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A new modification of NaCoPO₄ with the zeolite ABW structure

ANN M. CHIPPINDALE,^{a*} ANDREW R. COWLEY,^a JIESHENG CHEN,^{b*} QIUMING GAO^b AND RUREN XU^b

^aChemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, England, and ^bKey Laboratory of Inorganic Synthesis and Preparative Chemistry, Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China. E-mail: ann.chippindale@chem.ox.ac.uk

(Received 15 February 1999; accepted 17 March 1999)

Abstract

The title compound, sodium cobalt(II) phosphate, a new polymorph of NaCoPO₄, crystallizes as a monoclinic modification of the zeolite ABW structure. The five-coordinate Na⁺ cations reside within channels running through an open cobalt–phosphate framework constructed from four-, six- and eight-membered rings of alternating CoO₄ and PO₄ tetrahedra. The channels are enclosed by the eight-membered rings.

Comment

A number of phases of formula NaCoPO₄, in which Na⁺ cations reside in channels within three-dimensional cobalt–phosphate frameworks, have been characterized previously. The orthorhombic and hexagonal forms, α-NaCoPO₄ (pink) and β-NaCoPO₄ (blue), prepared originally by high-temperature solid-state reaction (Hammond & Barbier, 1996) and subsequently by hydrothermal synthesis at a moderate temperature (Feng *et al.*, 1997, 1997a), contain Co²⁺ in an octahedral and tetrahedral coordination, respectively. A third polymorph (dark red), also synthesized hydrothermally, contains trigonal-bipyramidal Co²⁺ cations (Feng *et al.*, 1997b).

We report here a new form of NaCoPO₄ which has the tetrahedron-based ABW zeolite framework topol-

ogy (Meier *et al.*, 1996). Although modifications of NH₄CoPO₄ and RbCoPO₄ also exhibit the ABW topology (Feng *et al.*, 1997), the structure of the title compound is distinct from these, as considerable distortion of the cobalt–phosphate framework occurs in order to provide the smaller Na⁺ cation with a more suitable coordination environment. The ability to accommodate Na⁺, as well as NH₄⁺ and Rb⁺ cations, demonstrates the flexibility of the ABW cobalt–phosphate framework.

The structure of the title compound is similar to that of NaZnPO₄ (Ng & Harrison, 1998). The asymmetric unit contains one Co and one P atom, each of which is coordinated by four O atoms to form CoO₄ and PO₄ tetrahedra, respectively. The CoO₄ tetrahedron has approximately regular geometry, with a mean Co—O bond length of 1.962 Å, which is typical for tetrahedral CoO₄ units. The PO₄ tetrahedron also has an approximately regular geometry, with a mean P—O bond length of 1.535 Å. These tetrahedra are vertex-linked alternately to form buckled chains of edge-sharing four-membered rings running parallel to the crystallographic *a* axis. Crosslinking of these chains forms a three-dimensional structure with the ABW topology, containing four-, six- and eight-membered rings of tetrahedra. The framework encloses channels running parallel to the *a* axis (Fig. 1). These are enclosed by very elongated elliptical eight-membered rings of tetrahedra, with cross-ring dimen-

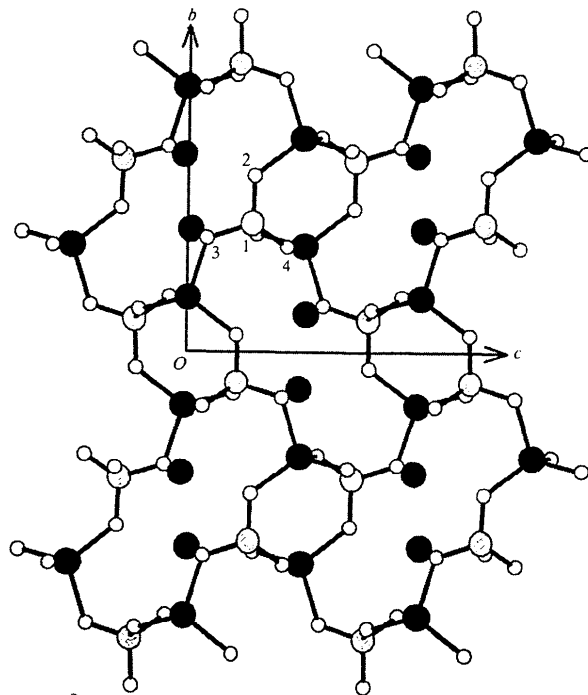


Fig. 1. View (ATOMS; Dowty, 1997) of the title compound along the crystallographic *a* axis, showing Na⁺ cations residing within channels bounded by highly elongated elliptical eight-membered rings of alternating CoO₄ and PO₄ tetrahedra. (Key: Co and Na black, P grey and O white.)

sions of $ca\ 3.8 \times 9.8\ \text{\AA}$. The Na⁺ cations, which reside within the channels, are coordinated to four O atoms at distances of between 2.293 (1) and 2.340 (1) Å, and a further O atom at a distance of 2.713 (1) Å.

Experimental

The title compound was prepared solvothermally from a mixture of Co(ethylenediamine)₃(HSO₄)₃, Al(ⁱPrO)₃, H₃PO₄, NaOH, ethylene glycol and water in the molar ratio 1.04:1.00:1.78:2.30:110:172. Aluminium triisopropoxide (1.0 g) and Co(en)₃(HSO₄)₃ (2.7 g), previously prepared by crystallization from an aqueous sulfuric acid solution of Co(Ac)₂·4H₂O and ethylenediamine, were stirred into a mixture of ethylene glycol (30 ml) and water (15 ml). NaOH (0.45 g) was then added and the reaction gel thus formed stirred vigorously. Dropwise addition of H₃PO₄ (85% aqueous by weight, 0.6 ml) was followed by further stirring and the mixture was then sealed in a Teflon-lined autoclave and heated at 413–433 K for 7 d under autogeneous pressure. The solid product mixture was washed with distilled water and dried at ambient temperature in air. Single crystals of the title compound in the form of deep-blue rectangular blocks could be readily selected under an optical microscope from deep-blue hexagonal bipyramids of NaCoPO₄·xH₂O [the Zn analogue of which has been reported previously by Harrison *et al.* (1996)] and a number of unidentified phases.

Crystal data

NaCoPO₄
M_r = 176.89
 Monoclinic
*P*2₁/*n*
a = 5.221 (1) Å
b = 9.983 (1) Å
c = 7.388 (1) Å
 β = 90.210 (4)^o
V = 385.07 Å³
Z = 4
D_x = 3.05 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 3378 reflections
 θ = 3.43–26.50^o
 μ = 4.83 mm⁻¹
T = 150 K
 Block
 0.40 × 0.20 × 0.15 mm
 Dark blue

Data collection

Enraf–Nonius DIP2000 diffractometer
 ω scans
 Absorption correction: multi-scan (Otwinowski & Minor, 1996)
T_{min} = 0.326, *T_{max}* = 0.484
 793 measured reflections
 752 independent reflections

Refinement

Refinement on *F*
R = 0.0182
wR = 0.0200
S = 1.0847
 683 reflections
 65 parameters

(Δ/σ)_{max} < 0.001
 $\Delta\rho$ _{max} = 0.44 e Å⁻³
 $\Delta\rho$ _{min} = -0.29 e Å⁻³
 Extinction correction: (Larson, 1967)
 Extinction coefficient: 59 (4)

Chebyshev polynomial with three parameters (2.31, -0.837, 1.90; Carruthers & Watkin, 1979)

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Na1	0.21602 (11)	0.38243 (7)	0.01491 (7)	0.0077
Co1	0.20259 (4)	0.330358 (18)	0.50677 (2)	0.0034
P1	0.69868 (7)	0.40172 (3)	0.27901 (4)	0.0025
O1	0.4126 (2)	0.37059 (12)	0.29603 (13)	0.0082
O2	0.7506 (2)	0.55224 (11)	0.28597 (13)	0.0079
O3	0.7830 (2)	0.3566 (1)	0.08752 (14)	0.0062
O4	0.8450 (2)	0.3274 (1)	0.42783 (14)	0.0069

Table 2. Selected geometric parameters (Å, °)

Na1—O1	2.3163 (11)	Co1—O3 ^v	2.0031 (10)
Na1—O2 ⁱ	2.3237 (11)	Co1—O4 ⁱⁱ	1.9544 (11)
Na1—O3 ⁱⁱ	2.3396 (13)	P1—O1	1.5313 (12)
Na1—O3 ⁱ	2.7133 (13)	P1—O2	1.5278 (11)
Na1—O4 ⁱⁱⁱ	2.2927 (11)	P1—O3	1.5502 (10)
Co1—O1	1.9494 (11)	P1—O4	1.5287 (11)
Co1—O2 ^{iv}	1.9430 (10)		
O1—Na1—O2 ⁱ	146.88 (5)	O1—Co1—O4 ⁱⁱ	107.72 (4)
O1—Na1—O3 ⁱⁱ	102.36 (4)	O2 ^{iv} —Co1—O4 ⁱⁱ	111.21 (5)
O2 ⁱ —Na1—O3 ⁱⁱ	109.04 (5)	O3 ^v —Co1—O4 ⁱⁱ	105.88 (4)
O1—Na1—O3 ⁱ	107.33 (4)	O1—P1—O2	111.70 (7)
O2 ⁱ —Na1—O3 ⁱ	57.55 (4)	O1—P1—O3	107.24 (6)
O3 ⁱⁱ —Na1—O3 ⁱ	99.94 (4)	O2—P1—O3	105.41 (6)
O1—Na1—O4 ⁱⁱⁱ	94.32 (4)	O1—P1—O4	109.10 (6)
O2 ⁱ —Na1—O4 ⁱⁱⁱ	87.98 (4)	O2—P1—O4	111.43 (6)
O3 ⁱⁱ —Na1—O4 ⁱⁱⁱ	104.39 (4)	O3—P1—O4	111.86 (6)
O3 ⁱ —Na1—O4 ⁱⁱⁱ	142.95 (4)	Co1—O1—P1	131.23 (6)
O1—Co1—O2 ^{iv}	115.83 (5)	Co1 ^{iv} —O2—P1	129.91 (6)
O1—Co1—O3 ^v	108.17 (5)	Co1 ^{iv} —O3—P1	118.86 (6)
O2 ^{iv} —Co1—O3 ^v	107.55 (4)	Co1 ^{iv} —O4—P1	132.95 (7)

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

Data collection: *XPRESS* (MacScience, 1989) in *DIP2000* software. Cell refinement: *DENZO* (Otwinowski & Minor, 1996). Data reduction: *DENZO*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996). Molecular graphics: *ATOMS for Windows* (Dowty, 1997). Software used to prepare material for publication: *CRYSTALS*.

Financial support from the National Natural Science Foundation of China and the EPSRC (UK) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1238). Services for accessing these data are described at the back of the journal.

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