



Synthesis, crystal structure, characterization and electrochemical properties of a new cyclohexaphosphate: $\text{Li}_2\text{Na}_2\text{CoP}_6\text{O}_{18} \cdot 12\text{H}_2\text{O}$



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ARTICLE INFO

Article history:

Received 18 April 2016

Received in revised form

18 June 2016

Accepted 20 July 2016

Available online 26 July 2016

Keywords:

Polyphosphate

Crystal structure

Li-ion battery

Electrical properties

ABSTRACT

A new cyclohexaphosphate with the $\text{Li}_2\text{Na}_2\text{CoP}_6\text{O}_{18} \cdot 12\text{H}_2\text{O}$ (LNCP) composition was prepared via a simple process at room temperature. This compound was characterized using X-ray diffraction (XRD), Infrared and UV–visible spectroscopy, Thermal analysis (TG), Cyclic voltammetry and Impedance spectroscopy. The results show that the LNCP was phased with a monoclinic structure and $C2/c$ space group. The crystal structure was solved by using 3893 independent reflections with a final R value of 0.055. The P_6O_{18} ring is centrosymmetrical. Its main geometrical features are those commonly observed in the atomic arrangements of cyclohexaphosphate. The atomic arrangement of this compound can be described by an organization in a three-dimensional framework, formed by the anions $(\text{P}_6\text{O}_{18})^{6-}$ and polyhedra of lithium and sodium. This structure has channels where octahedral cobalt is housed. By means of a cyclic voltammetry study, it is shown that this substrate undergoes a multistep anodic oxidation, leading to a thin and compact electroactive deposit. The electrical conductivity was studied using two-probe impedance spectroscopy and results showed that the conductivity of LNCP at 518 K was equal to $1.74 \times 10^{-4} \text{ Scm}^{-1}$.

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1. Introduction

The synthesis and characterization of new transition metal phosphates continues to be an attractive field of research for solid state chemists because these materials have interesting applications in different areas such as catalysis, ionic conductivity, industrial coatings, biosensor manufacture and electrochemistry [1–3]. In the structures formed, metals can adopt various coordination polyhedra (octahedron, trigonal bipyramid, tetrahedron, squared pyramid, etc.) which often display with the phosphate groups variable connecting modes giving rise to versatile frameworks [4]. Research on the synthesis of lithium transition-metal phosphates further intensified with the discovery of the electrochemical properties of the olivine-type phases LiMPO_4 ($M = \text{Mn}$ [5], Fe [6], Co [7], Ni [8]). As an important class of phosphate, cyclohexaphosphates have received considerable interest in the past few decades due to their high hydrolytic and

thermal stabilities, and pronounced complexation ability [9]. It is noteworthy that the metal cyclophosphate compounds show a hierarchy of structures with different dimensionalities. These include one-dimensional (1D) chains [10], two-dimensional (2D) layers [11] and a complex three-dimensional (3D) structure [12,13]. Although the study of metal phosphates is conspicuous and some inspiring results have been recently achieved, there is very scant information on the ternary alkali metal cyclohexaphosphates in the literature. So far only one case of a mixture of two alkalines and a cyclohexaphosphate with bivalent cations has been reported [13]. In industrial phosphoric acid, the high resistance of stainless steel to corrosion has been considered as the consequence of the formation of a porous polyphosphate film [14]. In this work, we report the synthesis of a novel dilithium disodium cobalt cyclohexaphosphate dodecahydrate, $\text{Li}_2\text{Na}_2\text{CoP}_6\text{O}_{18} \cdot 12\text{H}_2\text{O}$. The physicochemical properties were studied using X-ray diffraction and FTIR spectra. Then, the electrochemical oxidation of this cyclohexaphosphate was conducted by means of a potentiodynamic technique to obtain the corresponding electrodeposit. The electrical properties of the

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abovementioned material and its comparison to other results were studied.

2. Experimental section

2.1. Synthesis

0.808 g (10^{-3} mol) of $\text{Li}_6\text{P}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$, which has been prepared according to the Schülke and Kayser procedure [15], was mixed in 50 mL of distilled water to 0.237 g (10^{-3} mol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.170 g (2×10^{-3} mol) of NaNO_3 under mechanical stirring for 30 min, at room temperature. After this step, the obtained solution was allowed to stand in air until the formation of good quality pinkish single crystals. A yield of 67% was calculated for $\text{Li}_2\text{Na}_2\text{CoP}_6\text{O}_{18} \cdot 12\text{H}_2\text{O}$.

2.2. Analytical methods

UV–vis diffuse reflectance was performed on a Perkin Elmer Lambda-45 spectrophotometer coupled with an integration sphere type RSA-PE-20 in the 400–800 nm range with a speed of 960 nm min^{-1} and an aperture of 4 nm. The electronic absorption spectrum was obtained for an aqueous solution of the complex ($c = 1.24 \times 10^{-4} \text{ M}$) with a Perkin-Elmer Lambda-11 UV–vis spectrometer in the 400–800 nm range, using a 10 mm quartz cell. Infrared (IR) spectra were recorded at room temperature on a Nicolet IR 200 FTIR spectrophotometer in the $4000\text{--}400 \text{ cm}^{-1}$ region.

Powder X-ray diffractions (PXRD) were collected with a BRUKER D8 ADVANCE X-ray diffractometer using graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) for 2 h in the 2θ range from 9 to 40° .

X-ray data was collected on an Enraf Nonius Mach3 diffractometer, using graphite monochromated $\text{AgK}\alpha$ radiation ($\lambda = 0.5608 \text{ \AA}$). The structure was solved by direct methods and refined with full-matrix least-squares on F^2 using SHELXS-97 and SHELXL-97 [16,17]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in a difference Fourier map but constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The crystallographic data is reported in Table 1, the selected bond lengths and angles for the phosphoric ring and for all the cation polyhedra are listed in Table S1 and Table 2, respectively.

Table 1
Crystal data and structure refinement parameters of $\text{CoLi}_2\text{Na}_2\text{P}_6\text{O}_{18} \cdot 12\text{H}_2\text{O}$.

Formula	$\text{CoH}_{24}\text{Li}_2\text{Na}_2\text{O}_{30}\text{P}_6$
Formula weight (g mol^{-1})	808.80
Crystal system	Monoclinic
Space group	$C2/c$
a (\AA)	17.789 (11)
b (\AA)	10.243 (5)
c (\AA)	14.810 (11)
β ($^\circ$)	112.175 (5)
V (\AA^3)	2499 (3)
Z	4
Calculated density (g cm^{-3})	2.150
Absorption coefficient (mm^{-1})	0.64
Crystal size (mm)	$0.40 \times 0.35 \times 0.30$
F(000)	1636
Limiting indices	$-17 \leq h \leq 17, -5 \leq k \leq 12, -18 \leq l \leq 3$
Data/restraints/parameters	2186/23/222
Goodness-of-fit on F^2	1.04
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0547, wR2 = 0.1175$
R indices (all data)	$R1 = 0.0724, wR2 = 0.1280$
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}/\text{e \AA}^{-3}$	0.67; -0.70
CCDC	1456462

Table 2

Interatomic distances (\AA) and selected bond angles ($^\circ$) in the coordination polyhedra of the cobalt, sodium and lithium atoms. Esd are given in parentheses.

Selected bond lengths (\AA) and angles ($^\circ$) in $\text{Co}(\text{H}_2\text{O})_6$ Octahedron						
Co(1)	O(W4)	O(W5)	O(W6)			
O(W4)	2.111 (3)	3.020 (9)	2.980 (5)			
O(W5)	91.74 (12)	2.095 (3)	4.169 (5)			
O(W6)	90.75 (13)	177.09 (12)	2.075 (3)			
Selected bond lengths (\AA) and angles ($^\circ$) in NaO_6 octahedron						
Na (1)	O(W1)	O(W2)	O(W3)	O (E12) ^{vii}	O (E21) ⁱ	O (E31) ^{vi}
O(W1)	2.565 (4)	3.098 (6)	3.150 (5)	4.948 (6)	3.813 (13)	3.446 (6)
O(W2)	78.26 (15)	2.337 (5)	3.128 (7)	3.676 (7)	3.417 (9)	4.681 (8)
O(W3)	75.82 (13)	79.21 (16)	2.561 (4)	3.550 (12)	4.932 (16)	3.667 (8)
O (E12) ^{vii}	166.64 (14)	101.28 (16)	90.93 (13)	2.418 (4)	3.472 (5)	3.429 (5)
O (E21) ⁱ	100.73 (13)	92.71 (16)	171.68 (14)	92.64 (13)	2.384 (4)	3.412 (5)
O (E31) ^{vi}	88.35 (13)	166.48 (16)	95.84 (13)	91.30 (13)	91.60 (14)	2.377 (4)
Selected bond lengths (\AA) and angles ($^\circ$) in LiO_4 tetrahedron						
Li (1)	O (E11) ^{iv}	O (E32) ^{vi}	O(W1)	O(W3) ^{ix}		
O (E11) ^{iv}	1.926 (9)	3.270 (6)	3.133 (11)	3.272 (5)		
O (E32) ^{vi}	115.8 (4)	1.935 (9)	3.209 (8)	3.144 (6)		
O(W1)	107.2 (4)	110.6 (4)	1.967 (9)	3.049 (5)		
O(W3) ^{ix}	114.0 (4)	107.1 (4)	101.3 (4)	1.975 (9)		

Symmetry codes: (i) $-x, y, -z+1/2$; (iv) $-x+1/2, -y+1/2, -z+1$; (vi) $x, -y+1, z+1/2$; (vii) $x, -y, z+1/2$; (ix) $-x+1/2, y+1/2, -z+3/2$.

The bold digits correspond the bond lengths from the central ion to the oxygen atoms.

The TG-DTA experiments were carried out with 18.00 mg of LNCP. The sample was placed on an open platinum crucible and heated, under Argon at a heating rate of 5 K min^{-1} , from room temperature to 823 K; an empty crucible was used as reference.

The voltammetric study was performed using a Tacussel potentiostat (PGP 201) in a three-electrode cell with compartments separated by a porous glass. The working electrode was a gold disk ($\varnothing = 2 \text{ mm}$, EDI type Radiometer) and the counter electrode was a platinum wire. AgCl/Ag was used as the reference electrode. All experiments were carried out at room temperature ($25 \pm 2 \text{ }^\circ\text{C}$).

Electrochemical impedance spectra (EIS) were obtained using a Hewlett-Packard HP 4192 analyzer. The impedance measurements were taken in an open circuit using two electrode configurations with a signal amplitude of 50 mV and a frequency band ranging from 5 Hz to 13 MHz. Both pellet surfaces were coated with silver paste electrodes while the platinum wires attached to the electrodes were used as current collectors. All these measurements were performed at equilibrium potential at a temperature ranging between 313 K and 518 K. In order to obtain the ionic conductivity, the resulting data was analyzed using the equivalent circuit of the Z-View software.

3. Results and discussion

3.1. Crystal structure

The PXRD pattern of the synthesized product is in good agreement with the calculated pattern from the single crystal data, indicating its phase purity (Fig. 1a). The difference in intensity of some diffraction peaks may be attributed to the preferred orientation of the crystalline powder samples. Fig. 1b shows its equilibrium morphology, which was obtained using the WinXmorph program [18].

The single-crystal structure determination performed here confirms that $\text{Li}_2\text{Na}_2\text{CoP}_6\text{O}_{18} \cdot 12\text{H}_2\text{O}$ is isostructural to the previously reported $\text{Li}_2\text{Na}_2\text{NiP}_6\text{O}_{18} \cdot 12\text{H}_2\text{O}$ [13]. Thus, the title compound is the second cyclohexaphosphate with a mixture of two alkalines

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