

Hydrothermal Synthesis, Crystal Structure, and Characterization of Tetrasodium Tricobalt(II)-bis-Phosphate-bis-Hydrogenophosphate Octahydrate, $\text{Na}_4\text{Co}_3\text{H}_2(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$, with a New Structure Type

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A sodium cobalt hydrogen phosphate hydrate, $\text{Na}_4\text{Co}_3\text{H}_2(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$, was synthesized by the mild hydrothermal method, and the crystal structure was characterized by the single-crystal X-ray diffraction method. The layered structure possesses a new type with the following data: $M_r = 794.775$, monoclinic, $mP106$, $P2_1/c-e26d$ (No. 14), $a = 7.3547(9) \text{ \AA}$, $b = 9.222(1) \text{ \AA}$, $c = 15.186(2) \text{ \AA}$, $\beta = 95.18(1)^\circ$, $V = 1025.9(3) \text{ \AA}^3$, $Z = 2$, $D_x = 2.573 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 29.0 \text{ cm}^{-1}$, $F(000) = 790$, $T = 293 \text{ K}$, $R = 0.0346$, $wR = 0.0432$ for 198 variables and 2278 contributing unique reflections. The structure is characterized by corner- and edge-sharing deformed CoO_5 trigonal bipyramids with PO_4 tetrahedra forming an infinite ribbon along the [010] direction. The ribbons are connected by bridging CoO_6 octahedra resulting in a novel three-cobalt polymeric coordination unit and a polyhedral sheet. The same sheets are packed along the c -axis by sandwiching Na^+ cations and hydrogen-bonded water molecules to construct the whole structure. The temperature dependence of the magnetic susceptibility of the compound follows the Curie–Weiss law, and the effective magnetic moment of $4.69 \mu_B$ corresponds to high-spin Co^{2+} ion, confirmed by bond valence sum calculations. © 2000 Academic Press

Key Words: sodium cobalt hydrogen phosphate hydrate; hydrothermal synthesis; crystal structure; magnetic properties.

INTRODUCTION

In the last two decades, many one- or two-dimensional magnetically ordered transition-metal compounds have been characterized. They serve as model compounds with which the predictions of theory can be tested and refined. Although conventional chemical syntheses of transition metal phosphates can lead to a single-layered structure like $M(\text{I})M(\text{II})\text{PO}_4 \cdot \text{H}_2\text{O}$ (1) or $\text{K}_2M(\text{II})\text{P}_4\text{O}_{12} \cdot 5\text{H}_2\text{O}$ (2), three-dimensional microporous alkali metal phosphates (3–5) or

some mineral modifications (6–8) are normally obtained by conventional hydrothermal methods. Considering many examples of successful syntheses of new transition-metal phosphates and borophosphates (9–12, 17), it seems more promising to use mild hydrothermal methods, i.e., with lower temperature and pressure, to synthesize possible layered phosphates with complex structures. Here we report our synthesis and characterizations of a new two-dimensional cobalt(II) phosphate hydrate.

EXPERIMENTAL

Synthesis

The sample of the title compound was synthesized by the mild hydrothermal method. Starting materials were of analytical grade and used without further purification. A mixture of 0.381 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 2.149 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 0.228 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 0.8 ml 18% HCl (molar ratio of Na:Co:P:B = 8:1:4:6) was added to 1.0 mL distilled water. The mixture was sealed in glass tubes of about 25 cm in length. The solution was filled to about 30% of the tube volume. The glass tubes were placed in an oven, the temperature was increased slowly to 80°C , and the samples were prereacted for 1 week. The temperature was increased to 120°C and reacted for 2 weeks before the tubes were cooled to room temperature. The reaction was under auto-geneous pressure. The subsequent successful syntheses of the title compound under the same physical conditions in a shorter time but without the presence of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (only with $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and HCl) show the nonessentialness of this reactant. The blue-colored crystals with plate-like shapes were grown from the solution in the glass tubes and were easily isolated from the products in large quantities for powder XRD and magnetic measurements.

Structure Determination

A single crystal with a plate-like shape ($0.45 \times 0.20 \times 0.35 \text{ mm}^3$) was mounted on an Enraf-Nonius CAD4

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automatic four-circle diffractometer, MoK α radiation, with graphite monochromator. Crystallographic data for the title compound are summarized in Table 1. The unit cell parameters were refined from 2θ values of 25 randomly located reflections (MoK α , $\lambda = 0.71073$ Å, $31^\circ < 2\theta < 36^\circ$). A total of 3269 reflections were collected out to $(\sin \theta/\lambda) = 0.700$ ($-10 \leq h \leq 10, 0 \leq k \leq 13, -21 \leq l \leq 0$) in the ω - 2θ scan mode, yielding 2,278 unique observed reflections. Three standard reflections $-1\ 6\ -6, 1\ 2\ -12$, and $5\ 2\ -8$ were measured 32 times with maximum variations of less than 0.1%, showing no detectable decay during the data collection. The intensity data were corrected for Lorentz and polarization effects, and absorption correction was made according to eight ψ -scan reflections with maximum and minimum transmission factors of 0.7719 and 0.9983. The anomalous-dispersion coefficients were taken into account in the data processing. Systematic absences led to the only possible space group, $P2_1/c$ (International Tables for Crystallography, 1983, Vol. A). The structure was solved in space group $P2_1/c$ and confirmed by the full-matrix least-square structure refinement, based on F values using the SDP program package (13). The metal atoms were located by the direct method, and the remaining atoms were found from the successive difference Fourier maps. Attempts to refine the occupancies of the Na and Co atoms did not show any

TABLE 1
Crystallographic Data for Na₄Co₃H₂(PO₄)₄·8H₂O

Formula weight (amu)	794.775
Space group, Z	$P2_1/c, 2$
a (Å)	7.3547(9)
b (Å)	9.222(1)
c (Å)	15.186(2)
β (°)	95.18(1)
V (Å ³)	1025.9(3)
D_x (g cm ⁻³)	2.573
Temperature (K)	293
Radiation, monochromator	MoK α , graphite
Crystal shape, color	Plate, blue
Crystal size (mm)	0.45 × 0.20 × 0.35
Linear absorption coefficient (cm ⁻¹)	29.0
Scan type	ω - 2θ
Two-theta range (°)	3–60
hkl range	$-9 \rightarrow 9, 0 \rightarrow 12, -20 \rightarrow 0$
Total number of collected reflections	3,269
Number of observed unique reflections	2,278
Number of parameters	198
$F(000)$	790
Transmission factors T_{\min}, T_{\max}	0.7719, 0.9983
Final $R^a(F), R_w^b(F)$	0.0346, 0.0432
S	1.243
Shift/e.s.d. in the last cycle	0.00003
Residual peaks (hole) (eÅ ⁻³)	0.655 (–0.339)

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}, w = 1/\sigma^2(F).$$

TABLE 2
Atomic Positional and Displacement Parameters for Na₄Co₃H₂(PO₄)₄·8H₂O with Space Group $P2_1/c$

Atom	WP ^a	x	y	z	U_{eq} (100 Å ²) ^b
Na(1)	4e	0.5498(2)	0.1086(2)	0.7187(1)	1.80(3)
Na(2)	4e	0.2591(2)	0.0174(2)	0.8702(1)	1.61(3)
Co(1)	2d	1/2	0	1/2	0.85(1)
Co(2)	4e	0.02642(6)	0.23829(5)	0.50369(3)	0.870(8)
P(1)	4e	0.1046(1)	0.02331(9)	0.38326(6)	0.66(1)
P(2)	4e	0.7550(1)	0.4789(1)	0.42712(6)	0.74(1)
O(1)	4e	0.5780(3)	0.4464(3)	0.3743(2)	1.32(5)
O(2)	4e	0.8042(4)	0.3687(3)	0.5008(2)	1.13(5)
O(3)	4e	0.2366(4)	0.0554(3)	0.4649(2)	1.15(5)
O(4)	4e	0.9772(4)	0.1303(3)	0.6128(2)	1.07(4)
O(5)	4e	0.9519(3)	0.1381(3)	0.3885(2)	1.00(4)
O(6)	4e	0.2409(4)	0.3689(3)	0.5298(2)	1.20(5)
O(7)	4e	0.1944(4)	0.0379(3)	0.2973(2)	1.07(4)
O(8)	4e	0.9172(4)	0.4740(3)	0.3651(2)	1.31(5)
O(9)	4e	0.2578(4)	0.1821(3)	0.7483(2)	1.56(5)
O(10)	4e	0.7831(4)	0.1941(3)	0.2205(2)	1.57(5)
O(11)	4e	0.5326(4)	0.2007(3)	0.5654(2)	1.26(5)
O(12)	4e	0.5910(4)	0.0912(3)	0.3814(2)	1.71(5)
H(81)	4e	0.871	0.024	0.810	4.0 ^c
H(91)	4e	0.170	0.164	0.712	4.0 ^c
H(92)	4e	0.218	0.246	0.267	4.0 ^c
H(101)	4e	0.869	0.237	0.189	4.0 ^c
H(102)	4e	0.850	0.206	0.267	4.0 ^c
H(111)	4e	0.622	0.250	0.046	4.0 ^c
H(112)	4e	0.464	0.231	0.056	4.0 ^c
H(121)	4e	0.707	0.108	0.384	4.0 ^c
H(122)	4e	0.552	0.187	0.373	4.0 ^c

^a Wyckoff positions.

^b The U_{eq} were defined as one-third of the trace of the orthogonal U_{ij} tensor.

^c The atomic coordinates and displacement parameters for the H atoms are fixed in the refinements.

significant deviation from 100%, and the multiplicity was fixed at unity in the final refinements. One hundred and ninety-eight variables, including anisotropic displacement parameters for nonhydrogen atoms, were refined to $R = 0.0346$ and $wR = 0.0432$ [$w = 1/\sigma^2(|F|)$, $S = 1.243$] considering 2,278 contributing unique reflections with $F > 3\sigma(F)$. All the hydrogen atoms were located on the difference Fourier map but not refined. The maximum shift/e.s.d in the last cycle was 0.00003. Final residual electron density was $+0.655(-0.339)$ eÅ⁻³. The atomic positional and displacement parameters are given in Table 2, and the selected important interatomic distances are given in Table 3.

RESULTS AND DISCUSSION

Structure Description

The P(1) atom has a rather regular tetrahedron coordination with an average P–O distance of 1.537 Å and an angle

TABLE 3
Selected Important Interatomic Distances (Å), Angles, and Bond Valence Sums ($\sum s$) for the $\text{Na}_4\text{Co}_3\text{H}_2(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$ structure

[NaO ₆] polyhedra, $\sum s[\text{Na}(1)-\text{O}] = 1.11$, $\sum s[\text{Na}(2)-\text{O}] = 1.04$						
Na(1)-O(9)	2.334(3)	O(7)	2.347(3)	O(1)	2.407(3)	
O(11)	2.471(3)	O(10)	2.499(3)	O(12)	2.548(3)	
Na(2)-O(1)	2.364(3)	O(10)	2.392(3)	O(9)	2.394(3)	
O(2)	2.470(3)	O(8)	2.510(3)	O(6)	2.655(3)	
[CoO ₆] octahedra, $\sum s[\text{Co}(1)-\text{O}] = 2.04$						
Co(1)-O(3)	2.028(2)	O(11)	2.105(3)	O(12)	2.149(3)	
O(3)-O(3)	4.05	O(3)-Co(1)-O(3)	180.0			
O(11)-O(11)	4.21	O(11)-Co(1)-O(11)	180.0			
O(12)-O(12)	4.30	O(12)-Co(1)-O(12)	180.0			
O(3)-O(11)	2.97	O(3)-Co(1)-O(11)	91.8(1)			
O(3)-O(11)	2.87	O(3)-Co(1)-O(11)	88.2(1)			
O(3)-O(12)	3.02	O(3)-Co(1)-O(12)	92.5(1)			
O(3)-O(12)	2.89	O(3)-Co(1)-O(12)	87.5(1)			
O(11)-O(12)	3.04	O(11)-Co(1)-O(12)	91.2(1)			
O(11)-O(12)	2.98	O(11)-Co(1)-O(12)	88.8(1)			
[CoO ₅] trigonal-bipyramid, $\sum s[\text{Co}(2)-\text{O}] = 1.86$						
Co(2)-O(4)	1.994(3)	O(6)	1.996(3)	O(5)	2.011(3)	
O(2)	2.026(3)	O(3)	2.397(3)			
O(2)-O(3)	4.37	O(2)-Co(2)-O(3)	161.6(1)			
O(2)-O(5)	2.99	O(2)-Co(2)-O(5)	95.6(1)			
O(2)-O(4)	2.99	O(2)-Co(2)-O(4)	96.2(1)			
O(2)-O(6)	3.20	O(2)-Co(2)-O(6)	105.5(1)			
O(3)-O(5)	2.42	O(3)-Co(2)-O(5)	66.0(1)			
O(3)-O(4)	3.15	O(3)-Co(2)-O(4)	91.3(1)			
O(3)-O(6)	3.05	O(3)-Co(2)-O(6)	87.6(1)			
O(4)-O(5)	3.40	O(4)-Co(2)-O(5)	116.0(1)			
O(4)-O(6)	3.26	O(4)-Co(2)-O(6)	109.6(1)			
O(5)-O(6)	3.58	O(5)-Co(2)-O(6)	126.8(1)			
[PO ₄] tetrahedra, $\sum s[\text{P}(1)-\text{O}] = 4.97$						
P(1)-O(7)	1.521(3)	O(3)	1.533(3)			
O(4)	1.542(3)	O(5)	1.551(3)			
O(3)-O(4)	2.54	O(3)-P(1)-O(4)	111.5(2)			
O(3)-O(5)	2.52	O(3)-P(1)-O(5)	103.6(1)			
O(3)-O(7)	2.54	O(3)-P(1)-O(7)	112.6(2)			
O(4)-O(7)	2.48	O(4)-P(1)-O(7)	108.4(2)			
O(4)-O(5)	2.53	O(4)-P(1)-O(5)	109.8(1)			
O(5)-O(7)	2.53	O(5)-P(1)-O(7)	110.8(2)			
[PO ₄] tetrahedra, $\sum s[\text{P}(2)-\text{O}] = 4.94$						
P(2)-O(1)	1.497(3)	O(2)	1.531(3)			
O(6)	1.548(3)	O(8)	1.586(3)			
O(1)-O(2)	2.53	O(1)-P(2)-O(2)	113.3(1)			
O(1)-O(8)	2.52	O(1)-P(2)-O(8)	109.9(2)			
O(1)-O(6)	2.54	O(1)-P(2)-O(6)	113.0(1)			
O(2)-O(8)	2.49	O(2)-P(2)-O(8)	105.9(2)			
O(2)-O(6)	2.48	O(2)-P(2)-O(6)	107.4(1)			
O(6)-O(8)	2.52	O(6)-P(2)-O(8)	106.8(2)			
Hydrogen bonds in the $\text{Na}_4\text{Co}_3\text{H}_2(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$ structure						
A	A-B	B	B-C	C	A-B-C	A-C
O(7)	1.750	H(81)	0.878	O(8)	161.2	2.60
O(4)	1.995	H(91)	0.830	O(9)	173.1	2.82
O(7)	1.981	H(92)	0.792	O(9)	160.1	2.74
O(4)	1.906	H(101)	0.916	O(10)	160.1	2.79
O(5)	2.030	H(102)	0.828	O(10)	151.0	2.78
O(2)	1.904	H(111)	0.875	O(11)	175.6	2.78
O(6)	1.891	H(112)	0.812	O(11)	158.2	2.66
O(5)	1.814	H(121)	0.869	O(12)	178.2	2.68
O(1)	2.398	H(122)	0.938	O(12)	156.5	3.28

of 109.5° (range from 103.6° to 112.6°). The P-O distances are consistent with those typically seen in phosphates without hydrogen bonding (4–5, 14). But the tetrahedron around the P(2) atom has some deformation because of the O(8)H group. The anionic hydrogen connected to the P(2)O4 caused the significant elongation of the P-O(8) distance to 1.586 Å. It is 0.046 Å longer than the average 1.540 Å value around P(2). The average angle is 109.4° (range from 105.9° to 113.3°).

The two cobalt atoms have different oxygen coordinations, shown in Fig. 1. Co(1) occupies a special position with an inversion center and has a more symmetric neighborhood. The octahedron around Co(1) is rather regular: Four H₂O molecules form the basal plane at distances 2.105 and 2.149 Å while the O(3) atoms serve as the apical vertex with a slightly shorter distance of 2.028 Å. This makes the octahedron slightly compressed along the pseudo-fourfold O(3)-O(3) apical axis. Similar compression was observed in α -NaCoPO₄ (15). The average distance of Co(1)-O is 2.094 Å, very close to the 2.096 Å in NaCo₃(PO₄)(HPO₄)₂ (6) but smaller than the value 2.111 Å derived by Wildner (16). The O-O distances range from 2.89 to 3.04 Å, and the cis \angle O-Co(1)-O bond angles range from 87.5° to 92.5°. The trigonal-bipyramidal coordination polyhedron around the Co(2) atom is quite deformed. The distance of the cobalt atom from one of the apical oxygens (2.397 Å) is obviously elongated by comparison with the other four distances (ranging from 1.994 to 2.026 Å). The average distance is 2.085 Å, which is longer than the value 2.051 Å derived for polyhedra with coordination number 5 by Wildner (16). The O-O distances range from 2.42 to 3.58 Å, and the bond angle \angle O(2)-Co(2)-O(3) along the pseudo-threefold apical axis is 161.6°, far from 180°. The Co(2) atoms are no longer located at the centers of the trigonal-bipyramids but are shifted off the basal plane, which makes the coordination polyhedron approach a tetrahedron form if the O(3) atom is considered a capping atom. The strong deformation of the Co(2) polyhedron from the ideal trigonal-bipyramid is probably responsible for the blue color of the crystal, which is normally the case for tetrahedral coordination.

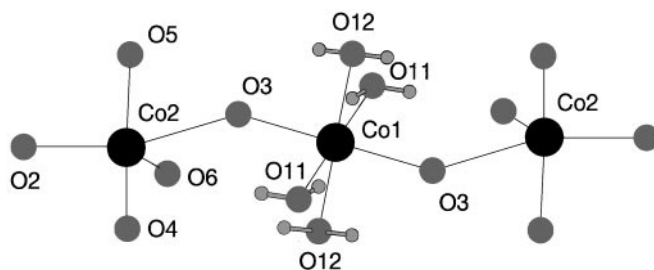


FIG. 1. The coordination environments of the two cobalt(II) ions in $\text{Na}_4\text{Co}_3\text{H}_2(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$.

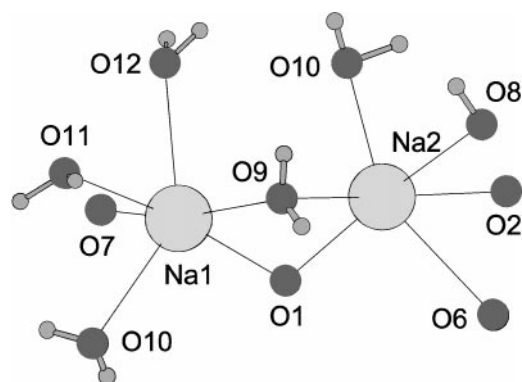


FIG. 2. The coordination environments of the two Na ions in Na₄Co₃H₂(PO₄)₄·8H₂O.

The Co(2)–Co(1)–Co(2) coordination polyhedra form a polymeric unit by bridging O(3) atoms with a \angle Co(1)–O(3)–Co(2) angle of 137.3° and a Co(1)–Co(2) distance of 4.123 Å. This kind of polymeric unit is so far, to our knowledge, the only example in cobalt phosphate structures, although edge-sharing octahedral polymeric units were recently observed in cobalt borophosphate (17). On the basis of bond strength calculations (18), both cobalt atoms are divalent. The calculated valence sums for metal atoms are listed in Table 3.

The two sodium atoms are at general positions. There is a very clear gap between 2.655 and 3.400 Å on the histogram of the Na–O distance distributions; therefore, the coordination polyhedra for the Na atoms are clearly defined as deformed oxygen octahedra; see Fig. 2. The Na–O distance of 2.655 Å is much smaller than the L_{\max} of 3.13 Å given by Donnay and Allmann (18). The angles are \angle O(10)–Na(1)–O(12) = 140.76° and \angle O(10)–Na(1)–O(6) = 146.42°. The average sodium–oxygen distances for Na(1) and Na(2) are 2.434 and 2.463 Å, respectively.

The Co(2) polyhedron, on one side, shares one edge and one corner with each of two P(1)O₄ tetrahedra and, on the other side, shares one corner with two P(2)O₄ tetrahedra. This connection forms an infinite polyhedral ribbon along the [010] direction. A polyhedral sheet is constructed by the ribbons connected by Co(1) octahedra, shown in Fig. 3. The same sheets are packed along the *c*-axis by sandwiching Na⁺ cations and hydrogen-bonded water molecules (O(9)H₂ and O(10)H₂) to construct the whole structure, shown in Fig. 4.

The connection of the layers is reinforced by hydrogen bonds formed between water molecules and other oxygen atoms coordinated to Co and P atoms. The O–H...O bond angles range from 151.0° to 178.2° and the oxygen distances range from 2.60 to 2.79 Å, which is quite normal for hydrogen bonds. The O(12)–H(122)...O(1) distance of 3.28 Å may be too long to be considered a bond, but the angle (156.5°) indicates a correct position for a hydrogen bond.

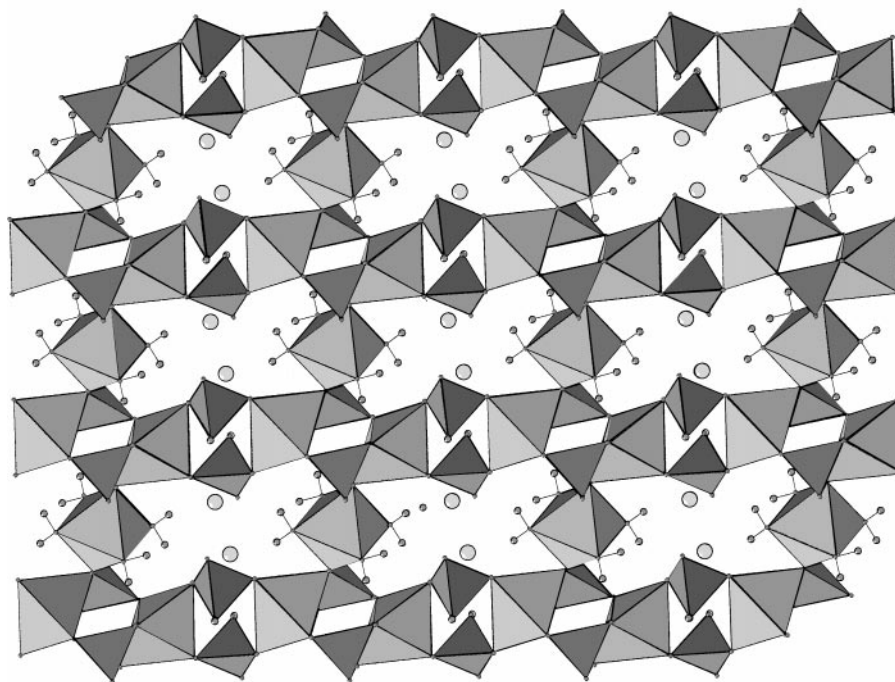


FIG. 3. Polyhedral representation of the connected sheet in Na₄Co₃H₂(PO₄)₄·8H₂O viewed along the [001] direction.

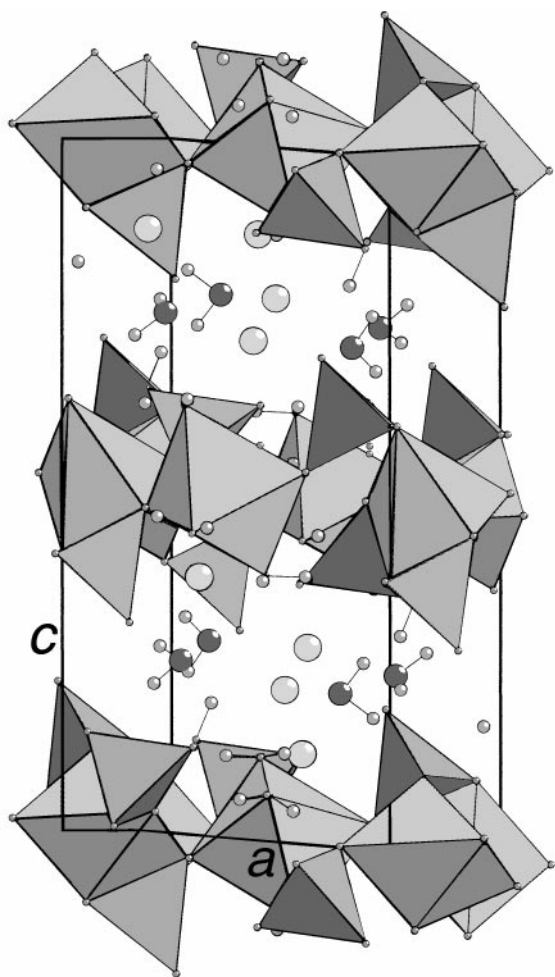


FIG. 4. Polyhedral representation of the $\text{Na}_4\text{Co}_3\text{H}_2(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$ structure, showing the packing of polyhedra sheets and sandwiched Na^+ and water molecules.

Magnetic Susceptibility

Figure 5 shows the temperature dependence of the magnetic susceptibility and reciprocal susceptibility for the $\text{Na}_4\text{Co}_3\text{H}_2(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$ compound. The variation follows the Curie–Weiss law over a wide range of temperatures (5–300 K). The effective magnetic moment/Co calculated from the derived Curie constant is $4.69 \mu_B$. This value falls in the range of the expected values of 4.30 to $5.20 \mu_B$ for the high-spin Co^{2+} ion (20). The extrapolated Weiss constant has a negative value of -8.6 K, which may imply that the possible superexchange interactions between neighboring Co atoms, i.e., Co(1)–O(3)–Co(2) units, are very weak and antiferromagnetic in character. The magnetic ordering transition was not observed at temperatures above 5 K.

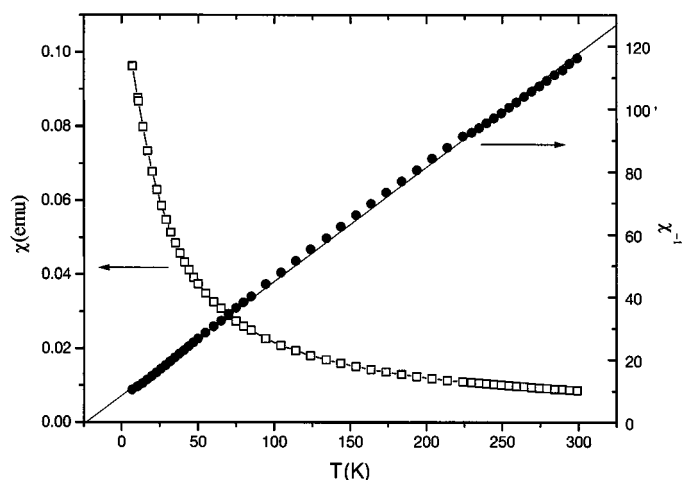


FIG. 5. Temperature dependence of the magnetic susceptibility and the inverse susceptibility for $\text{Na}_4\text{Co}_3\text{H}_2(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$.

CONCLUSIONS

The title compound was synthesized by the mild hydrothermal method, and the crystal structure was shown to possess a new type. A novel three-cobalt polymeric coordination unit was observed, and the whole structure was characterized by layers of corner- and edge-sharing cobalt and phosphorous coordination polyhedra sandwiched by sodium cations and water molecules through hydrogen bonds. Both the effective magnetic moment derived from magnetic susceptibility and the bond valence sum calculations confirmed the high-spin Co^{2+} ion.

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