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# Dicopper(II) trihydroxide cyanoureate dihydrate

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The title compound, poly[[$\mu$-cyanoureato-tri-$\mu$-hydroxido-dicopper(II)] dihydrate], $\{[Cu_2(C_2H_2N_3O)(OH)_3]\cdot 2H_2O\}_n$, is a new layered copper(II) hydroxide salt (LHS) with cyanoureate ions and water molecules in the interlayer space. The three distinct copper(II) ions have distorted octahedral geometry: one Cu (symmetry $\overline{1}$) is coordinated to six hydroxide groups (4OH + 2OH), whilst the other two Cu atoms (symmetries $\overline{1}$ and 1) are coordinated to four hydroxides and two N atoms from nitrile groups of the cyanoureate ions (4OH + 2N). The structure is held together by hydrogen-bonding interactions between the terminal $-NH_2$ groups and the central cyanamide N atoms of organic anions associated with neighbouring layers.

## Comment

In addition to the much studied layered double hydroxides (LDH), such as hydrotalcite, $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$, and related transition-metal substituted phases (Rives, 2001; Evans & Slade, 2006), a second class of materials with structures derived from brucite, $Mg(OH)_2$, namely the layered metal hydroxide salts (LHS), are gaining in scientific and technological importance (Arizaga *et al.*, 2007). This results from their potential uses as anion exchangers, catalysts and two-dimensional magnetic materials (Laget *et al.*, 1998, 1999; Yamanaka *et al.*, 1992). The LHS have the general formula $M^{2+}(OH)_{2-x}(A^{m-})_{x/m}\cdot nH_2O$, where $M$ is a divalent metal and $A$ is a counter-anion; examples include $M_2(OH)_3(A)$ ($M$ = Co, Ni, Cu; $A$ = $Cl^-$, $NO_3^-$, $CH_3COO^-$), $Cd(OH)NO_3\cdot H_2O$ and $Zn_5(OH)_8(NO_3)_2\cdot 2H_2O$ (Arizaga *et al.*, 2007). Most pertinent to this work are the copper hydroxide salts, $Cu_2(OH)_3(A)$, where $A$ can be a simple anion, as above, or a long-chain organic anion, such as an alkylsulfonate ($n$-$C_mH_{2m+1}OSO_2^-$; Park & Lee, 2005) or alkylcarboxylate ($n$-$C_mH_{2m+1}COO^-$; Fujita & Awaga, 1996, 1997). Adjusting the alkyl chain length in the organic anions enables the magnetic behaviour of the layered materials to be tuned by changing the relative importance of the intra- and interlayer interactions.

Full structural studies of $Cu_2(OH)_3(A)$ using single-crystal and powder X-ray diffraction have been reported in a number of cases [$A$ = $NO_2^-$ (Schmidt *et al.*, 1993), $NO_3^-$ (Effenberger, 1983; Guillou *et al.*, 1994), $Cl^-$ (Hawthorne, 1985), $Br^-$ (Oswald *et al.*, 1961) and $CH_3COO^-$ (Masciocchi *et al.*, 1997)]. These results, together with EXAFS studies of compounds with $A$ = $CH_3COO^-$ and $Br^-$ (Jiménez-López *et al.*, 1993), provide evidence for the coordination of $A$ to Cu atoms in the copper hydroxide layers. All reported structures exhibit a $Cu_2(OH)_3Cl$ botallackite-type structure, in which the Cu atoms lie in 4+2 (O + $A$) and 4+1+1 (O + O + $A$) environments.

In this work, we report the structure of a new inorganic–organic hybrid material $Cu_2(OH)_3[H_2NC(=O)NCN]\cdot 2H_2O$, in which cyanoureate ions and water molecules reside between the copper(II) hydroxide layers. The cyanoureate ions coordinate to Cu *via* the nitrile N atoms. Within the layers, there are three crystallographically distinct Cu atoms, two of which, Cu2 and Cu3, reside on inversion centres at special positions 2*a* and 2*c*, respectively, while the third, Cu1, lies on general position 4*e* (Fig. 1). Each Cu atom has an elongated octahedral coordination, with four shorter Cu—O bonds (~2 Å) and two longer bonds (>2.3 Å), in accordance with the Jahn–Teller distortion of Cu in a +2 oxidation state (Table 1). In the cases of atoms Cu1 and Cu2, the longer bonds are to atom N3, and for Cu3, to atom O3. Each O atom within the layer (O1, O2 and O3) is coordinated to three Cu atoms and a H atom. All the H atoms in the structure were located in difference Fourier maps. The copper hydroxide layers lie parallel to the *bc* plane and stack along the *a* axis in an ...*AA*... fashion. The $Cu^{II}$ ions within the layers form a triangular array (Fig. 2), with the shortest Cu···Cu distances in the range 3.010 (3)–3.164 (3) Å, comparable with those found in other $Cu_2(OH)_3A$ compounds

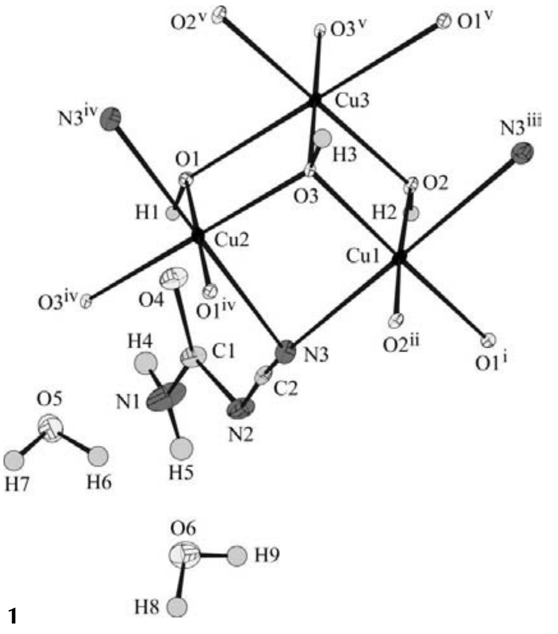

**Figure 1**
The local coordination in the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes are as in Table 1.

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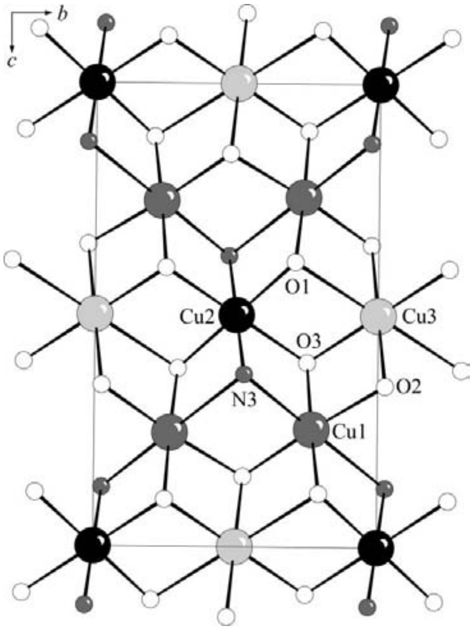

**Figure 2**
A view along the *a* axis of the inorganic layer, showing the triangular array of Cu1, Cu2 and Cu3 atoms within the $Cu_2O_3$ layers. Key: small white spheres are O atoms and small grey spheres are N3 atoms. The remaining atoms of the cyanoureate ions, together with the hydroxide H atoms, have been omitted.

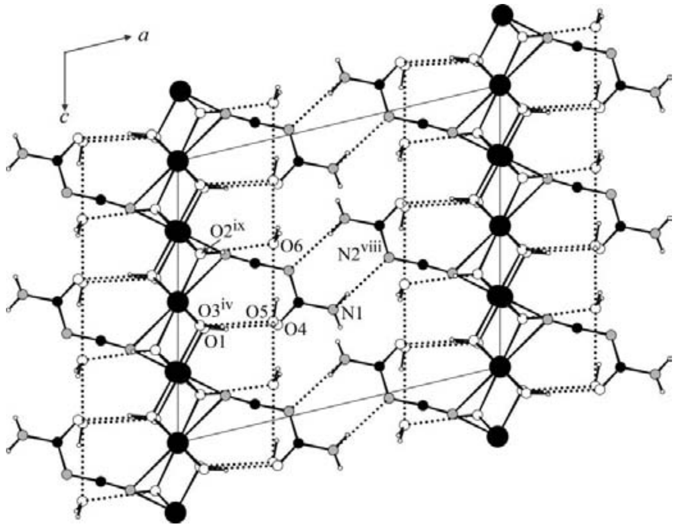

**Figure 3**
A view along the *b* axis, showing the ...*AA*... stacking of the copper hydroxide layers. Hydrogen-bonding interactions between the O1H, O2H and O3H hydroxide groups, the $H_2O5$ and $H_2O6$ water molecules, and the O4═C1 group, together with those involving the $N1H_2$ and N2 groups of adjacent cyanoureate ions, are shown as dotted lines. Key: large black spheres are Cu atoms, small white spheres are O atoms, small dark-grey spheres are N atoms, small black spheres are C atoms and very small white spheres are H atoms. The symmetry codes are as in Table 2.

known to exhibit intralayer magnetic interactions (Jiménez-López *et al.*, 1993).

The interlayer space contains cyanoureate ions, formed by the hydrolysis of dicyanamide anions, *viz.* $[N(CN)_2]^-$, under basic conditions, together with water molecules. The bond lengths and angles within the cyanourea moiety are in good agreement with those observed for the anions in $Ag^+[H_2NC({=}O)NCN]^-$ (Britton, 1987) and $NH_4^+[H_2N\text{-}C({=}O)NCN]^-$ (Lotsch & Schnick, 2004). The cyanoureate ion is almost planar, with a *cis* arrangement of the N3/C2/N2 and O4 groups. This conformation enables atom O4 of the C1═O4 carbonyl group to form a hydrogen bond with the O1—H1 hydroxide group of the layer, as well as with the interlayer water molecules $H_2O5$ and $H_2O6$ (Table 2 and Fig. 3). The other hydroxide groups, O2H2 and O3H3, also form hydrogen bonds with water molecules $H_2O6$ and $H_2O5$, respectively, which in turn interact with each other. Hydrogen-bonding interactions between the amide $N1H_2$ group and the central N2 atom of cyanoureate anions associated with adjacent layers serve to hold the layers together.

To the best of our knowledge, $Cu_2(OH)_3[H_2NC({=}O)NCN]\cdot 2H_2O$ is the first example of a layered solid in which the cyanoureate ion acts a ligand coordinating to a metal centre. Compounds are known in which the cyanoureate ion links metal atoms into dimers, *e.g.* in $[Cu_2\{NCNC({=}O)NH_2\}(R3Bm)](ClO_4)_3\cdot 4H_2O$ (where R3Bm is an *m*-xylyl-linked cryptand; Escuer *et al.*, 2004), and chains, *e.g.* in $Ag^+[H_2NC({=}O)NCN]^-$ (Britton, 1987). Interestingly, coordination to the Cu atoms occurs through atom N3 of the nitrile group rather than through atom N2, which formally carries the negative charge of the ion. In this respect, the behaviour of the ligand resembles that of the dicyanamide ion (Batten & Murray, 2003), particularly as observed in the two polymorphs of silver dicyanamide (Britton & Chow, 1977; Britton, 1990).

## Experimental

Single crystals of the title compound, in the form of blue–green blocks, were obtained from the hydrolysis of $[N(CN)_2]^-$ ions under alkaline conditions. Copper(I) dicyanamide (0.10 g) (Wang *et al.*, 1990) was dissolved in an aqueous ammonia solution (35%, 15 ml) containing 10 drops of hydrazine. This formed a deep-blue solution which, over the course of 10 min, turned through green to orange. After a few days, the solution had returned to the deep-blue colour and after 10 months a small number of crystals suitable for single-crystal X-ray diffraction had grown. Intense bands were observed in the IR spectrum recorded in Spectrosol over the range 4000–1300 $cm^{-1}$: 3467, 3354, 3312, 3220 ($\nu$ N—H, O—H); 2174, 2137 ($\nu$ C≡N); 1657, 1650 ($\nu$ C—O); 1535, 1529 ($\delta$ $NH_2$); 1412 ($\nu$ C—N).

*Crystal data*

$[Cu_2(C_2H_2N_3O)(OH)_3]\cdot 2H_2O$
$M_r = 298.22$
Monoclinic, $P2_1/c$
$a = 12.4648$ (5) Å
$b = 6.3096$ (2) Å
$c = 10.6032$ (5) Å
$\beta = 103.269$ (4)°
$V = 811.66$ (6) $Å^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 5.25$ $mm^{-1}$
$T = 150$ K
0.20 × 0.08 × 0.06 mm

*Data collection*

Oxford Diffraction Xcalibur area-detector diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.67$, $T_{max} = 0.73$
6870 measured reflections
2688 independent reflections
1731 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—O1$^{i}$ | 1.9145 (17) | Cu3—O1 | 2.3238 (15) |
| Cu1—O2 | 1.9736 (16) | Cu3—O2 | 2.0061 (18) |
| Cu1—O2$^{ii}$ | 1.9877 (16) | Cu3—O3 | 1.9923 (15) |
| Cu1—O3 | 1.9733 (17) | O4—C1 | 1.256 (3) |
| Cu1—N3 | 2.426 (2) | N1—C1 | 1.340 (3) |
| Cu1—N3$^{iii}$ | 2.658 (2) | N2—C1 | 1.359 (3) |
| Cu2—O1 | 1.9119 (14) | N2—C2 | 1.307 (3) |
| Cu2—O3 | 1.9925 (14) | N3—C2 | 1.159 (3) |
| Cu2—N3 | 2.532 (2) | | |
| | | | |
| N3$^{iii}$—Cu1—O2$^{ii}$ | 89.58 (6) | O2$^{v}$—Cu3—O1 | 74.31 (6) |
| N3$^{iii}$—Cu1—O1$^{i}$ | 88.94 (6) | O3$^{v}$—Cu3—O1 | 105.27 (6) |
| O2$^{ii}$—Cu1—O1$^{i}$ | 84.62 (7) | O2$^{v}$—Cu3—O2 | 180 |
| N3$^{iii}$—Cu1—O2 | 84.20 (6) | O3$^{v}$—Cu3—O2 | 99.27 (6) |
| O2$^{ii}$—Cu1—O2 | 173.67 (5) | O1—Cu3—O2 | 105.69 (6) |
| O1$^{i}$—Cu1—O2 | 96.40 (7) | O3$^{v}$—Cu3—O3 | 180 |
| N3$^{iii}$—Cu1—O3 | 89.92 (6) | O1—Cu3—O3 | 74.73 (6) |
| O2$^{ii}$—Cu1—O3 | 96.85 (7) | O2—Cu3—O3 | 80.73 (6) |
| O1$^{i}$—Cu1—O3 | 178.14 (6) | Cu3—O1—Cu1$^{vi}$ | 96.09 (6) |
| O2—Cu1—O3 | 82.01 (7) | Cu3—O1—Cu2 | 95.80 (6) |
| N3$^{iii}$—Cu1—N3 | 179.15 (2) | Cu1$^{vi}$—O1—Cu2 | 105.87 (7) |
| O2$^{ii}$—Cu1—N3 | 90.36 (7) | Cu3—O2—Cu1$^{iii}$ | 104.78 (8) |
| O1$^{i}$—Cu1—N3 | 91.90 (7) | Cu3—O2—Cu1 | 98.30 (7) |
| O2—Cu1—N3 | 95.84 (7) | Cu1$^{iii}$—O2—Cu1 | 105.85 (8) |
| O3—Cu1—N3 | 89.24 (7) | Cu2—O3—Cu3 | 104.69 (6) |
| N3$^{iv}$—Cu2—O1 | 92.82 (7) | Cu2—O3—Cu1 | 103.87 (7) |
| O3$^{iv}$—Cu2—O1 | 95.24 (6) | Cu3—O3—Cu1 | 98.77 (7) |
| O1$^{iv}$—Cu2—O1 | 180 | C1—N2—C2 | 116.8 (2) |
| N3$^{iv}$—Cu2—O3 | 94.12 (7) | Cu1—N3—C2 | 135.90 (18) |
| O3$^{iv}$—Cu2—O3 | 180 | Cu2—N3—C2 | 119.21 (19) |
| O1—Cu2—O3 | 84.76 (6) | Cu1$^{ii}$—N3—C2 | 145.31 (18) |
| N3$^{iv}$—Cu2—N3 | 180 | N2—C1—N1 | 114.0 (2) |
| O1—Cu2—N3 | 87.18 (7) | N2—C1—O4 | 125.73 (18) |
| O3—Cu2—N3 | 85.88 (7) | N1—C1—O4 | 120.3 (2) |
| O1$^{v}$—Cu3—O1 | 180 | N2—C2—N3 | 174.7 (3) |

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x, -y+1, -z+1$; (v) $-x, -y, -z+1$; (vi) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O1—H1$\cdots$O4 | 0.841 (9) | 1.954 (14) | 2.770 (2) | 163 (3) |
| O2—H2$\cdots$O6$^{vii}$ | 0.846 (9) | 1.943 (14) | 2.786 (2) | 175 |
| O3—H3$\cdots$O5$^{iv}$ | 0.841 (9) | 1.997 (16) | 2.824 (2) | 167 |
| N1—H5$\cdots$N2$^{viii}$ | 0.85 (3) | 2.21 (3) | 3.055 (3) | 174 |
| O5—H6$\cdots$O6 | 0.845 (10) | 2.216 (18) | 2.980 (3) | 150 (3) |
| O5—H7$\cdots$O4$^{ix}$ | 0.844 (9) | 1.943 (11) | 2.782 (3) | 172 |
| O6—H8$\cdots$O4$^{x}$ | 0.849 (10) | 2.12 (3) | 2.842 (3) | 142 |
| O6—H9$\cdots$O5$^{x}$ | 0.850 (30) | 2.17 (3) | 2.987 (3) | 161 |

Symmetry codes: (iv) $-x, -y+1, -z+1$; (vii) $x, y-1, z$; (viii) $-x+1, -y+1, -z+1$; (ix) $x, y+1, z$; (x) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

### *Refinement*

$R[F > 2\sigma(F)] = 0.031$
$wR(F) = 0.025$
$S = 1.11$
1731 reflections
151 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.96$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.81$ e Å$^{-3}$

All H atoms were located in difference Fourier maps and restrained to ride on their parent atoms [O—H = N—H = 0.85 (1) Å]. For the H atoms attached to framework atoms O1–O3, the fractional coordinates and isotropic displacement parameters were refined. For the remaining H atoms on water molecules $H_2O5$ and $H_2O6$ and amide fragment –N1$H_2$, the fractional coordinates were refined, with $U_{\rm iso}(H) = 1.2U_{\rm eq}(O)$ and $1.2U_{\rm eq}(N)$, respectively.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3026). Services for accessing these data are described at the back of the journal.

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