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Crystal structure of copper hydroxynitrite $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$

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ABSTRACT. The crystal structure of $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ has been determined by single crystal technique. Data were collected from X-ray diffractometer and the structure was refined by least squares method to a final R index of 4.4% ($R_w = 6.2\%$) from 732 reflections with $I > 4\sigma(I)$. The crystal structure can be roughly described in the monoclinic space group $P2_1/m$, but crystals are really triclinic (space group: $P-1$): $a = 5.609(3)$, $b = 6.039(6)$, $c = 6.622(3)$ Å, $\alpha = 90.07(6)$, $\beta = 95.43(4)$, $\gamma = 89.99(6)^\circ$, $V = 223.3$ Å³, $Z = 2$, $d_{\text{calc}} = 3.33$, $d_{\text{obs}} = 3.3$ g.cm⁻³. The structure of this hydroxysalt is built up by octahedral layers containing all the Cu^{2+} ions. The interlayer space is occupied by the nitrite group, characterized by a phenomenon of disorder involving one of its oxygens. The linkage between the successive layers is just due to strong hydrogen bonds.

INTRODUCTION

The solid phase $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ has already been mentioned by OSWALD in 1965 [1]. Since, no works about this phase, and particularly no crystal structure studies, have been published. Very recently and in parallel with this work the crystal structure, IR and Raman studies of the same compound have been published [16]. In this last paper the structure of $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ is described in the monoclinic system with a pseudosymmetrical space group $P2_1/m$.

$\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ belongs to the family of natural occurring copper hydroxy-salts, of formula type: $\text{Cu}_2(\text{OH})_3\text{X}$ ($\text{X} = \text{F}^-$, Cl^- , Br^- , NO_3^-), whose structures are related to the brucite type. $\text{Cu}_2(\text{OH})_3\text{Cl}$ exists under two allotropic varieties: atacamite [2] and paratacamite [3]. It is also the case for $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ which has two polymorphous forms; one monoclinic and the other orthorhombic [4]. The crystal structure of the monoclinic form, a metastable phase synthetically obtained, was determined in 1952 [5] and reviewed in [1979] [6] and [1983] [7] whereas the structure of the orthorhombic variety, a mineral named gerhardtite, was solved in 1982 [8]

In a previous publication [9], we have mentioned the existence of a new solid, $\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$. It was prepared by soft chemistry, from copper ammine complexes, obtained by dissolving a pure $\text{Cu}(\text{OH})_2$ in concentrated ammonia solutions. Recently we established that, in these conditions, ammonia was partly oxidized by dioxygen, to give rise to NO_2^- ion [10]. The structural determination led to the chemical formulation $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ and brings new data about copper hydroxy-salts.

EXPERIMENTAL

The preparation of pure $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ is not easy, because free nitrite has not a great stability. Nevertheless a small amount of this compound was obtained. Analysis of copper was performed by ICP spectrometry: $\text{Cu}_{\text{exp}} = 55.4\%$, $\text{Cu}_{\text{the}} = 56.71\%$. The presence of the nitrite group was confirmed by the AQUAMERCK analysis nitrite method.

Solutions containing copper nitrite ammine complexes, have been placed in boxes with KOH pellets and concentrated sulphuric acid, in order to fix slowly water and NH_3 gas. After several months at the temperature of a refrigerator, near 5°C , crystals were obtained in a mixture of CuO , $\text{Cu}(\text{OH})_2$ and other phases corresponding to copper ammine hydroxy-nitrites.

A pale-blue, thin plate single crystal of $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ was mounted on an ENRAF NONIUS CAD4 diffractometer. The experimental density, $d_{\text{obs}} = 3.3$ was determined with a crystal, by the flotation method, in a CLERICI solution.

The unit cell parameters (table I) were determined from a preliminary study in the triclinic system, by the photographic method. Then they were refined by a least squares treatment of 25 reflections, measured on an automated diffractometer. The symmetry of this structure can be described in the monoclinic system with the pseudosymmetrical space group $\text{P}2_1/\text{m}$ but the study of X-ray diffraction photographs realized with a small crystal obtained at 5°C , reveals important differences between the intensities of several $h\ k\ l$ and $h-k\ l$ reflections. A deeper examination, based on the comparison of several crystal samples of $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ shows that these differences can be variable from a sample to another one. This fact involves probably, some differences in the structure of each crystal sample.

The examination of the observed reflections of the used sample for the crystal structure study, shows differences between several reflections $h\ k\ l$ and $h-k\ l$ reaching 40%, whereas a lot of these reflections are quite identical. So the studied crystal is close to the monoclinic system, but its structure must be described in the lower symmetry $\text{P}-1$ triclinic system.

Data were corrected for Lorentz polarisation effects. Absorption corrections were applied according to WALKER and STUART method [11]. The other experimental recording conditions are given in table I. Scattering factors were from CROMER & WABER [12]. The structural determination was carried out on a MICROVAX computer using the SDP package [13]. The structure was solved by the heavy atom method with 732 unique reflections corresponding to $I > 4\sigma(I)$, which has been chosen because of the great number of very weak reflections.

The positions of copper atoms were deduced from the deconvolution of the three dimensional Patterson function. The refinement of these positions gave a conventional index $R = 22.3\%$. The positions of missing atoms were obtained from successive Fourier and differential synthesis maps. Further refinement of the structure carried out by Fourier synthesis and full matrix least squares cycles reduced R to 13.7% ($R_w = 20.7\%$).

After correcting absorption effects, the refinement including anisotropic thermal parameters for non hydrogen atoms improved the conventional R index to 5.4%. A three dimensional difference Fourier synthesis calculated with the reflections according to $0 < \sin\theta/\lambda < 0.7$, revealed the H-positions. The last refinement of all positions improved the conventional R index to 4.4% ($R_w = 6.2\%$). The weighting scheme used was the non-poisson contribution with $p = 0.04$. Corrections were made for anomalous dispersion and secondary extinctions effects ($g = 4.64 \times 10^{-6}$). The final fractional atomic coordinates, isotropic and anisotropic temperature factors are given in tables II and III. Selected interatomic distances and angles around copper and nitrogen are listed in table IV.

DISCUSSION

In $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$, all the copper atoms are octahedrally coordinated. Cu1 and Cu2 are strongly linked to four oxygens, respectively O1 (2x) and O3 (2x) for Cu1, O1 (2x) and O2 (2x) for Cu2. All these oxygens belong to hydroxyl groups OH. The mean Cu-OH bond length is 1.95 Å. The Hydroxyl groups build up an approximate square plane around Cu1 and Cu2 copper atoms. The surrounding of these two copper atoms is completed by two oxygens O4 belonging to the nitrite group. Cu1 and Cu2 are linked to O4 atoms which are located at a mean bond length of 2.49 Å from copper. The [4+2] resulting octahedra around Cu1 and Cu2 are typically a case of distortion by JAHN TELLER effect.

The copper atom Cu3 is surrounded by a very distorted octahedron composed of five oxygen atoms belonging to OH groups: O1, O2 (2x) and O3 (2x), and one oxygen of a nitrite group, O4. Four oxygen atoms [O2 and O3] build up an approximate square-plane containing four short Cu-O bonds with a mean bond length of 1.99 Å. O1 and O4 are located at a longer distance near 2.37 Å. The angular shifts of this octahedron, compared to the theoretical values of a regular octahedron, are very important: 17.1°.

All these octahedra are linked together to build up a sheet parallel to the (a,b) plane, at the mean position $z = 0$. Each octahedron of the layer shares six edges with the neighbouring octahedra. The distance separating two sheets is 6.56 Å and the mean thickness of each sheet is 2.13 Å. So it results that the structure contains an empty space which is partially occupied by two atoms belonging to the nitrite groups and the hydrogen of hydroxyl groups. A brucite type sheet and the projection of $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ along the *a* axis are represented in figures 1 and 2. In the crystal of $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$, the nitrite group is formed of one nitrogen atom bonded to O4, itself linked to three copper atoms, and one free oxygen atom. This last oxygen O5 occupies statistically two positions which have been labelled O5a and O5b in table I. The occupancy rates of the oxygen atom between the two positions O5a and O5b have been refined. Their values are very close to 50%. Therefore the position of the nitrite group in the $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ structure implies a phenomenon of disorder, which can be explained by the fact that the nitrite group, strongly linked to copper by O4 atom can twist around O4-N axis and consequently the second oxygen of nitrite group may occupy two positions O5a and O5b. In the studied crystal the nitrite group twists through 66 degrees around O4-N axis. However it is very probable that between two octahedral sheets, all the nitrite groups keep the same orientation defined for example by one group O4-NO5a. Consequently they are ordered in a whole plane parallel to (a,b). In fact a general phenomenon of disorder of the oxygen O5 belonging to the nitrite group, in the plane containing O5 atoms implies that some interatomic distances between O5 atoms become too short (2.2 Å). To explain the disorder of O5 we must then consider that the nitrite group takes statistically one of the orientation defined by O5a or O5b, for example O5a in a plane (parallel to (a,b)) and the other orientation O5b in another plane and as shown before these orientations are random. Thus it appears that the disorder of nitrite groups in $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ spreads just in the *c* direction. The two N-O bond lengths are very different 1.239 Å for N-O4 and about 1.34 Å for N-O5a or N-O5b. The O-N-O angles have very similar values for O4-N-O5a and O4-N-O5b, respectively 109.1° and 109.9°. The nitrite group of $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ appears in the classical nitrito form because the O-N-O group is strongly linked to an octahedral layer by the oxygen atom O4.

This nitrito form is quite different from the one of another copper nitrite $\text{Cu}(\text{NH}_3)_2(\text{NO}_2)_2$ whose structure has been published recently [14]. In this last compound the nitrite group appears both in nitro and nitrito forms. In the structure of $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$, the linkage between two neighbouring layers involves strong hydrogen bonds. A first group of H-bonds stands between H atoms of the hydroxyl groups and the oxygen O5a and O5b belonging to the nitrite group. As shown in table V the relative short distance between donor and acceptor atoms generates rather strong H-bonds. So the two oxygen positions O5a, O5b which are occupied by half an oxygen atom are strongly bonded to respectively H3 and H2. The similar donor- acceptor O...O distances related to H bond for O5a (2.72 Å) and for O5b (2.68 Å) implies that the two H-bonds have approximately the same strength. Consequently, it is normal that the oxygen atom may occupy the two sites O5a and O5b with the same probability. This fact agrees with the occupancy rates of oxygen in the two positions. If the

occupancy rates of O5a and O5b sites are strictly equal, the structure can be well described in the monoclinic system with the pseudosymmetrical space group P21/m, but the most stable structure corresponds to the ordered structure with an occupancy rate equal to 1 in O5a or O5b site. When the position of nitrite groups becomes ordered, the structure cannot be described in the monoclinic P21/m group but in a lower symmetry group. As observed notably on the X-ray diffraction photographs, the studied crystal corresponds to the triclinic P-1 system which permits a better description of the ordered structure. It is very probable that differences in intensities observed from different crystals correspond to partially ordered crystals. Due to the fact that the H-bonds are quite similar for oxygen in O5a or O5b position, the difference in stability between the ordered or the disordered structures is very weak.

A second set of H-bonds exists between nitrogen and H1 atoms. As shown in table V the distance donor- acceptor (3.01 Å) is longer than the first ones, so these H-bonds are less strong than in the preceding case. Nevertheless it is probable that this H-bond takes part in the bonding between two neighbouring sheets.

Table V: H- bond features

H bond	Distances(Å)		Angles(°)	Distances(Å)
	Donor-H	H··acceptor	O-H··acceptor	O··acceptor
O1-H1··N	0.90	2.14	161.1	3.01
O2-H2··O5b	0.84	1.93	149.3	2.68
O3-H3··O5a	0.84	1.96	149.5	2.72

Therefore in $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$, the H-bonds are very important for the structural cohesion. If we compare now this structure to the classical hydroxide structure such as brucite, we can remark that H-bonds are stronger in the nitrite compound, precisely because of the presence of the nitrite group. This fact permits to explain the relative stability of the studied nitrite, in comparison with $\text{Cu}(\text{OH})_2$ [15]. It is also interesting to compare the structure of $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ to that of the equivalent nitrate compound $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$. This last solid is present in two allotropic species whose crystal structures and properties have been studied earlier. One of them, the α variety may be compared easily to the nitrite compound. The cell parameters, c excepted, have quite similar values. In the nitrite, the c value is inferior because the nitrite group is less bulky than the nitrate group. The nitrate compound is also characterized by strong H-bonds which explain the good stability of this hydroxysalt compared to copper hydroxide.

REFERENCES

- [1] H.R.OSWALD and B.BRUNNER, Reactivity of solids, Proc., 5 I.S.R.S., Munich, Elsevier publ. Co., Amsterdam, 382, 1965.
- [2] J.B.PARISE and B.G.HYDE, Acta Cryst., 1986, C42, p.1277.
- [3] M.E.FLEET, Acta Cryst., 1975, B31, p.183.
- [4] H.R.OSWALD, Z.Kristallogr., 1961, 116, p.210.
- [5] W.NOWACKI and R.SCHEIDEGGER, Helv.Chim.Acta, 1952, 35, p.375.
- [6] J. P AUFFREDIC, D. LOUER and M.LOUER. Journal of Thermal analysis, 1979, 16, p. 329.
- [7] H.EFFEBBERGER, Z.Kristallogr, 1983, 165, p.127.
- [8] B.BOVIO and S.LOCCHI, J. Crystallogr. Spectro. Research, 1982, 12(6), p.507.
- [9] Y.CUDENNEC, A.LECERF, A.RIOU and Y.GERAULT, Eur.J.Solid State Inorg. Chem., 1990, 27, p.411.
- [10] Y.CUDENNEC, A.RIOU, K.ROCHDI, Y.GERAULT and A.LECERF, Eur.J.Solid State Inorg. Chem., 1993, 30, p.77.
- [11] N.WALKER and D.STUART, Acta cryst., 1983, A39,p.158.
- [12] D.T.CROMER and J.T.WABER, Acta cryst., 1965, 18, p.104.
- [13] B.A.FRENTZ, The Enraf-Nonius C.A.D.-4 S.D.P. system, Delft univ. Press, DELFT,HOLLAND, 1978.
- [14] K.ROCHDI, A.RIOU, Y.CUDENNEC, Y.GERAULT and A.LECERF, Eur.J.Solid State Inorg. Chem., 1993, 30, p.427.
- [15] Y.CUDENNEC, A.LECERF, A.RIOU and Y.GERAULT, Eur.J.Solid State Inorg. Chem., 1988, 25, p.351.
- [16]M.SCHMIDT, H.MOLLER and H.D.LUTZ, Z.Anorg.Allgem.Chem., 1993, 619, p.1287.

Table I: Experimental Data.

crystal data:	
crystal size (mm):	0.3x 0.2x 0.02
space group	P-1 (2)
cell parameters	a= 5.609(3) Å b= 6.039(6) Å c= 6.622(3) Å α = 90.07 (6)° β = 95.43 (4)° γ = 89.99 (6)°
Volume	223.3 Å ³
Z	2
calculated density (g cm ⁻³)	3.33

Intensity measurement:	
(λ Mo K α)	0.71073 Å
Monochromator	Graphite plate
scan mode	ω -2 θ
scan width (°)	2.00+0.60 tan θ
slit amplitude(mm)	1.00+0.35tan θ
max θ (°)	35.00°
range of h k l	0<h<8, -9<k<9, -10<l<10
standard reflections	3: measured every 2 hours(no decay): (1 2 -2), (2 0 2), (1 -2 -3)
measured reflections	2135
reflections with I> 4 σ (I)	732
μ (cm-1)	94.816

Structure solution and refinement:	
parameters refined	86
agreement factors	R=0.044, R _w =0.062
Δ/σ	0.00
$\Delta\sigma$	< 0.8e ⁻ /Å ³

Table II: Final atomic coordinates and equivalent isotropic temperature factors of $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$.

Atom	x/a	y/b	z/c	Beq	occupancy rate
Cu1	0.0	0.0	0.0	0.96(2)	1
Cu2	0.0	0.5	0.0	0.99(2)	1
Cu3	0.5056(2)	0.2500(2)	-0.0013(2)	0.94(1)	1
O1	0.9011(9)	0.249(1)	0.1518(9)	1.0(1)	1
O2	0.3356(9)	0.4938(9)	0.1243(9)	0.93(9)	1
O3	0.3358(9)	0.0055(9)	0.1244(9)	0.94(9)	1
N	0.179(1)	0.250(2)	0.564(1)	3.7(3)	1
O4	0.169(1)	0.251(1)	0.750(1)	2.2(1)	1
O5a	0.367(3)	0.130(3)	0.520(2)	3.8(4)	0.48
O5b	0.366(3)	0.374(3)	0.516(2)	3.8(4)	0.52
H1	-0.045	0.268	0.283	4.0*	1
H2	0.375	0.500	0.250	4.0*	1
H3	0.375	0.0	0.250	4.0*	1

* These atoms have not been refined.

$$\text{Beq} = \frac{4}{3} \sum \beta_{ij} a_j$$

Table III: anisotropic temperature factors.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Cu1	0.53(4)	0.87(5)	1.46(5)	0.18(4)	0.05(4)	-0.17(4)
Cu2	0.52(4)	0.81(5)	1.63(5)	0.06(4)	0.08(4)	0.09(4)
Cu3	0.58(2)	0.72(3)	1.56(3)	0.13(2)	0.27(2)	-0.01(2)
O1	0.6(2)	0.9(2)	1.5(2)	0.2(1)	-0.0(2)	-0.3(2)
O2	0.5(1)	0.5(2)	1.8(2)	0.1(1)	-0.1(1)	-0.2(2)
O3	0.4(1)	0.9(2)	1.5(2)	0.0(1)	0.2(1)	-0.3(2)
N	2.3(4)	6.8(7)	1.9(4)	-0.1(4)	-0.3(3)	-0.3(4)
O4	2.5(3)	1.8(3)	2.2(3)	0.4(2)	0.4(2)	0.3(2)
O5a	2.8(6)	7(1)	1.7(6)	1.6(6)	0.4(5)	-0.5(7)
O5b	3.0(6)	6(1)	2.2(6)	-1.3(6)	-0.1(5)	0.6(7)

Table IV: Selected bond length (Å) and angles (°).
 Atoms noted ' correspond to equivalent positions.

(2x)Cu1-O1	1.917(4)Å	O1-Cu1-O4	91.1(2)
(2x)Cu1-O3	1.983(4)Å	-O4'	89.0(2)
(2x)Cu1-O4	2.497(6)Å	O1-Cu1-O3	85.4(2)
		-O3'	94.6(2)
		O3-Cu1-O4	82.0(2)
		-O4'	98.0(2)
(2x)Cu2-O1	1.931(4)Å	O1-Cu2-O2	94.4(2)
(2x)Cu2-O2	1.982(4)Å	-O2'	85.6(2)
(2x)Cu2-O4	2.490(6)Å	O1-Cu2-O4	91.0(2)
		-O4'	89.0(2)
		O2-Cu2-O4	81.8(2)
		-O4'	98.2(2)
Cu3-O2	1.979(4)Å	O1-Cu3-O2	107.1(2)
Cu3-O2'	1.998(5)Å	-O2'	74.9(2)
Cu3-O3	1.983(5)Å	O1-Cu3-O3	106.7(2)
Cu3-O3'	1.992(5)Å	-O3'	74.6(2)
Cu3-O1	2.350(4)Å	O2-Cu3-O4	84.7(2)
Cu3-O4	2.385(6)Å	O2'-	94.1(2)
		O2-Cu3-O2'	81.2(2)
		O2-Cu3-O3	96.2(2)
		O2'-Cu3-O3'	101.5(2)
		O3-Cu3-O4	84.9(2)
		O3'-	94.3(2)
		O3-Cu3-O3'	81.2(2)
N-O4	1.239(8)Å	O4-N-O5a	109.1(8)
N-O5a	1.335(12)Å	O4-N-O5b	109.9(8)
N-O5b	1.35(2)Å		

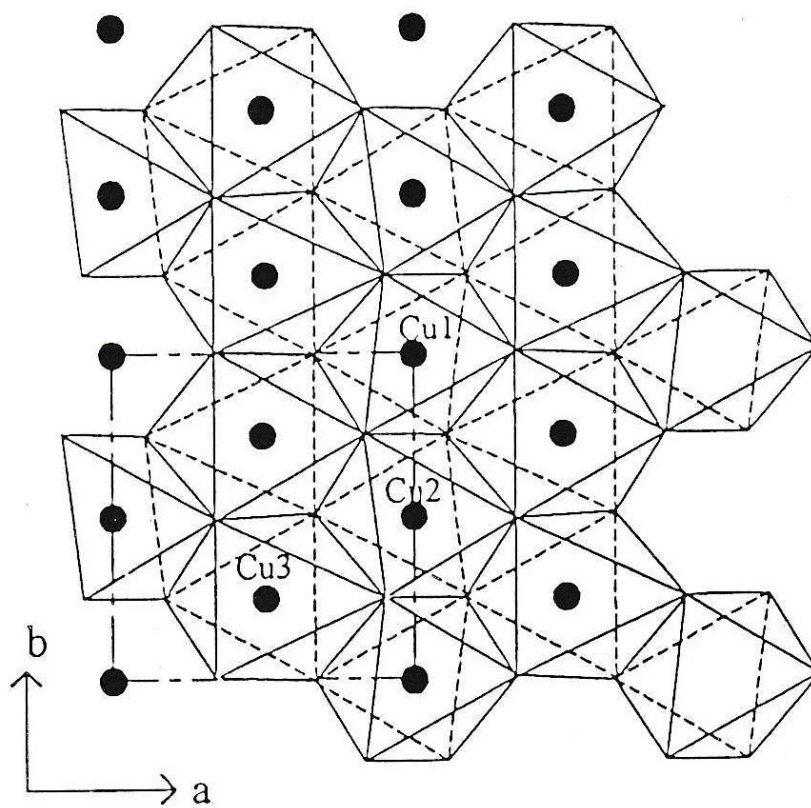


Fig : The brucite sheet parallel to the plane (a,b).

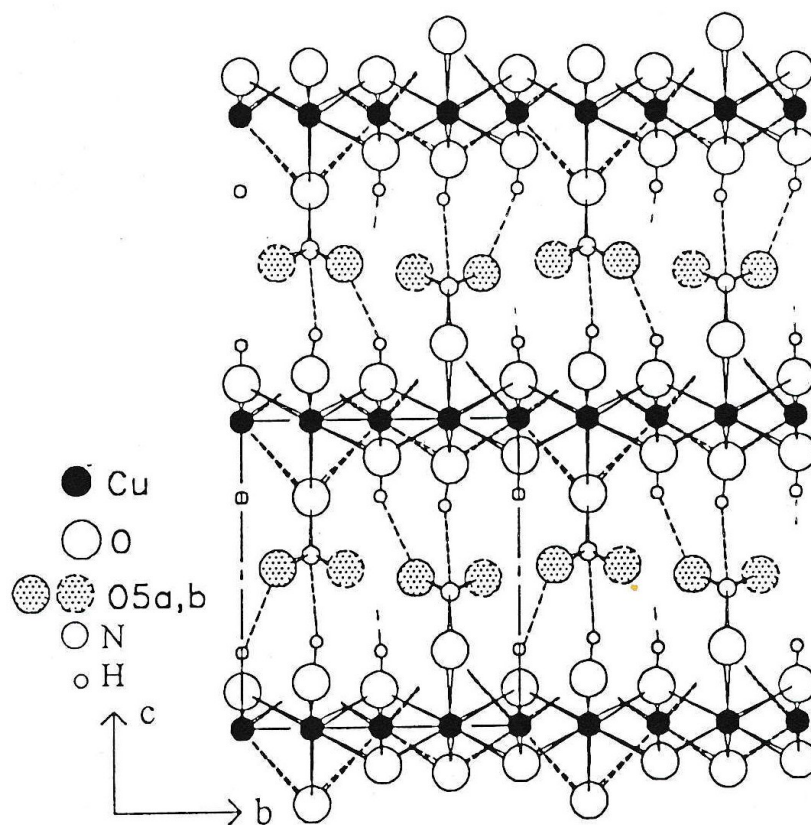


Fig 2: The projection of the $\text{Cu}_2(\text{OH})_3(\text{NO}_2)$ along the a axis.