

(interdimer separation 3.54, 3.56 and 3.61 Å). This configuration maximizes the S...S bonding (Lowe, 1980) [the intradimer S...S distances range from 3.27 to 3.50 Å (Table 3)]. On the other hand, three interdimer types of overlaps are observed showing the irregularity of the packing. The intermolecular contacts (Table 3) reveal strong interactions between the [Fe(CN)₆]³⁻ anions and the organic molecules. [Fe(CN)₆]³⁻ units and H₂O molecules are associated through hydrogen bonding. Magnetic measurements of this material are in progress and will be reported elsewhere.

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Copper Disodium Tetrahydroxide

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Abstract. CuNa₂(OH)₄, *M_r* = 177.55, orthorhombic, *Pna*2₁, *a* = 6.750 (3), *b* = 6.726 (5), *c* = 8.993 (5) Å, *V* = 408.3 (7) Å³, *Z* = 4, *D_x* = 2.888 Mg m⁻³, *Mo Kα*, *λ* = 0.71069 Å, *μ* = 5.442 mm⁻¹, *F*(000) = 348, room temperature, *R* = 0.030 for 549 reflections. The structure contains [NaO₆] octahedra and [CuO₄] square planes. It can be described as deriving from the NaCl type. 3/4 of the octahedral sites formed by O atoms are occupied by Na or Cu atoms, 1/4 by H atoms. A study of the hydrogen bonds shows that they are very weak.

Introduction. In 1933, Scholder described several new compounds belonging to the ternary system Na₂O, MO, H₂O (*M*: divalent metal). Since then, several papers have been published; the synthesis was published in 1966 (Scholder & Schwochow, 1966). In all the previous studies, the syntheses gave rise to powders and no crystallographic study has ever been mentioned. The chemical formula of these compounds, mostly Na₂*M*(OH)₄, was deduced only from chemical analysis.

These compounds, which are unstable in air, have never been obtained for other alkali metals.

In a recent paper (Cudennec, Lecerf, Riou & Gerault, 1988), we proposed a new method of synthesis for one compound belonging to these systems: Na₂Cu(OH)₄. This method made possible the growth of crystals; therefore a complete crystallographic study became possible. This paper reports the results of the structure determination and discusses peculiar properties.

Experimental. As stated in our previous publication, crystals of Na₂Cu(OH)₄ were prepared from a system containing 1 mol of CuO, 10 mol of NaOH and 40 mol of H₂O. The mixture was placed in a dry box using KOH at room temperature for several weeks to be slowly dehydrated and protected from CO₂. Well formed blue octahedral-shaped crystals appeared, of average size about 0.1 mm. Crystals could not be isolated and washed because of their instability;

Table 1. Final atomic coordinates and equivalent isotropic temperature factors for $\text{Na}_2\text{Cu}(\text{OH})_4$

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Cu	0.26417 (5)	0.00723 (6)	0.000	0.793 (6)
Na(1)	0.5007 (3)	0.7148 (3)	0.7539 (3)	1.26 (3)
Na(2)	0.2558 (2)	0.0060 (2)	0.4950 (4)	1.25 (2)
O(1)	0.2623 (4)	0.0113 (4)	0.7753 (4)	1.37 (6)
O(2)	0.2827 (5)	0.9925 (4)	0.2137 (4)	1.43 (6)
O(3)	0.0538 (4)	0.8078 (4)	0.0044 (4)	1.08 (4)
O(4)	0.4643 (4)	0.2164 (4)	0.0059 (3)	1.05 (4)
H(O1)	0.58 (1)	0.96 (1)	0.240 (9)	4.0*
H(O2)	0.25 (1)	0.33 (1)	0.74 (1)	4.0*
H(O3)	0.499 (9)	0.24 (1)	0.60 (1)	4.0*
H(O4)	0.50 (1)	0.25 (1)	0.91 (1)	4.0*

* Atoms refined isotropically, $B = 4.0 \text{\AA}^2$.Table 2. Selected bond distances (\AA) for $\text{Na}_2\text{Cu}(\text{OH})_4$ and hydrogen-bonding geometry

Cu—O(1)	2.021 (3)	Na(2)—O(1)	2.522 (5)
Cu—O(2)	1.929 (3)	Na(2)—O(2)	2.537 (5)
Cu—O(3)	1.954 (3)	Na(2)—O(3)	2.438 (3)
Cu—O(3)	2.883 (3)	Na(2)—O(3)	2.404 (3)
Cu—O(4)	1.951 (3)	Na(2)—O(4)	2.412 (3)
Cu—O(4)	2.749 (3)	Na(2)—O(4)	2.452 (3)

Na(1)—O(1)	2.569 (3)	O(1)—H(O1)	1.12 (9)
Na(1)—O(1)	2.339 (3)	O(2)—H(O2)	1.13 (10)
Na(1)—O(2)	2.479 (4)	O(3)—H(O3)	1.04 (10)
Na(1)—O(2)	2.455 (4)	O(4)—H(O4)	0.94 (10)
Na(1)—O(3)	2.286 (5)		
Na(1)—O(4)	2.291 (4)		

O—H...O	O—H (\AA)	H...O (\AA)	O—H...O ($^\circ$)	O...O (\AA)
O(1)—H(O1)...O(2)	1.12 (9)	2.05 (9)	160. (6)	3.121 (5)
O(2)—H(O2)...O(1)	1.13 (10)	2.18 (10)	170. (7)	3.298 (5)
O(3)—H(O3)...O(2)	1.04 (10)	2.39 (7)	147. (7)	3.313 (5)
O(4)—H(O4)...O(1)	0.94 (10)	2.67 (8)	137. (6)	3.421 (5)

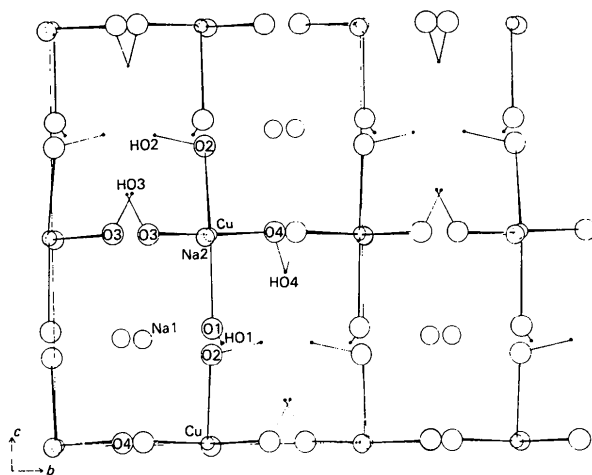
therefore, for all the crystallographic studies, small single crystals were quickly sealed inside a 0.3 mm Lindemann-glass capillary. A suitable crystal (0.1 × 0.1 × 0.1 mm) was mounted on an Enraf-Nonius CAD-4 diffractometer. Unit-cell constants were determined from a preliminary study by the photographic method, and then refined on the basis of 25 carefully centred reflections in the angular range $2 < 2\theta < 32^\circ$. Data were collected in the ω - 2θ scan mode, with ω scan width $(2.00 + 0.45 \tan\theta)^\circ$ and scan amplitude $(1.00 + 0.35 \tan\theta)$ mm; $\theta_{\text{max}} = 25^\circ$. 1603 reflections were measured which were merged to a unique set of 860, $R_{\text{int}} = 0.031$. Of these, 549 were regarded as observed reflections according to $I > \sigma(I)$. Data were corrected for Lorentz and polarization effects, no absorption correction was applied. A periodic check of 3 standard reflections showed no significant intensity variation. The hkl range was $0 \leq h \leq 10$; $0 \leq k \leq 10$; $0 \leq l \leq 13$. The structure was solved by direct methods and the positions of one Cu, one Na and three O atoms belonging to the asymmetric unit were deduced from one of the most

probable E maps. The structure was completed from successive Fourier and difference Fourier maps. Full-matrix least-squares refinement was based on F and the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w(F) = 1/\sigma^2(F)$. For the seven non-H atoms, which were assigned anisotropic thermal parameters, the refinement converged to $R = 0.050$ and $wR = 0.056$ for all observed data. At this stage a difference Fourier map revealed the positions of the four H atoms. Further refinement including the H atoms led to a final R value of 0.030 and $wR = 0.031$. The H atoms were refined isotropically. The weighting scheme was a non-Poisson contribution with $p = 0.050$. Corrections were made for anomalous-dispersion and secondary-extinction effects, $g = 1.86 \times 10^{-7}$. During the last refinement cycle, the r.m.s. shift/e.s.d. was 0.05. The final difference Fourier map showed no features higher than 0.8 e \AA^{-3} . All crystal structure analyses and refinements were carried out on a PDP 11/60, using the *SDP* package (Frenz, 1978). Scattering factors were from Cromer & Waber (1965)*.

Discussion.

Coordination polyhedra. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1. Fig. 1 shows a view of the unit cell of $\text{Na}_2\text{Cu}(\text{OH})_4$. Bond lengths and angles are given in Table 2. The structure contains one crystallographic Cu site and two distinct Na sites. The coordination of the Cu atom in the structure is fourfold square planar.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51496 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. The unit cell of $\text{CuNa}_2(\text{OH})_4$.

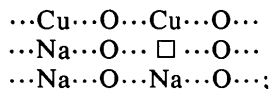
Cu is coordinated by four O atoms belonging to OH groups. The average distance is 1.964 Å with values in the range 1.929–2.021 Å. Two O atoms, more distant from Cu, complete a very distorted octahedron. Nevertheless, these two O atoms, whose distances from Cu are 2.749 and 2.883 Å, are very weakly linked. Na(1) and Na(2) atoms are each coordinated by six atoms in the form of distorted octahedra. Na(1) displays Na–O distances in the range 2.286–2.569 Å with a mean value of 2.403 Å. Na(2) shows a less-distorted octahedron than Na(1). The average Na(2)–O distance is 2.461 Å with values in the range 2.404–2.537 Å.

Hydrogen bonding. The geometrical features of expected H bonds are given in Table 2. Distances and angles involving the H atoms are satisfactory. H(O1), which is attached to O(1), forms an H bond with O(2) which is 2.05 Å distant from it. This H bond, which deviates significantly from linearity [$O(1)–H(O1) \cdots O(2) = 160^\circ$], must be considered as relatively weak. Nevertheless, this is the strongest one in the structure. H(O2) forms a very weak H bond with O(1) which is 2.18 Å distant from it. As shown in Table 2, H(O3) and H(O4) are too far from their nearest neighbours O(1) and O(2) to allow H-bond formation. The present results are in good agreement with the IR study. The IR spectrum displays effectively four absorption bands corresponding to the four distinct hydroxyl groups. Of these, two are slightly shifted to the low frequencies (3525 and 3490 cm^{-1}) whereas the two other bands are not significantly shifted (3600 and 3570 cm^{-1}).

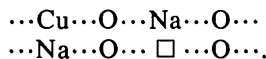
Crystal packing. As suggested in Fig. 1, the four distinct O atoms present in the $\text{Na}_2\text{Cu}(\text{OH})_4$ structure are also sixfold coordinated in the form of very distorted octahedra. These octahedra are built of Na, Cu and H cations. O(1) and O(2) environments are similar; their nearest neighbours are one Cu, three Na and two H atoms. One of the H atoms surrounding O(1) or O(2) corresponds to an H bond where the atoms O(1) and O(2) are acceptors. The distorted octahedra surrounding O(3) and O(4) involve two Cu, three Na and one H atoms. In this case, one of the two Cu atoms is very weakly linked to the corresponding O(3) or O(4) atom. The similarity between Na, Cu and O octahedral environments suggests that $\text{Na}_2\text{Cu}(\text{OH})_4$ is derived from the NaCl-type structure.

The structure is built of atomic rows parallel to $[110]$, $[\bar{1}\bar{1}0]$ and $[001]$ axes. These rows form networks respectively parallel to (100), $(\bar{1}\bar{1}0)$ and (001) planes. They are constituted of cations alternating with O atoms. There are three types of rows forming the

networks parallel to (110) or $(\bar{1}\bar{1}0)$ planes. In this case, the atoms appear in the following order:



on the other hand, the networks parallel to (001) involve two types of rows corresponding to:



The symbol \Box represents an octahedral site occupied by four H atoms.

Each atom occupies an octahedral site as in the NaCl structure, but an important difference is the presence here of an 'octahedral hole' occupied by four H atoms.

All the H atoms are thus confined inside an octahedral hole. So if we consider the four octahedral sites reserved for the cations, three are occupied by Cu or Na atoms and the fourth by the H atoms. If we now compare the structure of $\text{Na}_2\text{Cu}(\text{OH})_4$ with that of NaOH, it appears that the new compound is more nearly the NaCl type. The structure of NaOH, stable at room temperature, is built up of slices of the NaCl structure in which Na has five nearest neighbours at five of the vertices of an octahedron, whereas $\text{Na}_2\text{Cu}(\text{OH})_4$ contains sixfold-coordinated Na atoms. Another difference between these structures is that Na–O–H bonds are collinear in NaOH while the mean angle for Na–OH bonds in $\text{Na}_2\text{Cu}(\text{OH})_4$ is 144° .

Structural instability. One of the principal features of the compound studied is its poor stability. There are probably several explanations for this, but the presence of four H atoms confined to a narrow octahedral site is undoubtedly the main reason. Moreover, it is probable that the ionic radius, and consequently the nature of the alkali atom, determines the size of the 'octahedral hole' available to the H atoms. This could be the reason why alkali hydroxymetallates $M_2M^{II}(\text{OH})_4$ have been obtained only for sodium.

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