5). Although this does not contain an organic template, it has some similarity to the present compound in possessing an aquated octahedral transition metal. Interestingly this phase may only be synthesized using a large excess of Ni ($>15:1$) wrt Al, whereas in the present case, 1:1 stoichiometry of reagents gives excellent yield and reduces the contaminant phases.

Other mixed-metal phosphate systems are being uncovered, and recently a mixed V(IV)–Fe(III) phosphate $2[enH_2][enH][Fe(VO)_8(PO_4)_8H_4(OH)_4(OH_2)_2] \cdot 4H_2O$ was reported, which also used ethylene diamine as the structure-directing organic base (6). In this case, the synthesis of the bimetallic compound followed the initial preparation of the mixed-valence all-vanadium analogue.

The current synthesis of compound 1 may also be compared with studies involving either indium or cobalt metals alone. In the indium/en/PO_4/F system, which we have studied with the Jilin group (7), several intriguing phases have been synthesized, including $[In_5(PO_4)_4F_3(en)_3(OH_2)_2]$, a neutral 3-D material with 10-membered rings spanned by ethylene diamine bridges and the neutral 2-D sheet compound $[In(PO_4)F(enH)]$, which has pendant monoprotonated $[NH_2(CH_2)_2NH_3]$ groups (7).

Other indium phosphate phases not incorporating fluoride or coordinated amine are also found, including the 2-D sheet compound $0.5[enH_2][In(PO_4)(OH)]$ (7), which is isostructural with Ga and Fe analogues (11, 12). In addition, Dhingra and Haushalter have reported the acidic phosphate phase $0.5[enH_2][In(HPO_4)_2]$ through use of ethylene diamine as the organic base (13).

Cobalt substitution into metal phosphates such as ALPOs and GaPOs has been shown to be relatively straightforward, and cobalt-phosphate framework compounds have been the subject of recent study. Stucky et al. explored the preparative conditions for $[A][CoPO_4]$,

TABLE 6
Supplementary Material for Yu, Sung and Williams; Anisotropic Displacement Coefficients ($\mathring{A}^2 \times 10^3$) for 1

	$U11$	$U22$	$U33$	$U12$	$U13$	$U23$
In(1)	9(1)	9(1)	10(1)	4(1)	4(1)	5(1)
Co(1)	9(1)	3(1)	9(1)	2(1)	5(1)	2(1)
P(1)	9(1)	10(1)	9(1)	5(1)	4(1)	4(1)
F(1)	28(1)	10(1)	21(1)	0(1)	13(1)	4(1)
O(1)	14(1)	45(2)	19(1)	17(1)	9(1)	20(1)
O(2)	17(1)	17(1)	18(1)	8(1)	11(1)	8(1)
O(3)	42(2)	13(1)	20(1)	15(1)	14(1)	6(1)
O(4)	14(1)	16(1)	9(1)	3(1)	3(1)	2(1)
O(5)	23(1)	43(2)	20(1)	19(1)	7(1)	11(1)
N(1)	17(1)	15(1)	22(2)	8(1)	8(1)	9(1)
C(2)	17(2)	16(1)	24(2)	6(1)	7(1)	12(1)

Note. The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U11 + \cdots + 2hka^*b^*U12)$.

$[A] = NH_4$, Na, K, Rb, which may facilitate future synthesis of such materials (14) and recently published an extensive set of zeolite analogues based on cobalt phosphate (15). One example of an open 3-D framework cobalt-phosphate is $0.5[enH_2][CoPO_4]$, which is in fact templated by ethylene diamine. This has tetrahedral Co^{2+} and 8-membered ring channels (16). No evidence was found for the presence of this particular phase, or the various indium-containing phases mentioned above, under the conditions used to prepare 1.

The use of fluoride in the synthesis of 1 is obviously critical due to its stoichiometric incorporation into the structure. To date we have not been successful in synthesizing crystalline mixed In-Co phosphate phases in its absence. As discussed above, the purely indium system is also much modified by the inclusion of stoichiometric quantities of F^-. We have also recently discovered a highly fluorinated phase $3[pnH_2]3[H_3O][In_9(PO_4)_6(HPO_4)_2F_{11}]$, {$pn$ = 1,3-diaminopropane} with large elliptical 14-membered rings, which resulted from use of 8 mol. eq. of HF in the synthesis conditions (8).

CONCLUSIONS

Organically templated mixed-metal phosphate phases containing quite disparate metals, such as cobalt and indium, can be formed in high yield under appropriate conditions. In the case of $[enH_2][CoIn(PO_4)_2H(OH_2)_2F_2]$, 1, reported here, the Co(II) and In(III) metal centers, though both octahedrally coordinated, have different chemical environments. Consequently the use of the two metals leads to a new structural type not accessible from either metal alone. Furthermore, the use of stoichiometric quantities of fluoride assisted synthesis of the mixed-metal phase 1 through generation of stable fluoride bridges, and may be advantageous for certain other metal combinations.

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