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$NaCo(H_2PO_2)_3$: Crystal structure and physical study

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ABSTRACT

$NaCo(H_2PO_2)_3$ was synthesized in solution and its structure was studied by single-crystal X-ray diffraction. It crystallizes in the cubic space group $P2_13$ (#198), Z = 4, a = 9.2563(16) Å, V = 793.1(2) $Å^3$. Final residual factors of the refined structure model R/Rw were 0.0367/0.0941. The cations Na^+ and Co^{2+} are both octahedrally coordinated. $[NaO_6]$ and $[CoO_6]$ share edges to form channels propagating along [1,−1, −1] with the $[H_2PO_2]$ pseudo-pyramids adjusted inside the channels to the above mentioned octahedra. The IR and Raman spectroscopic studies show the expected bands of the hypophosphite anion. $NaCo(H_2PO_2)_3$ did not show any electrochemical activity under the electrochemical test conditions (2.4–4.5 V vs. Na/Na+).

1. Introduction

Bibliographic survey of the hyphosphite materials revealed us just a few phases in the system A-M-H_2PO_2 (A = alkaline, M = 3d metal transition and/or Earth-alkaline) compared to their homologs with phosphates and phosphites compounds. We found reports on several hypophosphites of transition metals and lanthanides [1–7], and few mixed hypophosphites: $NaCa(H_2PO_2)_2$ [8] and $Co_{0.5}(H_2O)_6Ni_{0.5}(H_2PO_2)_2$ [9]. Several other simple phases are known, e.g., AH_2PO_2, A = K, Rb, Cs [10], $Mg(H_2O)_6(H_2PO_2)_2$ [11], $Mn(H_2PO_2)_2.H_2O$ [12], $Co(H_2O)_6(H_2PO_2)_2$ [9,13], and $Cu(H_2PO_2)_2$ [14]. Some powder crystallographic data are also known: $M(H_2PO_2)_2$, Co(H2PO2)2.0.53H2O [15], and $VO(H_2PO_2)_2.H_2O$ [16]. This class of materials was studied in both chemistry and material science due to their industrial applications as mild reducing agents, reagents in catalytic syntheses and antioxidants [17,18]. As applications of such phosphite materials, we mention the use of sodium hypophosphite as catalyser for the formation of cyclic anhydrides intermediates polycarboxilic acids [19]. Zinc hypophosphite $Zn(H_2PO_2)_2.H_2O$) was also reported as an anti-corrosive agent [20].

In the present paper we report on the synthesis, crystal structure, spectroscopic studies and electrochemical properties of a new mixed hypophosphite $NaCo(H_2PO_2)_3$ as the first result of our ongoing investigation of the complete series $AM(H_2PO_2)_3$.

2. Experimental

2.1. Synthesis

The crystals subject to the present study were prepared by mixing NaH_2PO_2 (0.2762 g, 3.37 mmol) and $CoCl_2$ (0.5689 g, 3.38 mmol) in 5 mL distilled water. The mixture was stirred for 1 h before to be left at ambient (P, T) conditions. Two kinds of crystals deposited, pink and a soft white powder with the analysis results elucidated below.

2.2. X-rays study

2.2.1. Powder

The powder diffraction study was performed at room temperature with the PANalytical Empyrean powder diffractometer. The sample was ground and placed into the 0.3 mm borosilicate glass capillary which was measured in transmission mode from 8° to 100° 2Theta with $CuK\alpha_{1,2}$ focused by the incident focusing mirror.

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The step size was set to 0.013° 2-Theta.

The phase analysis, which was performed in the HighScore Plus software using the PDF-4+ 2011 database, found $Co(PH_2O_2)_2$ and NaCl phases and also confirmed the presence of the $NaCo(H_2PO_2)_3$ phase with the crystal structure subject of the present paper. Results are depicted in Fig. 1.

2.2.2. *Single crystal*

The X-ray diffraction data for the title compound were collected at 298 K in a four-circles diffractometer Gemini of Oxford Diffraction (now Rigaku Oxford Diffraction), using graphite monochromatized MoKα radiation ($\lambda = 0.7173$ Å) collimated with Mo-Enhance collimator, and the Atlas S1 CCD detector. A numerical absorption correction based on the crystal shape was carried out with the program CrysAlis RED [21]. The structures were solved by the Direct Methods procedure of SIR97 [22] and refined by a full-matrix least-squares technique based on F^2 with Jana2006 [23].

Table 1 reports the crystallographic data and experimental details about data collection and structure refinements. Atomic coordinates and equivalent thermal parameters are reported in Table 2, selected bond distances in Table 3. The structural graphics were created using DIAMOND program [24].

Supplementary tables of crystal structures and refinements, notably the full list of bond lengths and angles, and anisotropic thermal parameters have been deposited with the Inorganic Crystal Structure Database, FIZ, Hermann von Helmholtz Platz 1, 76344 EggensteinLeopoldshafen, Germany; fax: (+49) 7247 808 132; Email: crysdata@fiz-karlsruhe.de. CCDC deposition number is **886031**.

3. Raman spectrum

All Raman spectra were obtained with a HR800 Horiba integrated Raman microscope equipped with a × 50, NA 0.7 objective. All measurements were carried out using a He–Ne laser ($\lambda_0 = 633$ nm, laser power: 20 mW, exposure time: 1 s, accumulation time: 10, acquisition mode: static, resolution of 1 cm^{-1}). Wavelength calibration was performed by means of a silicon wafer through a × 50 objective, evaluating the first-order phonon band of Si at 520 cm^{-1}.

The measurements were carried out by focusing the laser beam on the crystals and each analysis was repeated at least 3 times. The spectra were processed by using the OriginPro 7.5 program (OriginLab Corporation Northampton, U.S.A) in order to obtain accurate peak values.

Table 1
Crystallographic data and details of X-ray diffraction analysis for $NaCo(H_2PO_2)_3$.

NaCo(H2PO2)3	$M_r = 276.90$ (g mol^{-1})
S. G.: $P2_13$	$F_{000} = 548$
Radiation: $Mo_{K\alpha,}$ $\lambda = 0.7107$ Å,	Cell parameters:
$T = 300$ K	$a = 9.2563$ (16) Å, $\alpha = 90°$
Number of parameters: 35	$b = 9.2563$ (16) Å, $\beta = 90°$
	$c = 9.2563$ (16) Å, $\gamma = 90°$
	$V = 793.1$ (2) Å^3, $Z = 4$
$\theta = 3.11–29.45°$	$\mu = 2.802$ mm^{-1}
$T_{min} = 0.558$, $T_{max} = 1$	0.286 × 0.211 × 0.184 mm
Reciproque space:	R/wR[F2 > 3σ(F2)] =
$-11 < h < 7$, $-8<k < 12$, $-12 < l<9$	0.0367/0.0941 (593/670 reflexions)

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $NaCo(H_2PO_2)_3$.

	x	y	z	U_{iso}*/U_{eq}
Co1	0.5831 (1)	0.4169 (1)	0.9169 (1)	0.01772 (15)
P1	0.4473 (2)	0.7552 (2)	0.9030 (2)	0.0389 (4)
Na1	0.3787 (2)	0.1213 (2)	0.8787 (2)	0.0200 (4)
O1	0.5507 (4)	0.6375 (3)	0.8719 (4)	0.0334 (10)
O2	0.4435 (3)	0.8847 (3)	0.8102 (3)	0.0273 (9)
H2	0.4595	0.7932	1.0343	0.04670*
H3	0.3208	0.7032	0.9142	0.04670*

4. Discussion

Both Na and Co atoms lie on a three-fold axis (Wyckoff position 4a) and they are octahedrally coordinated, while P is in a general position (Fig. 2). Fig. 3 shows the projection of the structure of the title compound on the ac plane. The structure forms a 3D network built upon [NaO_6] and [CoO_6] octahedrons and [H_2PO_2] tetrahedrons which share corners and edges. More detailed look shows that [CoO_6] shares respectively the edge O1–O2 and O2–O2′ with neighbouring [NaO_6] octahedrons giving rise to a zig-zag channels running along [100]. Two such channels share the edge O1–O2 to extend in the b direction. Finally, a 3D framework is formed with large channels along [1,–1, –1] and with [H_2PO_2] tetrahedrons bind inside the channels. Other view shows that one loop of this network can be formulated as [$Co_5H_{60}Na_5O_{60}P_{30}$] (Fig. 4).

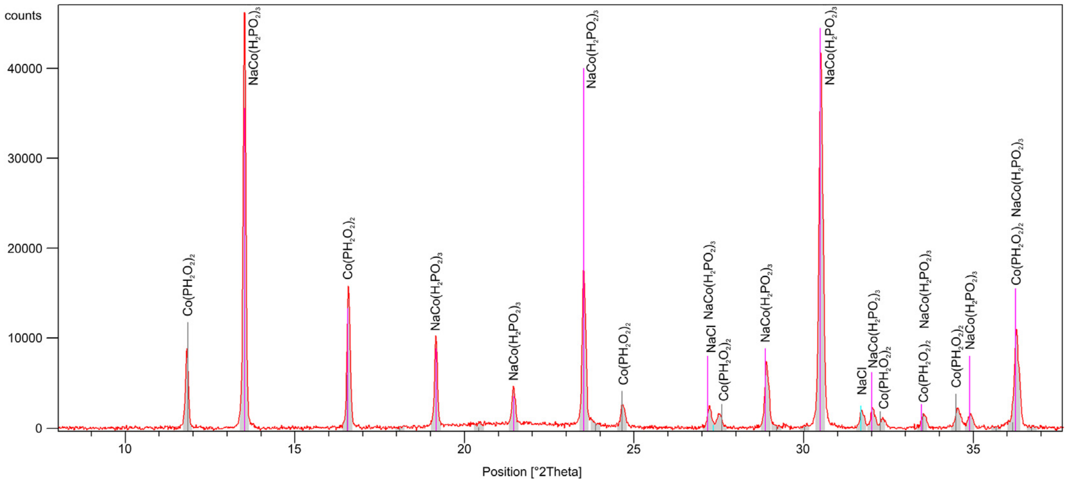

Fig. 1. The measured powder pattern (background subtracted) shows that sample is a mixture of two major $NaCo(H_2PO_2)_3$ and $Co(PH_2O_2)_2$ phases and minor NaCl phase.