

A Novel Copper Oxalate, $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$

Wenjiao Yao,^[a] A. Robert Armstrong,^[a] and Philip Lightfoot*^[a]

Dedicated to Professor A. K. Cheetham, on the occasion of his 70th birthday

Abstract: A novel copper oxalate $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ was synthesised through a hydrothermal method and characterized by single-crystal X-ray diffraction. It crystallizes in monoclinic system, $P2_1/n$ space group with $a = 72578(3)$ Å, $b = 5.7711(4)$ Å, $c = 8.6604(8)$ Å, $\beta = 106.948(9)^\circ$. The structure displays a novel stacking pattern of $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units connected through electrostatic attraction via Na^+ cations. Structural comparisons are made to related compounds.

Introduction

Coordination polymers based on carboxylate ligands have the potential of combining the interesting physical properties arising from metal atoms/ions (such as magnetism, luminescence, and electrochemistry) and the structural-chemical diversity derived from the relatively flexible coordination of the molecular ligands. Tony Cheetham has been one of the leaders in this field.^[1] The molecular ligands also enable great synthetic flexibility to realize structure design. In particular, the simplest dicarboxylate ligand (oxalate) is found to be very versatile in its coordination modes to metal ions, acting as mono-dentate, bidentate, tridentate or tetradentate, resulting in structures formed of chains, layers, or three dimensional networks.^[2] In terms of synthesis method, oxalic acid is found to act as both reductant and template. It is a common and relatively mild reducing agent, which can reduce metal ions to variable states depending on the synthesis environment.^[3] Moreover, the oxalate bridge has great ability to transmit electronic effects between metal centers.^[3] For the last decades, lots of work has been done in transition metal-oxalate systems. The initial research focused on structural diversity of metal-oxalate compounds, as reported in, for example, $\text{M}_2[\text{Mo}_2\text{O}_5(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$, $\text{M}_2[\text{MoO}_3(\text{C}_2\text{O}_4)]$ ($\text{M}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$), $\text{Na}_2\text{U}_2\text{M}(\text{C}_2\text{O}_4)_6(\text{H}_2\text{O})_4$ ($\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{and Zn}^{2+}$) and $\text{K}_3\text{VO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_3$.^[4-6] Later, the magnetic properties of hydrothermally-prepared $\text{Na}_2\text{M}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}$) and $\text{K}_2\text{M}(\text{C}_2\text{O}_4)_2$ ($\text{M}=\text{Fe}, \text{Co}$) were studied.^[7-11] More recently, Hussain et al reported the photoemission of $\text{K}_2\text{Ni}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot 8\text{H}_2\text{O}$, obtained via a slow evaporation method.^[12-13] In all of these compounds, the transition metals (V, Fe, Co, Ni, Mo) are coordinated to six oxygen atoms of oxalate moieties and/or water molecules, forming distorted octahedra. The oxalate groups in these compounds also act as bridges to connect $[\text{MO}_6]$ octahedra together, forming 1D, 2D, or 3D frameworks. In a few

cases, the framework is zero-dimensional, the adjacent groups stabilized through electrostatic attraction with alkali metals.^[7] For example in copper oxalates the most common configuration is a rectangular $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ unit. An ideal $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ unit has D_{2h} symmetry, while in a crystal field it is usually slightly distorted. Furthermore, inclusion of different cations or the incorporation of water of crystallization may lead to different stacking patterns. A typical example is $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ ($x = 0, 2, 4$).^[14-16] As x changes from zero to two to four, the structure evolves from $P2_1/n$ (monoclinic) to $P-1$ (trigonal) to $P2_1/n$ (monoclinic). The anhydrous phase was obtained by heating the corresponding hydrated phases (either tetra-hydrate or di-hydrate) at elevated temperature.^[14] In the sodium-copper-oxalate system, only one phase has been reported so far, viz. $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$.^[16-19] As part of a current interest in the exploration of novel transition metal-oxalate compounds in our group, here we report the synthesis and novel crystal structure of anhydrous sodium copper oxalate, namely $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$. The compound was obtained together with the known phase $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ through hydrothermal synthesis, but displayed a very different crystallization habit. Structural characterization reveals that it displays a novel stacking pattern of $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ groups compared to all the known alkali copper oxalates.

Results and Discussion

A mixture of copper (II) fluoride, oxalic acid and sodium carbonate was initially preheated at 393 K for overnight and then transferred into a Teflon-lined autoclave with distilled water as solvent for hydrothermal synthesis (see Experimental section). Reaction for three days at 433 K gave rise to a large amount of bright blue strip crystals together with a small amount of grey blue block crystals. The blocks are easily ignored with the naked eye but they are quite clear under an optical microscope (40 \times) and scanning electron microscope (SEM). As shown by the SEM image in Figure 1, the strips are typically in the size range $5 \times 0.5 \times 0.5$ mm³, with the blocks being $0.1 \times 0.1 \times 0.1$ mm³. The integrated EDX spectrum indicates F didn't incorporate into either crystals. Both crystals were then chosen to collect single crystal X-ray diffraction (SXRD) data to determine the crystal structure. The results show that the strips are the known sodium bis(oxalate) cuprate $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ^[16], while the blocks were determined to be a new compound, formulated $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$.

Table 1 lists the final atomic parameters. The details of the structure refinement are specified in the experimental section. $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ crystallizes in the monoclinic system, $P2_1/n$ space group. In the asymmetric unit cell, there is one, one, two and four sites for Na, Cu, C and O atoms, respectively. The Cu^{2+} lies on an inversion centre, rectangularly-coordinated by two bidentate

[a] Prof. Dr. P. Lightfoot
School of Chemistry
University of St Andrews
St Andrews, UK
Phone: +44 (0)1334 463841
E-mail: pl@st-andrews.ac.uk

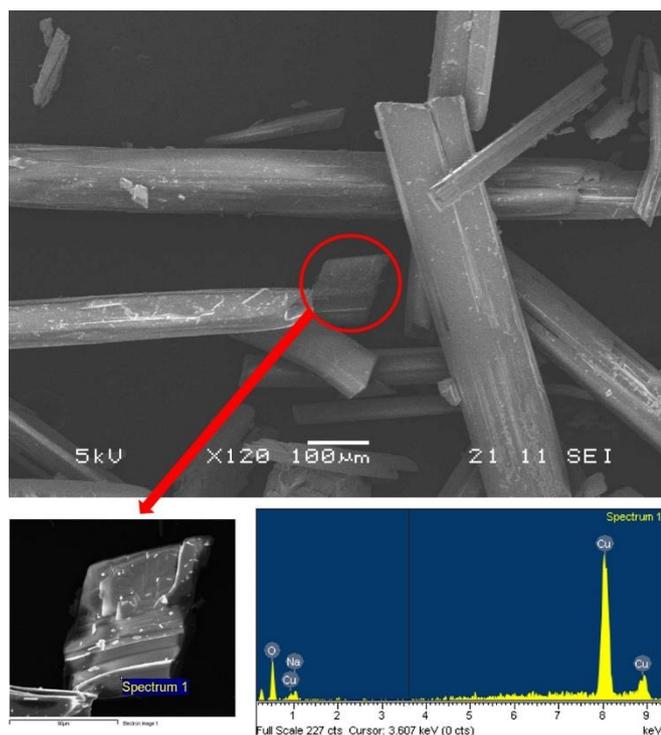


Figure 1. SEM images of the crystalline mixture obtained from hydrothermal reaction.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters in $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$

Atom	Wyck.	x/a	y/b	z/c	U_{eq} (\AA^2)
Cu1	2d	1.0000	1/2	1/2	0.0107(2)
Na1	4e	0.26357(13)	1.00141(8)	0.35664(11)	0.0158(3)
O1	4e	0.46058(13)	0.69208(17)	0.36247(11)	0.0119(3)
O2	4e	0.77498(14)	0.68746(18)	0.48961(11)	0.0121(3)
O3	4e	0.49635(14)	0.24530(17)	0.25797(11)	0.0131(3)
O4	4e	0.81136(14)	0.26717(16)	0.38761(11)	0.0130(3)
C1	4e	0.6201(2)	0.5999(2)	0.39855(17)	0.0092(3)
C2	4e	0.6407(2)	0.3491(3)	0.33917(17)	0.0088(3)

oxalate anions with Cu-O bond lengths of 1.939(1) Å to 1.962(3) Å. The intra-oxalate O-Cu-O bond angle is 84.411(2)°. The C-C and C-O bond lengths are in the normal range: 1.558 Å and 1.229 - 1.277 Å, respectively. All the atoms in one $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ unit are nearly coplanar, the dihedral angle of the $[\text{CuO}_4]$ plane and $[\text{C}_2\text{O}_4]$ plane being 9.781(5)°. The $[\text{Cu}(\text{C}_2\text{O}_4)_2]$ planes are coincident with the (0 1 1) direction. The apical, intermolecular Cu-O distance between adjacent $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units (Figure 2a) is 2.652 Å. This is longer than the 2.5 Å of the elongated Cu-O octahedron in the previously reported copper compounds.^[15] Therefore, during the synthesis, the $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ unit may be considered as a building

block in this compound. However, this Cu-O length is much shorter than in $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ (2.8034 Å). We suppose that the shorter intermolecular Cu-O length contributes to stronger binding between different building blocks. Therefore, after the initial crystal nucleation in the hydrothermal condition, it is easier for building blocks to stack in three directions and finally construct into block-shaped crystals. This may explain the different morphology of $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ and $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$. Regarding Na-O coordination, each Na atom is surrounded by five O atoms from four $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units, as displayed in Figure 2b, with the bond lengths ranging from 2.279 Å to 2.531 Å and bond angles from 71.29° to 141.27°. The adjacent $[\text{NaO}_5]$ polyhedra share edges with two others and form zigzag chains along the *b* axis, as indicated in Figure 2c. The $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units connect the chains together. Bond Valence Sum (BVS) calculation reveals the valence for Cu and Na is +2.118 and +1.016, respectively. These values agree well with other similar compounds.^[14-19]

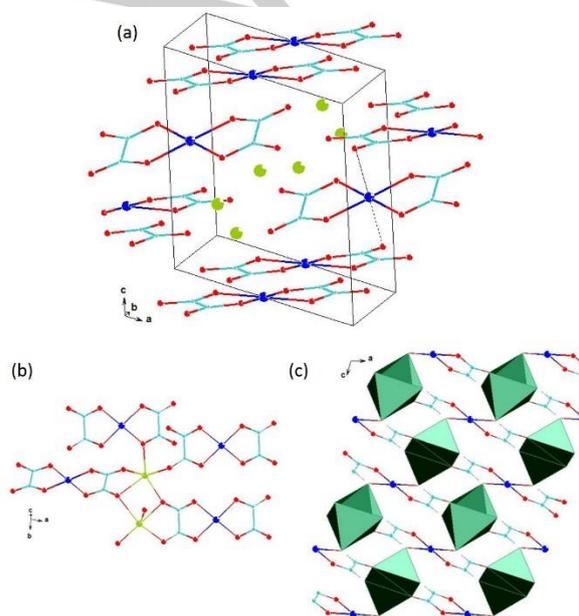


Figure 2. Crystal structure of $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$. (a) Unit cell (b) Coordination of the $[\text{NaO}_5]$ polyhedron (c) $[\text{NaO}_5]$ zigzag chains connected by $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units. Blue: Cu. Lemon: Na. Red: O. Aqua: C. Green polyhedra: NaO_5 . Dashed line in (a) indicates the weak binding of Cu-O.

It is worth to point out that the stacking pattern of $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units in this compound is quite different from the known copper oxalates. Figure 3 displays the typical representatives reported so far, namely the title compound $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$, $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ and $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$. The $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units in $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ arrange in the same way as in $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, and those in $\text{Cu}(\text{HC}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ ^[20] and $\text{Rb}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ^[21] the same as in $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, thus not displayed in Figure 3. $\text{Cs}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ^[22] no longer retains $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ building units due to extraordinarily large Cs^+ cation, thus also not taken into consideration. It is clearly seen that in $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$, the dihedral angle for different $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$

planes is obviously larger than in the other compounds. In detail, for the compounds a-d in Figure 3, the dihedral angle is $43.483(6)^\circ$, 0° , $14.801(9)^\circ$, and $10.498(6)^\circ$, respectively. The first case is almost three times that of even the maximum of the rest. This abnormal dihedral angle may be attributed to both the different size of the cations and different degrees of hydration. As a general rule, the smaller the cation and the smaller the water content, the bigger the dihedral angle. This can be interpreted that if the cation and water molecules are taken as "separators", smaller cations and less water-containing compounds provide less space among the $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units, therefore the $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units tend to stagger in a more anisotropic way to decrease the mutual repulsive force originating from their overlapped conjugated orbitals.

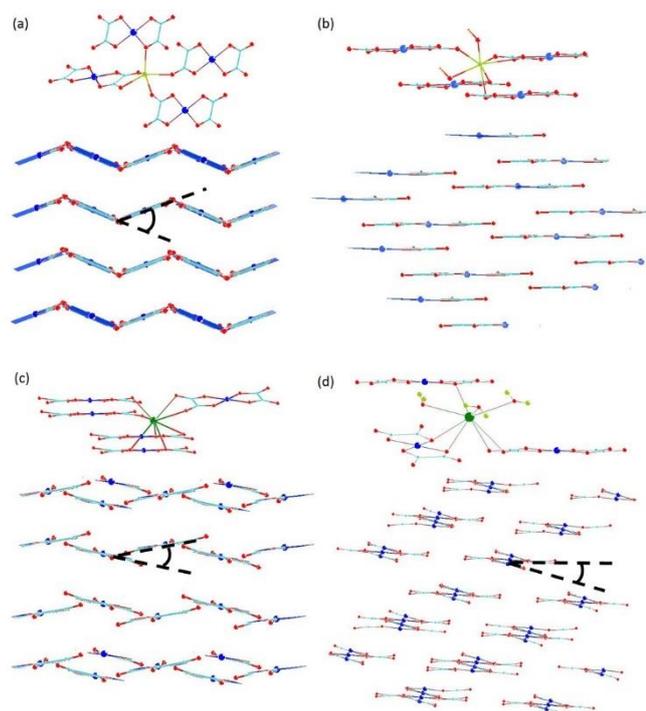


Figure 3. Structural comparison of $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ stacking patterns in copper oxalates. (a) $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ (b) $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ (c) $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ (d) $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$. Blue: Cu. Lemon: Na. Green: K. Red: O. Aqua: C.

As reported in the synthesis of $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2$,^[15] we also tried to obtain the pure $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ sample from heating its hydrated phase. According to the thermogravimetric (TG) analysis of wheatleyite,^[18] the dehydration of $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ under flowing nitrogen atmosphere occurs between 78°C and 111°C . The next phase transition starts from 255°C . Therefore, the mixed samples obtained from hydrothermal synthesis were placed in an oven filled with nitrogen and underwent heat treatment until the PXRD didn't change significantly. The final sample showed no obvious change regarding colour or shape of crystallites. The IR spectrum of the sample showed no absorption in the frequency range $3700\text{--}3100\text{ cm}^{-1}$, indicating all the water molecules had been successfully removed (Figure 4). The powder X-ray

diffraction (PXRD) of the slowly-cooled and quenched remains showed no noticeable difference. They both showed much lower peak intensity of the hydrated phase, similar intensity of $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$, and several new peaks which cannot be indexed. This indicated most of $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ transformed to another phase while the $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ remained intact. Attempts to collect SXRD on the unknown phase failed.

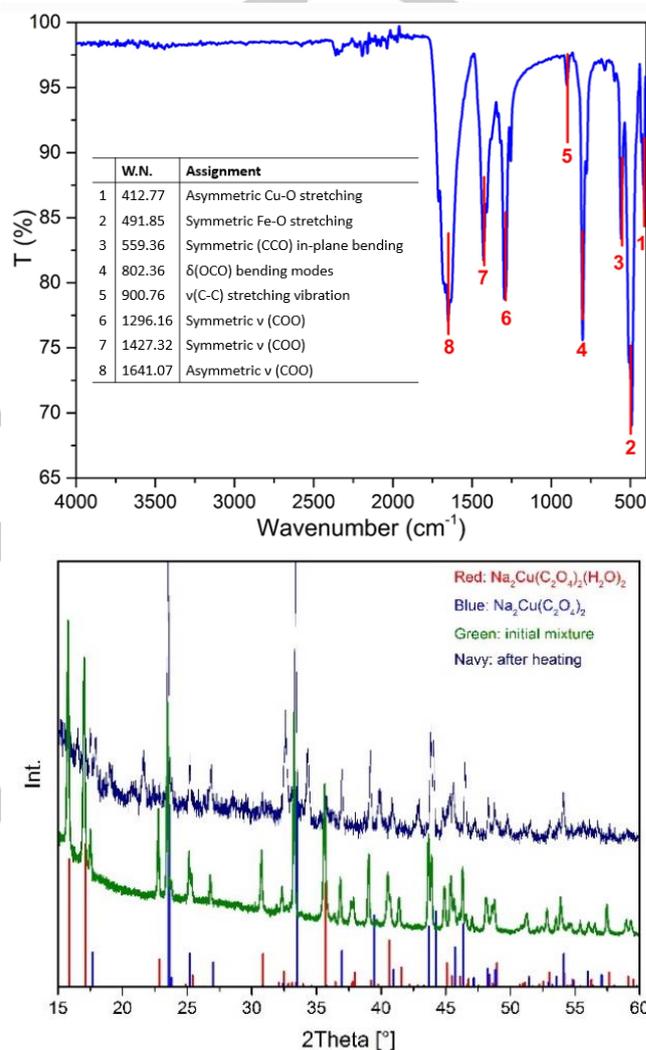


Figure 4. Top: IR spectrum of dehydrated sample. Bottom: PXRD of mixed samples before and after dehydration.

Conclusions

In summary, we have demonstrated the hydrothermal synthesis of a new sodium copper oxalate $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$. Its crystal structure is well determined by SXRD and PXRD. This compound displays a novel 'buckled' stacking pattern of $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units compared to other known alkali copper oxalates. Specifically, the $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units in the title compound form a markedly large dihedral angle, three times or even more than the others. The

compound cannot be obtained by dehydration of its di-hydrated phase. Further studies will focus on slow evaporation and synthesis in variable conditions, such as temperature, pH, and mineralizer, in order to prepare phase-pure $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ and also to check for further sodium copper oxalate phases.

Experimental Section

Synthesis. Single crystals of the title compound are synthesised by a pre-heating and hydrothermal method. Typically, CuF_2 (5 mmol), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (15 mmol), Na_2CO_3 (10 mmol) as commercially obtained were mildly ground in a mortar and transferred to a Teflon-lined autoclave. The sealed sample was heated to 393 K, held overnight, and cooled to room temperature by switching off the oven. The autoclave was then opened and distilled H_2O (1 mL) was added as solvent. The autoclave was then put heated at 433 K overnight and then cooled down in air. The corresponding product was washed with distilled water and acetone dried at 333 K.

Heat treatment. Mixed crystals obtained from hydrothermal synthesis were placed in an oven filled with nitrogen and slowly heated to 403 K and held for at least overnight before the first cooling-down by switching off the oven. A small amount of sample was taken each time to check the phase evolution by PXRD. The heat treatment and PXRD cycle was repeated until no obvious change appeared between the last two PXRD patterns.

Single crystal X-ray diffraction (SXRD). Bright blue strips and grey blue blocks were chosen to be mounted on nylon loops in inert oil and SXRD data were collected with a Rigaku SCX Mini diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173 K. Rigaku CrystalClear 2.0 was employed to index and process the data. The structures were solved by direct methods and refined using SHELX-2014^[23] incorporated into the WinGX program. Absorption corrections was performed semi-empirically from equivalent reflections on basis of multi-scans. All atoms were refined anisotropically. The bright blue strips were solved as triclinic, P-1, with cell parameters, 7.536(5) \AA , 9.472(6) \AA , 3.575(3) \AA , 81.91(6) $^\circ$, 103.74(2) $^\circ$, 108.10(7) $^\circ$, which agrees well with $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ in ICSD (No. 40090). The grey-blue blocks, $0.20 \times 0.14 \times 0.14 \text{ mm}^3$, belong to the monoclinic system, $P2_1/n$, with $a = 7.2578(3) \text{ \AA}$, $b = 5.7711(4) \text{ \AA}$, $c = 8.6604(8) \text{ \AA}$, $\beta = 106.948(9)^\circ$, $V = 346.99(5) \text{ \AA}^3$, $Z = 2$, $F(000) = 278$, $d_{\text{calc}} = 2.733 \text{ g/cm}^3$. No. of reflections 2776, No. of refined parameters 70, in the range of 2.5–27.5 $^\circ$. Crystallographic data (including structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1481337. (Fax: +44-1223-336-033; deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Powder X-ray diffraction (PXRD). Hand-ground samples were adhered between two poly-films using high vacuum grease. PXRD patterns were recorded on a Stoe STADI/P diffractometer operating in transmission mode with Fe K α_1 radiation ($\lambda = 1.936 \text{ \AA}$) in the 2θ range 15 $^\circ$ –60 $^\circ$. Step scan mode, step size 0.02 $^\circ$, steps time 60 s.

SEM image. Secondary electron image of the synthesized sample was taken on JSM-5600 with a tungsten filament electron source using accelerating voltage 5 kV. The EDX spectrum was collected with an Oxford Inca EDX system using accelerating voltage 20 kV.

IR spectroscopy. IR spectroscopy was carried out with the objective of specifying and comparing the coordination of atoms in the dehydrated to confirm the water molecules were totally removed. The mid-infrared spectrum was obtained at room temperature via a Perkin Elmer Spectrum GX IR spectrometer. The spectroscopy was collected in a range from 400 to 4000 cm^{-1} with resolution of 1 cm^{-1} .

Acknowledgements

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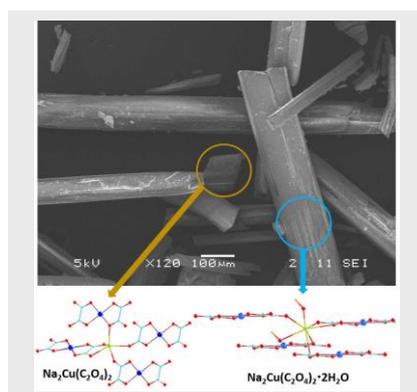
Keywords: Copper oxalate • Hydrothermal synthesis • Single crystal structure • Powder X-ray diffraction •

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Entry for the Table of Contents

FULL PAPER

A novel anhydrous copper oxalate $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ was synthesized via the hydrothermal method. The compound is found to be co-crystallised with its hydrous phase. The structure determined from single-crystal X-ray diffraction shows it contains unusual stacking pattern of $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units. Further studies indicated it cannot be obtained from dehydration of $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$.



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