

# Low-temperature flux synthesis of a novel one-dimensional copper (II) chlorophosphate: crystal structure and magnetic property of $\text{Na}_3[\text{CuO}(\text{HPO}_4)\text{Cl}]$

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## Abstract

A novel one-dimensional copper (II) chlorophosphate,  $\text{Na}_3[\text{CuO}(\text{HPO}_4)\text{Cl}]$  has been prepared by using the low-temperature flux method. It crystallizes in the orthorhombic system, space group  $Pnma$ ,  $a = 11.096(2)$ ,  $b = 6.5703(13)$  and  $c = 8.3623(17)$  Å,  $V = 609.7(2)$  Å<sup>3</sup>,  $Z = 4$ . Its crystal structure presents a one-dimensional character in such a way that the edge-sharing  $\text{CuO}_4\text{Cl}_2$  building blocks yield a novel linear octahedral chains via Cu–O–Cu and Cu–Cl–Cu bridges. The  $\text{HPO}_4$  groups, as the modifier, are grafted onto these chains and sodium ions are located between the chains to satisfy the charge balance. The magnetic susceptibility obeys a Curie–Weiss law above 120 K with  $C = 0.38$  (emu K)/mol and  $\theta = -150$  K, showing the  $\text{Cu}^{2+}$  character and antiferromagnetic interactions.

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**Keywords:** Hydrothermal synthesis; Crystal structure; Phosphate; Magnetic property

## 1. Introduction

Transition metal phosphates in  $A-M-P-O$  quaternary systems, where  $A$  = an electropositive cation,  $M$  = a transition metal cation, are of great interest from both the industrial and academic point of view due to their applications as catalysts, ion exchangers, or molecular sieves [1]. Of particular interest is the family of copper phosphates due to the structural multiplicity attributed to the Jahn–Teller distortion ( $d^9$ ). Thus, during the past decade, a large number of  $\text{CuPO}$ s have been structurally characterized, including  $\text{Sr}_2\text{Cu}(\text{PO}_4)_2$ ,  $\text{K}_2\text{Cu}(\text{P}_2\text{O}_7)$ ,  $\beta\text{-Na}_2\text{CuP}_2\text{O}_7$ ,  $\text{Ba}_2\text{Cu}(\text{PO}_4)_2$ ,  $[\text{C}_3\text{N}_2\text{H}_5][\text{Cu}(\text{H}_2\text{PO}_4)_2\text{Cl}] \cdot \text{H}_2\text{O}$  with one-dimensional chains [2–6],  $\text{Na}_2$

$\text{CuP}_2\text{O}_7$ ,  $\beta\text{-NaCuP}_2\text{O}_4$ ,  $\alpha\text{-Na}_2\text{CuP}_2\text{O}_7$  with layered structure [4,7,8],  $\text{Rb}(\text{CuPO}_4)$ ,  $\text{BaCuPO}_4\text{Cl}$ ,  $\text{Cu}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Cu}_2(\text{P}_8\text{O}_{22})$ ,  $\text{Na}_2\text{Cs}_2\text{Cu}_3(\text{P}_2\text{O}_7)_2\text{Cl}_2$  with open framework structure [9–13]. Among them, one-dimensional copper materials have attracted more interest from chemists and physicists owing to their novel structure chemistry and rather unique physical properties. For example, due to the simplified electron localization within the copper chains, these solids are very useful for experimental and theoretical developments of magnetic models, and charge ordering in the Cu–O chains has been investigated intensively. Structurally, owing to the introduction of  $\text{PO}_4$  tetrahedra as building blocks, O–P–O bridges instead of –O– bridges between copper atoms present in most of copper phosphates with one-dimensional structure. The well-isolated chains with Cu–O–Cu linkages are rare in oxide chemistry.

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Although most copper phosphate phases have been prepared by either conventional high-temperature, solid-state precursor methods or hydrothermal techniques, new synthetic methods, e.g., changing temperature, reaction mechanism, and basicity/acidity, have been explored extensively in order to discover new compounds due to these changes in reaction conditions [10]. Very recently, our group prepared successfully a novel fluoro-borophosphate,  $\text{NH}_4\text{BPO}_4\text{F}$  with the GIS topology by using low-temperature flux method ( $\text{B}_2\text{O}_3$  as flux) [14]. In this paper, we try synthesizing new materials in copper–phosphate system by employing a new low-melting flux,  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  at low temperature, and interestingly lead to the isolation of the title compound,  $\text{Na}_3[\text{CuO}(\text{HPO}_4)\text{Cl}]$ , **1** which exhibits a novel one-dimensional structural feature with polymeric chains consisting of Cu–O/Cl–Cu units, suggesting that a similar method may be exploited in the preparation, for example, of novel magnetic materials.

## 2. Experimental

### 2.1. General

The reagents used were commercially obtained with analytical purities and used without further purification. The products were examined by powder X-ray diffraction (Rigaku D/max 2550 V diffractometer,  $\text{CuK}$ ) in order to confirm their phase identity and purity. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were carried out on an EPMA-8705QH<sub>2</sub> electron microscope equipped with a LINKS ISIS. The elemental analysis was performed on ICP-AES (Vista AX ICP-AES). IR spectra were collected on a Digilab-FTS-80 spectrophotometer from 4000 to  $400\text{ cm}^{-1}$  using pressed KBr pellets of the samples. Thermogravimetric analyses and differential scanning calorimetry (TGA and DSC) were performed using an STA-409PC/4/H LUXX DSC-TGA instrument at a heating rate of 10 K/min in a flow of nitrogen gas from room temperature to 1273 K. The magnetic susceptibility measurements were carried out with a SQUID magnetometer (Quantum-Design, MPMS XL-7) in the temperature range 2–300 K.

### 2.2. Synthesis and characterizations of $\text{Na}_3[\text{CuO}(\text{HPO}_4)\text{Cl}]$

The new compound was synthesized via low-temperature flux of  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  with low melting points of 353 K. The mixture of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.68 g),  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (4.64 g) in a molar ratio of 1:6 was placed in a Teflon-lined stainless steel autoclave and heated to 443 K for 5 days, cooled at 2 K/h–373 K, and then cooled to room temperature. The light blue rod crystals

were isolated by vacuum filtration, washed thoroughly with hot deionized water and ethanol, and dried in air. The yield: 1.005 g (90% based on  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ). Anal. Calc. for  $\text{Na}_3[\text{CuO}(\text{HPO}_4)\text{Cl}]$ : Cu, 22.69; P, 11.07; Na, 24.64. Found: Cu, 22.75%; P, 11.12%; Na, 24.38%. The presence of Cl in the title compound was confirmed by EDS analysis. IR (KBr):  $\nu/\text{cm}^{-1} = 3397, 2927, 1913, 1550, 1411, 1118, 1029, 995, 948, 825, 601, 574$ . TGA showed a mass loss of 3.1% in the range of 663–743 K with an exothermal peak corresponding to the removal of a half molar equivalent of water through condensation P–OH groups (calcd. 3.2%), and then no weight loss was observed up to 973 K. Further mass loss of 12.4% between 973 and 1223 K with a broad endothermic peak is consistent with the release of the chlorine (calcd. 12.7%).

### 2.3. Crystal structure determination

Crystals of **1** were selected under a polarizing microscope, glued to a thin glass fiber with cyanoacrylate (superglue) adhesive, and inspected for singularity. One of them were chosen, ( $0.20 \times 0.10 \times 0.10\text{ mm}$ ), and data sets was collected at 295 K on a Nonius Kappa CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source ( $\text{MoK}\alpha$  radiation,  $\lambda = 0.71073\text{ \AA}$ ) operating at 50 kV and 40 mA. The data were corrected for absorption using the SADABS program [15]. The structure was solved by direct methods and refined against  $|F^2|$  with the aid of the SHELXTL-97 package [16]. The copper, phosphor, chlorine, sodium and most of the oxygen atoms were located from the structure solution, whereas some oxygen and hydrogen atoms were found in the difference Fourier maps. The analysis of the structures was carried out with PLATON [17]. Additional information about the data collection and structure refinement is presented in Table 1, and the atomic positional and displacement parameters are given in Table 2. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; E-mail: [crysdata@fiz.karlsruhe.de](mailto:crysdata@fiz.karlsruhe.de)) on quoting the depository number CSD 391263.

## 3. Results and discussion

### 3.1. Description of the structure

The structure of  $\text{Na}_3[\text{CuO}(\text{HPO}_4)\text{Cl}]$  is built up from isolated infinite  ${}^1_{\infty}\{[\text{CuO}(\text{HPO}_4)\text{Cl}]^{3-}\}$  chains running along the *b*-axis, and sodium ions as guests occupy the interspaces among these chains (Fig. 1). The asymmetric unit of **1** contains 9 non-hydrogen atoms, of which 7

Table 1  
Crystal data and structure refinements for Na<sub>3</sub>[CuO(HPO<sub>4</sub>)Cl]

Empirical formula	ClCuHN <sub>3</sub> O <sub>5</sub> P
Formula weight	279.94
Wavelength (Å)	0.71073
Temperature (K)	293
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
<i>a</i> (Å)	11.096(2)
<i>b</i> (Å)	6.5703(13)
<i>c</i> (Å)	8.3623(17)
<i>V</i> (Å <sup>3</sup> )	609.7(2)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.852
$\mu$ (MoK $\alpha$ ) (mm <sup>-1</sup> )	4.21
$\theta$ range (deg)	3.05–27.10
Total data collected	2823
Unique data	731
<i>R</i> <sub>int</sub>	0.0563
<i>S</i>	0.956
<i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> ), <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0377, 0.0719
Final <i>R</i> indices, <i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>a</sup>	0.0634, 0.0775

$$^a w = 1/[\sigma^2(F_o)^2 + (0.0882P)^2] \text{ where } P = [F_o^2 + 2F_c^2]/3.$$

Table 2  
Selected bond distances (Å) and angles (deg) for Na<sub>3</sub>[CuO(HPO<sub>4</sub>)Cl]

Cu1–O2 <sup>a</sup>	1.969(3)	Na1–O1 <sup>i</sup>	2.567(4)
Cu1–O2	1.969(3)	Na1–O1 <sup>e</sup>	2.567(4)
Cu1–O1	1.994(3)	Na1–Cl1 <sup>a</sup>	2.739(2)
Cu1–O1 <sup>a</sup>	1.994(3)	Na1–Cl1 <sup>m</sup>	2.791(2)
Cu1–Cl1	2.875(3)	Na2–O2 <sup>j</sup>	2.320(3)
Cu1–Cl1 <sup>a</sup>	2.875(3)	Na2–O2 <sup>c</sup>	2.320(3)
P1–O4	1.517(5)	Na2–O1 <sup>e</sup>	2.951(7)
P1–O3	1.523(5)	Na2–O3	2.393(5)
P1–O2	1.556(3)	Na2–O4	2.596(5)
P1–O2 <sup>f</sup>	1.556(3)	Na2–Cl1 <sup>m</sup>	2.961(3)
Na1–O4 <sup>c</sup>	2.351(4)	Na2–Cl1 <sup>p</sup>	3.105(3)
Na1–O2 <sup>m</sup>	2.431(4)		
O2 <sup>a</sup> –Cu1–O2	180.00(16)	O1 <sup>a</sup> –Cu1–Cl1	86.25(5)
O2 <sup>a</sup> –Cu1–O1	93.15(16)	Cl1–Cu1–Cl1 <sup>a</sup>	180.0(13)
O2–Cu1–O1	86.85(16)	O3–P1–O2 <sup>f</sup>	109.79(16)
O1–Cu1–O1 <sup>a</sup>	180.0(2)	O2–P1–O2 <sup>f</sup>	108.3(3)
O2 <sup>a</sup> –Cu1–O1 <sup>a</sup>	86.85(11)	O4–P1–O2 <sup>f</sup>	109.28(17)
O2–Cu1–O1 <sup>a</sup>	93.15(6)	O4–P1–O3	110.3(3)
O1–Cu1–Cl1	93.75(5)	O4–P1–O2	109.28(17)
O2–Cu1–Cl1	88.56(13)	O3–P1–O2	109.79(16)
[CuO <sub>4</sub> Cl <sub>2</sub> ] octahedron, $\sum s[\text{Cu–O/Cl}] = 1.95$			
[PO <sub>4</sub> ] tetrahedron, $\sum s[\text{P–O}] = 4.79$			
[Na(1)O <sub>4</sub> Cl <sub>2</sub> ] octahedron, $\sum s[\text{Na(1)–O/Cl}] = 1.04$			
[Na(2)O <sub>4</sub> Cl <sub>2</sub> ] octahedron, $\sum s[\text{Na(2)–O/Cl}] = 1.04$			

(a)  $-x, -y, -z$ ; (e)  $-x, -y, -z + 1$ ; (f)  $x, -y + 1/2, z$ ; (i)  $x + 1/2, -y - 1/2, -z + 1/2$ ; (j)  $-x, y + 1/2, -z + 1$ ; (m)  $x - 1/2, y, -z + 1/2$ ; (p)  $x, y, z + 1$ .

atoms belong to the framework and 2 atoms to the guest species. There is one crystallographically independent Cu and one P atom in the structure. The copper atom shares two oxygen atoms and two chlorine atoms with neighboring octahedra ( $d_{\text{av}}[\text{Cu–O}] = 1.922 \text{ \AA}$  and

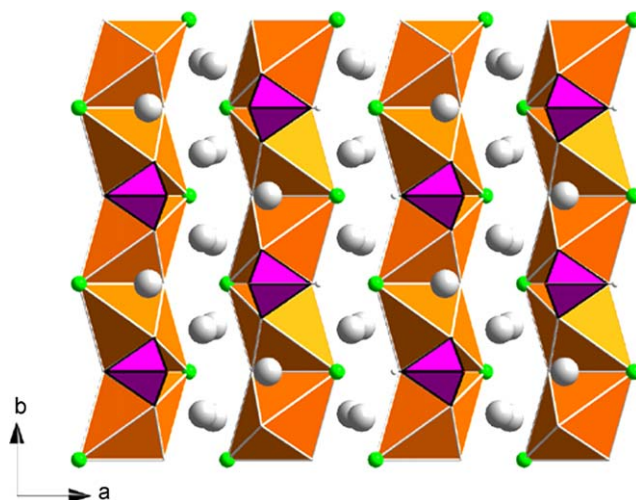


Fig. 1. View along *c* of the structure of Na<sub>3</sub>[CuO(HPO<sub>4</sub>)Cl] showing a novel linear CuO<sub>4</sub>Cl<sub>2</sub> octahedral chain decorated by PO<sub>4</sub> groups and sodium atoms occupy the open spaces in the structure (CuO<sub>4</sub>Cl<sub>2</sub>: yellow; PO<sub>4</sub>: violet; Cl atom: green sphere; Na atom: gray sphere).

$d_{\text{av}}[\text{Cu–Cl}] = 2.875 \text{ \AA}$ ), and two O-corners with two PO<sub>4</sub> tetrahedra ( $d_{\text{av}}[\text{Cu–O}] = 1.970 \text{ \AA}$ ), respectively, which results in a largely distorted octahedral geometry. Each phosphorous atom shares two of the oxygen atoms with two copper octahedra and also possesses two terminal P–O linkages. The average P–O distances and O–P–O bond angles are 1.555 Å and 109.41°, respectively, which fall in the range of the values observed in many phosphate materials [18,19]. Bond valence sum calculations clearly indicate the oxidation state of +2 for the Cu ion [20]. The complete list of bond distances along with their bond valence sum (SBV) values are given in Table 2.

The anionic framework,  ${}^1_{\infty}\{\text{CuO}(\text{HPO}_4)\text{Cl}\}^{3-}$  is built up from CuO<sub>4</sub>Cl<sub>2</sub> octahedral linear chains along the *b*-axis, decorated by PO<sub>4</sub> tetrahedra. Each chain is constructed from a central core constituted by a continuous string of edge-sharing CuO<sub>4</sub>Cl<sub>2</sub> octahedra, bridging through their oxygen and chlorine apices (see Fig 2a). This arrangement results in a linear configuration with a Cu–Cu separation of 3.285 Å. The chlorine vertices of the copper-centered octahedra are found on the opposite sides of the chains, and hence their terminal nature can be considered as one reason for the lower dimensionality of the structure, i.e., it is impossible to form links between the chains via halogen atoms. The HPO<sub>4</sub> groups, as the modifier, are grafted onto these chains in such a way that two consecutive octahedra are linked by one tetrahedron to form a three-membered ring (see Fig. 2b). The remaining two vertexes of PO<sub>4</sub> groups as one terminal and one protonated oxygen protrude away from the chains, roughly in the *c* direction. These chains arrange themselves into two pseudo-(010) sheets with the separation of

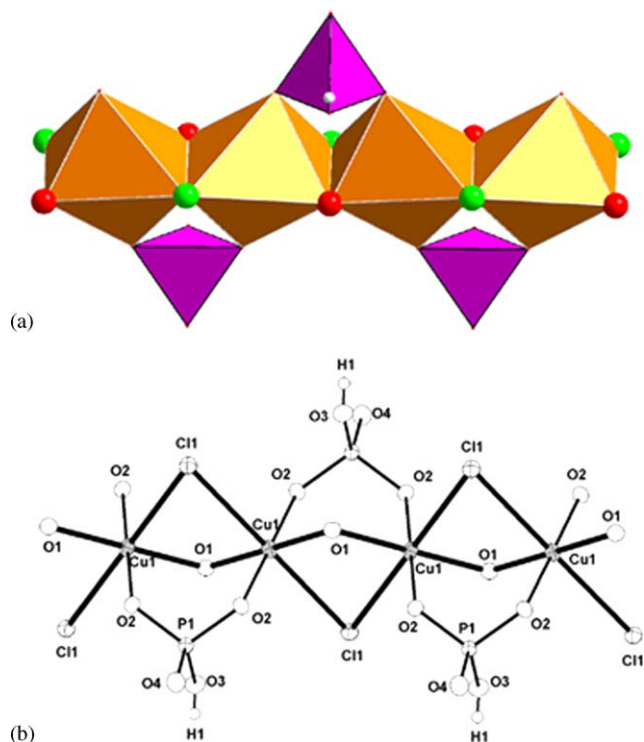


Fig. 2. (a) View of copper octahedral chain decorated by PO<sub>4</sub> tetrahedra (CuO<sub>4</sub>Cl<sub>2</sub>: yellow; PO<sub>4</sub>: violet; Cl atom: green sphere); (b) Thermal ellipsoid plot (50% probability) and atomic labelling scheme for the inorganic chains.

approximately 3.0 Å. Two such sheets configure themselves in the *ABAB* stack extending along the [010] direction. Furthermore, the chlorine ions participate in strong hydrogen bonding with the –OH group of neighboring chains to connect these chains into the whole framework (Cl...H–O = 2.68 Å) (Fig. 3).

The guest Na<sup>+</sup> ions, occupy the opening space among the chains to keep the structural stability and satisfy the charge balance. Na(1)<sup>+</sup> ions are located between these sheets, while Na(2)<sup>+</sup> ions are filled in dentate space between adjacent PO<sub>4</sub> tetrahedra in each chain. Na(1) is surrounded by four oxygen and two chlorine atoms, defining the geometry of a distorted octahedron with  $d_{\text{av}}[\text{Na–O}] = 2.48 \text{ \AA}$  and  $d_{\text{av}}[\text{Cl–O}] = 2.77 \text{ \AA}$ , while Na(2) is coordinated by five oxygen and two chlorine atoms, giving rise to a irregular geometry. The Na–O bond distances are quite diverse, ranging from 2.32 to 2.98 Å and the Na–Cl bond distances are from 2.962 to 3.102 Å.

The copper chlorophosphate chains bear close resemblance to those observed in [C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>][Cu(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>Cl]·H<sub>2</sub>O [13]. Although both of them have the similar central copper chains with the Cu–O/Cl–Cu linkage, interestingly, a additional PO<sub>4</sub> tetrahedra are found to connect with the chains by sharing one three-coordinated oxygen in [C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>][Cu(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>Cl]·H<sub>2</sub>O, which leads to a more complex chain topology.

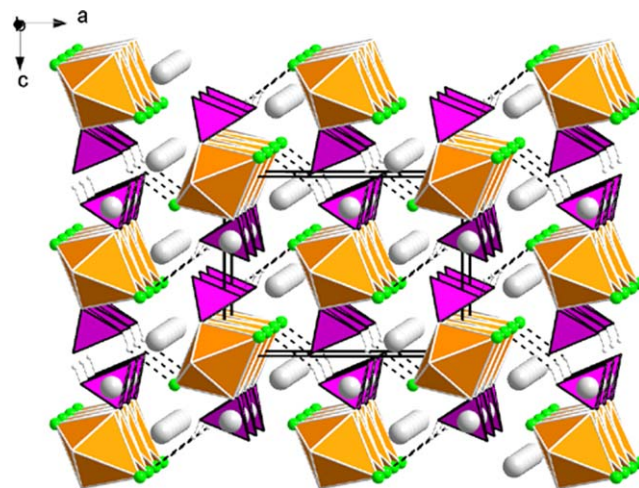


Fig. 3. Polyhedral view of the structure Na<sub>3</sub>[CuO(HPO<sub>4</sub>)Cl] along the *b*-axis, showing these chains arrange themselves into two pseudo-(010) sheets in *ABAB* all-up/all-down extend in the [010] direction. Sodium atoms occupy the intersheet spaces and the dentate spaces between adjacent PO<sub>4</sub> tetrahedra in each chain. The dotted lines represent the hydrogen bond interactions between Cl and H ions (CuO<sub>4</sub>Cl<sub>2</sub>: yellow; PO<sub>4</sub>: violet; Cl atom: green sphere; Na atom: gray sphere).

Similarly, such copper octahedral chains are also closely related to some of the chain topologies known in copper oxy salt minerals. For example, infinite chain with edge-sharing copper polyhedra with one or two-connected sulfate tetrahedra are observed in Pb<sub>5</sub>[Cu(CO<sub>3</sub>)(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>6</sub>] and Pb<sub>2</sub>[Cu(SO<sub>4</sub>)(OH)<sub>2</sub>], respectively [21,22]. In addition, the edge-sharing metal octahedral chains resembling closely to the chains in the title compound are also found in PbMBO<sub>4</sub> (*M* = Cr, Mn, Fe) [23].

### 3.2. Magnetic property

Magnetic susceptibility data of a microcrystalline sample at 2000 Oe field are plotted in Fig. 4 as both molar susceptibility ( $\chi$ ) and  $\chi^{-1}$  vs. temperature (*T*). The features of the  $\chi^{-1}$  vs. *T* curve can be divided into two temperature regions. At the high temperatures, ca. 120–300 K, a nearly perfect Curie–Weiss paramagnetic behavior is shown. The low-temperature region, ca. 2–120 K, exhibits a gradual decrease in  $\chi^{-1}$  as the temperature is lowered, which indicates a weak antiferromagnetic coupling. The high-temperature magnetic susceptibility data are fitted with the Curie–Weiss equation,  $\chi = C/(T - \Theta)$ , giving rise to  $C = 0.38$  (emu K)/mol, and  $\Theta = -150$  K. The large negative Weiss constant suggests an antiferromagnetic-like ordering, which is consistent with the downward progression of the  $\chi^{-1}$  vs. *T* curve in the low-temperature region. Consideration of the structure in relation to likely exchange pathways suggests that the strongest interaction should be across the shared edge of the



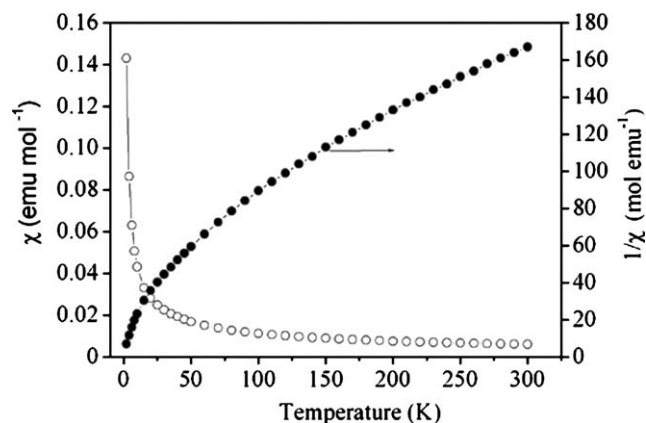


Fig. 4. Temperature dependence of the magnetic susceptibility and the inverse susceptibility for  $\text{Na}_3[\text{CuO}(\text{HPO}_4)\text{Cl}]$ .

copper octahedra, through Cu–O–Cu bridge parallel to the *b*-axis. The internuclear coupling constant  $J_{\text{Cu–Cu}}$  can be calculated on the basis of the Cu–O–Cu bridge angle,  $\varphi$ . The equation used here for the evaluation of  $J$  values is obtained from the report of the di-oxo-bridged copper(II) molecular complexes [24]. By use of the bridging angles,  $111.1^\circ$ , the  $J$  values are calculated to be  $-1010.3 \text{ cm}^{-1}$ . The relatively large negative  $J$  value suggest a significant antiferromagnetic coupling between the  $\text{Cu}^{2+}$  magnetic centers in the Cu(II)–O chain. Such an exchange pathway gives rise to the complicated magnetic properties observed in the title compound at low-temperature region.

#### 4. Conclusion

A new copper chlorophosphate,  $\text{Na}_3[\text{CuO}(\text{HPO}_4)\text{Cl}]$ , has been synthesized by a novel low-temperature flux method for the first time. The structure of the title compound contains isolated infinite  $[\text{CuO}(\text{HPO}_4)\text{Cl}]^{3-}$  chains running along the *b*-axis, which is constructed from edge-sharing  $\text{CuO}_4\text{Cl}_2$  octahedra, bridging through their oxygen and chlorine apices, and the  $\text{HPO}_4$  groups lying on the opposite sides of these chains. The sodium ions as guests occupy the interspaces among these chains to satisfy the charge balance. The magnetic measurement of the title compounds indicates the existence of antiferromagnetic interactions, which are propagated along Cu–O–Cu single chains. The successful synthesis not only completes the family of copper–phosphate system, but also provides important information for further developing novel inorganic materials by using the low-temperature method.

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