

- Leligny, H., Labbe, Ph., Ledesert, M., Hervieu, M., Raveau, B. & McCarroll, W. H. (1993). *Acta Cryst.* **B49**, 444–454.
- Leligny, H., Ledesert, M., Labbe, Ph., Raveau, B. & McCarroll, W. H. (1990). *J. Solid State Chem.* **87**, 35–43.
- Lindblom, B. & Strandberg, R. (1989). *Acta Chem. Scand.* **43**, 825–828.
- McCarley, R. E. (1986). *Polyhedron*, **5**, 51–61.
- Mattausch, H., Simon, A. & Peters, E. M. (1986). *J. Am. Chem. Soc.* **25**, 3428–3433.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Schimek, G. L. & McCarley, R. E. (1994). *J. Solid State Chem.* **113**, 345–354.
- Shannon, R. D. & Prewitt, C. D. (1969). *Acta Cryst.* **B25**, 925–946.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Stout, G. & Jensen, L. H. (1968). In *X-ray Structure Determination*. London: McMillan.
- Torardi, C. C. & McCarley, R. E. (1979). *J. Am. Chem. Soc.* **101**, 3963–3964.
- Torardi, C. C. & McCarley, R. E. (1981). *J. Solid State Chem.* **37**, 393–397.

Acta Cryst. (1996). **C52**, 1867–1869

Lithium Dicobalt Tripolyphosphate and Lithium Dinickel Tripolyphosphate

FATIMA ERRAGH,^{a,b} ALI BOUKHARI^a AND ELIZABETH M. HOLT^{c*}

^aLaboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, Université Mohammed V, Avenue Ibn Batouta, Rabat, Morocco, ^bLaboratoire de Chimie Physique de Matériaux, Département de Chimie, Faculté des Sciences, El Jadida, Morocco, and ^cDepartment of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA. E-mail: chememh@osucc.bitnet

(Received 16 August 1995; accepted 5 December 1995)

Abstract

Isotypic lithium dicobalt triphosphate, $\text{LiCo}_2\text{P}_3\text{O}_{10}$, and lithium dinickel triphosphate, $\text{LiNi}_2\text{P}_3\text{O}_{10}$, have been synthesized and characterized by single-crystal X-ray diffraction. These are the first observations of non-hydrated mixed-metal tripolyphosphates. The $\text{P}_3\text{O}_{10}^{5-}$ groups are situated on a mirror plane, with successive PO_3 moieties displaying both staggered and eclipsed conformations. Octahedrally coordinated Co^{2+} and Ni^{2+} ions form a staggered chain [$\text{Co} \cdots \text{Co}$ 3.286(1) and 3.133(1) Å, $\text{Ni} \cdots \text{Ni}$ 3.201(1) and 3.023(1) Å], with successive metal ions bridged by two O atoms.

Comment

The literature contains numerous structural studies of solid materials containing the $\text{P}_3\text{O}_{10}^{5-}$ group. Most, however, are hydrated systems in which hydrogen-bonding

interactions play a role in determining the packing, for example, $\text{Zn}_5(\text{P}_3\text{O}_{10})_2 \cdot 17\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1975; Averbuch-Pouchot, Durif & Guitel, 1975), $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ (Dyroff, 1965), $\text{CuNa}_3\text{P}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ (Jouini, Dabbabi, Averbuch-Pouchot, Durif & Guitel, 1984), $\text{NaZn}_2\text{P}_3\text{O}_{10} \cdot 9\text{H}_2\text{O}$ (powder data; Corbridge & Tromans, 1958) and $\text{Na}_3\text{NiP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ (powder data; Corbridge & Tromans, 1958). Another group of $\text{P}_3\text{O}_{10}^{5-}$ -containing complexes reflect their preparation from solution by the inclusion of ammonia in the stoichiometry of the solid, for example, $(\text{NH}_4)\text{Be}_2\text{P}_3\text{O}_{10}$ (Bagieu-Beucher, Durif & Averbuch-Pouchot, 1976; Averbuch-Pouchot, Durif, Coing-Boyat & Guitel, 1977). A third type of complex is both hydrated and contains NH_4^+ , for example, $(\text{NH}_4)_4\text{NaP}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1985). There are few examples of pure ceramics of the type $M_x\text{P}_3\text{O}_{10}$. Only $\text{Ag}_5\text{P}_3\text{O}_{10}$ (ATD data only; Lee, 1968) and two forms of $\text{Na}_5\text{P}_3\text{O}_{10}$ (Corbridge, 1960; Davies & Corbridge, 1958) are known.

We have prepared the first non-hydrated mixed-metal tripolyphosphates. Lithium dicobalt tripolyphosphate and lithium dinickel tripolyphosphate are isotypic and crystallize with alternating layers of metal atoms and tripolyphosphate groups. The $\text{P}_3\text{O}_{10}^{5-}$ groups are situated on a mirror plane passing through the P atoms, the bridging O atoms and one O atom of each terminal group. The central P atom of each $\text{P}_3\text{O}_{10}^{5-}$ group is eclipsed with one neighboring PO_4 group and shows a staggered arrangement of O atoms with the other neighboring group. P—O—P angles between staggered oxyphosphorus groups are large [143.3(2) and 142.5(3)° for the Co and Ni structures, respectively], but smaller when the adjacent groups are eclipsed [124.8(3) and 126.4(3)° for the Co and Ni structures, respectively] (Fig. 1).

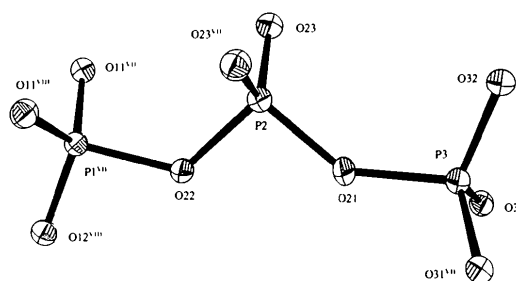


Fig. 1. View of the P_3O_{10} group of lithium dicobalt tripolyphosphate showing the conformation. Displacement ellipsoids are plotted at the 50% probability level.

The transition metal atoms display distorted octahedral coordination geometry with no visible Jahn–Teller distortion for Co [average Co—O 2.136(3) Å and average Ni—O 2.074(3) Å]. The Co and Ni octahedra share edges to form staggered chains. These chains are bridged by edge-sharing octahedral lithium motifs (Fig. 2). The Li atoms are situated on inversion cen-

ters with four O-atom near neighbors [average Li—O 2.066 (3) and 2.041 (3) Å for the Co and Ni complexes, respectively] and two distant ones [Li—O 2.961 (3) and 2.907 (3) Å for the Co and Ni complexes, respectively].

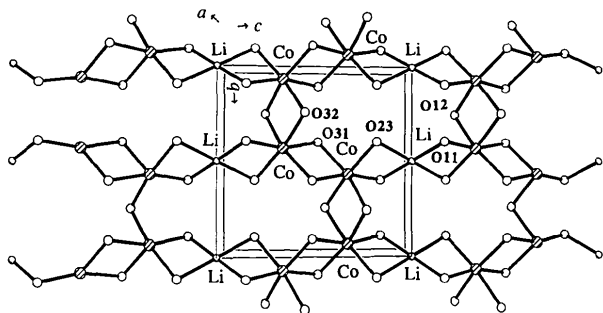


Fig. 2. A projection view of the metal layer of lithium dicobalt triphosphosphate showing the bonded O atoms.

These structures may be compared with those of Na₅P₃O₁₀, in which P₃O₁₀⁵⁻ ions crystallize with a twofold axis (through the central P atom), a staggered conformation of adjacent tetrahedra is found (P—O—P 122 and 121°) and the P₃O₁₀⁵⁻ ions are distorted from mirror symmetry. The two allotropic forms of Na₅P₃O₁₀ differ in the coordination geometry of Na, one containing Na atoms in octahedral coordination and the second showing both four- and sixfold coordination of the Na atoms.

Experimental

LiCo₂P₃O₁₀ was prepared by fusion of a mixture of CoCl₂·6H₂O, Li₂CO₃ and (NH₄)₂HPO₄ in a stoichiometry calculated to produce Li₂CoP₂O₇. Crystalline material was obtained on heating the mixture to 1123 K in a quartz crucible followed by slow cooling (3 K h⁻¹). LiNi₂P₃O₁₀ was prepared in a similar manner using NiCl₂·6H₂O instead of CoCl₂·6H₂O.

LiCo₂P₃O₁₀

Crystal data

LiCo₂P₃O₁₀

M_r = 377.7

Monoclinic

*P*2₁/*m*

a = 4.655 (2) Å

b = 8.565 (3) Å

c = 9.103 (3) Å

β = 97.80 (1)°

V = 359.4 (2) Å³

Z = 2

D_x = 3.490 Mg m⁻³

Data collection

Syntex P4 automated

diffractometer

θ/2θ scans

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 45

reflections

θ = 10.2–12.85°

μ = 5.329 mm⁻¹

T = 298 K

Chunk

0.1 × 0.1 × 0.1 mm

Blue–purple

610 observed reflections

[*F* > 4.0σ(*F*)]

R_{int} = 0.0371

Absorption correction:

semi-empirical from ψ
scans (*XEMP*; Siemens,
1991)

T_{min} = 0.65, *T_{max}* = 0.72

1054 measured reflections

680 independent reflections

Refinement

Refinement on *F*

R = 0.034

wR = 0.046

S = 1.13

680 reflections

86 parameters

w = 1/[σ²(*F*) + 0.0008*F*²]

(Δ/σ)_{max} < 0.001

θ_{max} = 25.0°

h = -1 → 5

k = -1 → 10

l = -10 → 10

3 standard reflections

monitored every 97

reflections

intensity decay: <5%

Δρ_{max} = 0.67 e Å⁻³

Δρ_{min} = -0.48 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Table

2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for LiCo₂P₃O₁₀

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Co1	0.0379 (1)	0.0671 (1)	0.3346 (1)	0.024 (1)
P1	0.4616 (3)	1/4	0.1433 (2)	0.022 (1)
P2	-0.6675 (3)	1/4	0.8227 (2)	0.023 (1)
P3	-0.3970 (3)	1/4	0.5361 (3)	0.023 (1)
O11	0.2861 (6)	0.1012 (4)	0.1564 (3)	0.028 (1)
O12	0.7615 (9)	1/4	0.2385 (4)	0.026 (1)
O21	-0.4343 (9)	1/4	0.7111 (4)	0.028 (1)
O22	-0.4433 (9)	1/4	0.9743 (4)	0.024 (8)
O23	-0.8404 (7)	0.1006 (4)	0.8140 (3)	0.029 (1)
O31	-0.2267 (6)	0.1002 (4)	0.5151 (1)	0.025 (1)
O32	-0.6999 (9)	1/4	0.4465 (4)	0.024 (1)
Li1	0	0	0	0.047 (5)

Table 2. Selected geometric parameters (Å) for LiCo₂P₃O₁₀

Co1—O11	2.136 (3)	P1—O11 ^{vi}	1.527 (4)
Co1—O31	2.201 (3)	P1—O12	1.540 (4)
Co1—O12 ⁱ	2.138 (3)	P1 ⁱⁱⁱ —O22	1.658 (4)
Co1—O23 ⁱⁱ	2.098 (3)	P2—O21	1.584 (5)
Co1—O31 ⁱⁱⁱ	2.090 (3)	P2—O23	1.508 (4)
Co1—O32 ^{iv}	2.155 (3)	P2—O22	1.613 (4)
Li1—O11	2.009 (3)	P2—O23 ^v	1.508 (4)
Li1—O23 ⁱⁱ	2.122 (3)	P3—O31 ^{vi}	1.534 (3)
Li1—O23 ^{iv}	2.122 (3)	P3—O31	1.534 (3)
Li1—O11 ^{vi}	2.009 (3)	P3—O21	1.626 (4)
P1—O11	1.527 (4)	P3—O32	1.530 (4)

Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) -1 - *x*, -*y*, 1 - *z*; (iii) -*x*, -*y*, 1 - *z*; (iv) 1 + *x*, *y*, *z*; (v) 1 + *x*, *y*, *z* - 1; (vi) -*x*, -*y*, -*z*; (vii) *x*, ½ - *y*, *z*; (viii) *x* - 1, *y*, 1 + *z*.

LiNi₂P₃O₁₀

Crystal data

LiNi₂P₃O₁₀

M_r = 377.3

Monoclinic

*P*2₁/*m*

a = 4.576 (1) Å

b = 8.356 (1) Å

c = 8.921 (1) Å

β = 98.08 (1)°

V = 337.77 (5) Å³

Z = 2

D_x = 3.709 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 45

reflections

θ = 10.4–12.5°

μ = 6.334 mm⁻¹

T = 298 K

Plate

0.3 × 0.3 × 0.08 mm

Yellow

Data collection

Syntex P4 automated diffractometer	792 observed reflections
$\theta/2\theta$ scans	$[F > 6.0\sigma(F)]$
Absorption correction:	$R_{\text{int}} = 0.0355$
semi-empirical from ψ scans (XEMP; Siemens, 1991)	$\theta_{\text{max}} = 23.0^\circ$
$T_{\text{min}} = 0.25$, $T_{\text{max}} = 0.68$	$h = -1 \rightarrow 6$
1368 measured reflections	$k = -1 \rightarrow 11$
931 independent reflections	$l = -12 \rightarrow 12$
	3 standard reflections
	monitored every 97 reflections
	intensity decay: <5%

Refinement

Refinement on F	$\Delta\rho_{\text{max}} = 1.80 \text{ e } \text{\AA}^{-3}$
$R = 0.052$	$\Delta\rho_{\text{min}} = -1.74 \text{ e } \text{\AA}^{-3}$
$wR = 0.063$	Extinction correction: none
$S = 1.20$	Atomic scattering factors
931 reflections	from <i>International Tables</i>
86 parameters	for <i>X-ray Crystallography</i>
$w = 1/[\sigma^2(F) + 0.0008F^2]$	(1974, Vol. IV, Table
$(\Delta/\sigma)_{\text{max}} = 0.006$	2.2B)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for $\text{LiNi}_2\text{P}_3\text{O}_{10}$

	x	y	z	U_{eq}
Ni1	0.0366 (1)	0.0691 (1)	0.3363 (1)	0.007 (1)
Li1	0	0	0	0.030 (4)
P1	0.4637 (3)	1/4	0.1452 (1)	0.006 (1)
P2	-0.6669 (3)	1/4	0.8209 (1)	0.006 (1)
P3	-0.3979 (3)	1/4	0.5346 (1)	0.006 (1)
O11	0.2891 (6)	0.0985 (3)	0.1597 (3)	0.008 (1)
O12	0.7700 (9)	1/4	0.2381 (4)	0.009 (1)
O21	-0.4319 (10)	1/4	0.7100 (4)	0.011 (1)
O22	-0.4459 (9)	1/4	0.9756 (4)	0.008 (1)
O23	-0.8400 (7)	0.0985 (3)	0.8107 (3)	0.010 (1)
O31	-0.2283 (6)	0.0972 (3)	0.5129 (3)	0.008 (1)
O32	-0.7074 (9)	1/4	0.4462 (4)	0.009 (1)

Table 4. Selected geometric parameters (\AA) for $\text{LiNi}_2\text{P}_3\text{O}_{10}$

Ni1—O12 ⁱ	2.059 (3)	P1—O11 ^{vii}	1.513 (3)
Ni1—O23 ⁱⁱ	2.040 (3)	P1 ^{viii} —O22	1.624 (4)
Ni1—O31 ⁱⁱⁱ	2.044 (3)	P1—O12	1.525 (4)
Ni1—O31	2.132 (3)	P2—O21	1.560 (4)
Ni1—O11	2.095 (3)	P2—O22	1.592 (4)
Ni1—O32 ^{iv}	2.072 (3)	P2—O23	1.489 (3)
Li1—O11	1.982 (3)	P2—O23 ^{vii}	1.489 (3)
Li1—O23 ^v	2.100 (3)	P3—O21	1.594 (4)
Li1—O11 ^{vi}	1.982 (3)	P3—O32	1.521 (4)
Li1—O23 ⁱⁱⁱ	2.100 (3)	P3—O31	1.521 (3)
P1—O11	1.513 (3)	P3—O31 ^{vii}	1.521 (3)

Symmetry codes: (i) $x-1, y, z$; (ii) $-1-x, -y, 1-z$; (iii) $-x, -y, 1-z$; (iv) $1+x, y, z$; (v) $1+x, y, z-1$; (vi) $-x, -y, -z$; (vii) $x, \frac{1}{2}-y, z$; (viii) $x-1, y, 1+z$.

A variable scan rate was used with a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$. Refinement was completed using full-matrix least-squares methods.

For both compounds, data collection: XSCANS (Siemens, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); program(s) used to refine structures: SHELXTL-Plus (Sheldrick, 1992); molecular graphics: XP (Siemens, 1990).

The authors express their thanks to the National Science Foundation for assistance in the form of a grant to permit collaborative investigation and to the Moroccan–American Commission for a Fulbright grant to EMH.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Averbuch-Pouchot, M. T. & Durif, A. (1975). *J. Appl. Cryst.* **8**, 564.
 Averbuch-Pouchot, M. T. & Durif, A. (1985). *Acta Cryst.* **C41**, 1553–1555.
 Averbuch-Pouchot, M. T., Durif, A., Coing-Boyat, J. & Guitel, J. C. (1977). *Acta Cryst.* **B33**, 203–205.
 Averbuch-Pouchot, M. T., Durif, A. & Guitel, J. C. (1975). *Acta Cryst.* **B31**, 2482–2486.
 Bagieu-Bucher, M., Durif, A. & Averbuch-Pouchot, M. T. (1976). *J. Appl. Cryst.* **9**, 412.
 Corbridge, D. E. C. (1960). *Acta Cryst.* **13**, 263–269.
 Corbridge, D. E. C. & Tromans, E. R. (1958). *Anal. Chem.* **30**, 1101–1110.
 Davies, D. R. & Corbridge, D. E. C. (1958). *Acta Cryst.* **11**, 315–319.
 Dyroff, D. R. (1965). Thesis, University of California, USA.
 Jouini, O., Dabbabi, M., Averbuch-Pouchot, M. T., Durif, A. & Guitel, J. C. (1984). *Acta Cryst.* **C40**, 728–730.
 Lee, J. D. (1968). *J. Chem. Soc.* pp. 2881–2882.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1992). *SHELXTL-Plus*. Release 4.21/V. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Siemens (1990). *XP. Interactive Molecular Graphics Program*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). **C52**, 1869–1872

Zigzag Chain Structure of Hexaammonium Enneamolybdate Pentahydrate

TOSHIHIRO YAMASE, MORIYASU SUGETA AND ERI ISHIKAWA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatuta Midori-ku, Yokohama 226, Japan

(Received 23 July 1995; accepted 21 November 1995)

Abstract

The title compound, $(\text{NH}_4)_6[\text{Mo}_9\text{O}_{30}]\cdot 5\text{H}_2\text{O}$, contains an $\{[\text{Mo}_8\text{O}_{26}(\text{MoO}_4)]^{6-}\}_n$ anion with a zigzag chain structure, in which two adjacent Mo_8O_{26} moieties are linked by an MoO_4 tetrahedron.