



HAL
open science

Structural study of $\alpha\text{-Cu}(\text{NO}_2)_2(\text{NH}_3)_2$

K Rochdi, A Riou, Yannick Cudennec, Y Geràult, A Lecerf

► **To cite this version:**

| K Rochdi, A Riou, Yannick Cudennec, Y Geràult, A Lecerf. Structural study of $\alpha\text{-Cu}(\text{NO}_2)_2(\text{NH}_3)_2$. European Journal of Solid State and Inorganic Chemistry, 1993, 30, pp.427-433. hal-03198622

HAL Id: hal-03198622

<https://hal.science/hal-03198622>

Submitted on 14 Apr 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Structural study of α -Cu(NO₂)₂(NH₃)₂

K. ROCHDI, A. RIOU, Y. CUDENNEC, Y. GERÀULT and A. LECERF

Laboratoire de Chimie des Matériaux Inorganiques et de Cristallographie, I.N.S.A.,
20, avenue des Buttes de Coësmes, 35043 Rennes Cedex, France.

(M.T., received October 20, 1992; accepted November 25, 1992.)

ABSTRACT. - The crystal structure of α -Cu(NO₂)₂(NH₃)₂ has been determined. Data were collected from X-ray diffractometer and the structure was refined by least squares method to a final R index of 2.6% (R_w = 3.5%) for 1133 reflections.

Crystals are triclinic. (Space Group P-1): $a = 4.418(2) \text{ \AA}$, $b = 5.603(2) \text{ \AA}$, $c = 6.075(2) \text{ \AA}$, $\alpha = 78.62(3)^\circ$, $\beta = 76.26(3)^\circ$, $\gamma = 79.58(3)^\circ$, $Z = 1$, $V = 141.8(2) \text{ \AA}^3$, $d_{\text{calc}} = 2.22 \text{ g.cm}^{-3}$, $d_{\text{obs}} = 2.2 \text{ g.cm}^{-3}$. Each copper is surrounded by an approximately square planar arrangement of two ammonia groups (1.977 Å) and two nitrites (2.056 Å), this last short distance Cu-N involves the complexing property of the nitrite group. Two oxygens belonging to a nitrite group complete a distorted octahedron at 2.540 Å from copper. All these octahedra are linked by oxygens of nitrite groups, to form chains parallel to a -axis. The interactions between these chains, only due to hydrogen bonds, are very weak.

INTRODUCTION

In a recent paper[1], the previous works about ammine cupric nitrites have been reminded. We have shown that ammonia of tetraammine cupric complex solutions obtained by dissolution of cupric hydroxide in a concentrated ammonia solution, can be partially oxidized when exposed to air, at room temperature. This oxidation gives rise to ammine cupric nitrites and is probably due to the catalytic property of divalent copper ions. Several ammine cupric nitrites were prepared by this way:

- Cu(NO₂)₂(NH₃)₄ which crystallizes in two allotropic species α and β .
- Cu(NO₂)₂(NH₃)₂ which has also two allotropic forms α and β .

At the present time, little is known about the crystal structure and the structural properties of such compounds [2] [3]. The purpose of the present paper is the crystal structure determination of α -Cu(NO₂)₂(NH₃)₂, previously unknown.

EXPERIMENTAL

Dark pinked parallelepipedical crystals of average size 0.2 mm were obtained by a soft action at room temperature of water vapour on the α -Cu(NO₂)₂(NH₃)₄ variety.

The crystal used for the data collection appears as a pink single crystal irregularly shaped with approximate dimensions: 375 x 175 x 87 μm^3 .

The unit cell parameters in the triclinic system were deduced from a preliminary study by the photographic method. Then, they were refined by a least squares treatment of 2 θ values of 25 reflections measured on an ENRAF-NONIUS CAD4 diffractometer. Graphite monochromated Mo K α radiation was used ($\lambda = 0.7107 \text{ \AA}$).

Data were collected in the ω -2 θ scan mode, with ω scan width $(2.00 + 0.60 \tan\theta)^\circ$ and slit amplitude $(1.00 + 0.35 \tan\theta) \text{ mm}$. 1146 reflections were collected but only 1133 reflections were kept as observed reflections according to $I > \sigma(I)$ and used in the structural refinement.

Data were corrected for LORENTZ-POLARIZATION effects and absorption corrections were applied according to WALKER and STUART method [4] ($\mu = 38.332 \text{ cm}^{-1}$).

A periodic check of 3 standard reflections showed no significant variation of intensity. The hk1 range was $0 < h < 6$, $-8 < k < 8$, $-9 < l < 9$ ($2\theta < 68^\circ$).

The structure was solved by the heavy atom method. The positions of copper atoms were deduced by deconvolution of the three-dimensional Patterson function. Some positions of oxygen and nitrogen were also deduced from this function. The refinement of these positions gave a conventional index $R = 22.1\%$. 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 (including the scale factor and individual isotropic thermal parameters) reduced R to 10.1% ($R_w = 13.6\%$). After correcting absorption effects [4], the refinement including anisotropic thermal parameters for non-hydrogen atoms improved the conventional R index to 3.4% ($R_w = 4.2\%$). At this stage, 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 2.6% ($R_w = 3.5\%$) with [shift/err = 0.00].

The weighting scheme used was the non-poisson contribution with $p = 0.04$. Corrections were made for anomalous dispersion and secondary extinction effects ($g = 4.069 \cdot 10^{-6}$).

The last differential Fourier map showed no features higher than $0.8 \text{ e} \cdot \text{\AA}^{-3}$. Scattering factors were from CROMER and WABER [5]. The structural determination was carried out on a MICROVAX computer using the SDP package [6]. Final fractional atomic coordinates and anisotropic temperature factors are given in Table I and Table II.

DISCUSSION

A projection of the structure along the c -axis is represented in Fig 1. Selected bond lengths (\AA) and angles ($^\circ$) are listed in Table III.

Each copper atom is octahedrally coordinated. The nitrogen atoms N1(NO₂) and N2(NH₃) make an approximately square planar surrounding. Another ligand O1 complete a distorted octahedron at a longer distance. The [4+2] resulting distorted octahedron is typically a case of JAHN TELLER distortion effect. The four nitrogen atoms are bonded to Cu at 1.977 \AA and, 2.056 \AA , whereas the oxygen atoms O1 of nitrite group give longer distances (2.54 \AA). The last oxygen atom O2 is too far from copper atom (2.885 \AA), and can not belong to the copper surrounding.

The nitrogen N1 involves two short bonds of 1.236 \AA and 1.240 \AA with two oxygen atoms in order to form the nitrite group.

The nitrogen N2, belonging to ammonia group, is bonded to three independent hydrogen atoms. Therefore, it occupies the center of a tetrahedron where copper is placed at the vertex and the three

hydrogen atoms form the bottom. The angles H-N2-H and Cu-N2-H are in the range between 106.0° and 111.8°.

In the α -Cu(NO₂)₂(NH₃)₂ structure, the linkage between the octahedra previously described, is mainly due to oxygens of the nitrite group. The oxygen O1 of a nitrite group is shared with a copper atom of another octahedron, while the second oxygen atom O2 belonging to the nitrite group is free. Thus, the octahedra alternate with nitrite groups to build chains parallel to *a*-axis. The bond distance Cu-O1 is 2.54 Å, then the interaction between octahedra is relatively weak.

The interaction between the chains is due to hydrogen bonds formed between hydrogen atoms of the ammonia group and oxygen atoms of the nitrite one.

The linkage along *b* and *c* directions is only due to the hydrogen bonds. The hydrogen atom H2 is bonded to the oxygen O1, whereas the hydrogen atom H3 is weakly linked to O2 (The oxygen atom of nitrite group which is not linked to copper atoms). Only these two hydrogen bonds are involved in the linkage between the chains along the *b*-axis. The hydrogen atom H1 belonging to ammonia group is linked to O2 by a weak hydrogen bond at 2.130 Å. This hydrogen bond permits the linkage along the *c*-axis, thus the chains are weakly linked to their neighbours along this direction.

In view of the distances and angles of hydrogen bonds, we can deduce that these bonds are very weak, this fact added to the relative weakness of the Cu-O bonds within the chains, is probably the reason of the poor stability of the compound when it is exposed to air. The distances and angles characterizing these hydrogen bonds are presented in Table IV.

N-H...O	N-H(Å)	H...O(Å)	N-H...O(°)	N...O(Å)
N2-H1...O2	0.998	2.130	155.71	3.07
N2-H2...O1	0.810	2.321	177.39	3.13
N2-H3...O2	0.723	2.465	154.8	3.13

TABLE IV -Distances (Å) and angles (°) of hydrogen bonds.

CONCLUSION

The present study shows unquestionably the presence of nitrite groups in the crystal structure of the compound. As stated in our recent memory [1], these results bring an additional proof that a solution of cupric tetraammine complex can be oxidized in contact with air at room temperature. It seems that the presence of Cu²⁺ within a complex form in this solution, generates a catalytic effect. In fact, several tests carried out recently, in the same conditions with other divalent metals (Ni, Co), show that ammonia is not oxidized.

The structural study of α -Cu(NO₂)₂(NH₃)₂ reveals the presence of both nitro (-NO₂) and nitrito (-O-NO) forms. The nitro form is present in the square planar surrounding of copper, since two vertex of the square, in trans positions, are occupied by nitrogen atoms belonging to NO₂ groups. This particular situation of NO₂ group with respect to copper is due to the complexing properties of the nitrite ion and is undoubtedly responsible of the original pink color of α -Cu(NO₂)₂(NH₃)₂.

The nitrito form is equally present since two oxygen atoms belonging to different NO₂ groups are directly linked to copper by longer bonds. These two oxygens thus complete an octahedron distorted by JAHN TELLER effect.

In addition, the same nitrite group presents the nitro form for one copper and the nitrito form for another copper of the same chain (Fig.1).

The presence of nitrite group under two different forms is a current phenomenon. In our recent paper [1], we have mentioned the existence of a solid phase β -Cu(NO₂)₂(NH₃)₄, where both nitro form and free nitrite ions are present in the structure which will be soon published. That also is the case for other structures, related mainly to organic, copper(II) complexes [7] [8] [9], cobalt(III) complexes [10] [11] and nickel(II) complexes [12].

If we consider now, the transformation which occurs at a temperature near 30°C:



We can formulate the hypothesis that it is simply due to the fact that the oxygen nitrito brings nearer the copper atom, even when correlatively, the nitrogen of NO₂ group moves farther.

This transformation which reverses the bond lengths Cu-ONO and Cu-NO₂, corresponds to a weak exchange of energy and would justify the low temperature of the transition between solids, and the possibility of the opposite transformation β to α when the temperature decreases below 30°C. Moreover the inversion of the distances Cu-ONO and Cu-NO₂ can explain the color change characterizing this transition. This hypothesis could be verified after establishing the crystal structure of the β green phase.

REFERENCES

- [1]Y.CUDENNEC, A.RIOU, K.ROCHDI, Y.GERAULT and A.LECERF, Eur.J.Solid State Inorg.chem., (to be published, accepted in July, 21, 1992).
 [2]M.A.PORAI-KOSHITS and M.BYKOVSKA, Kristallografya, 1961, 3, p.381-388.
 [3]Y.MORI, H.INOUE and M.MORI, Inorg.chem., 1975, 14(5), p.1002-1005.
 [4]N.WALKER and D.STUART, Acta cryst., 1983, A39, p.158-166.
 [5]D.T.CROMER and J.T.WABER, Acta cryst., 1965, 18, p.104-109.
 [6]B.A.FRENTZ, The Enraf-Nonius C.A.D.-4 S.D.P. system, Delft Univ. Press, DELFT, HOLLAND, 1978.
 [7]R.ALLMANN, S.KREMER and D.KUCHARZCYK, Inorg. Chem. Acta, 1984, 85(1), p.19-21.
 [8]A.PAJUNEN and S.PAJUNEN, Acta Cryst., 1979, B35(12), p.3058-3060.
 [9]K.A.KLANDERMAN, W.C.HAMILTON and I.BERNAL, Inorg.Chim. Acta, 1977, 23(1), p.117-129.
 [10]I.BERNAL, J.CETRULLO and S.BERHANE, Struct. Chem., 1990, 1(4), p.631-366.
 [11]I.KRSTANOVIC and M.CELAP, Cryst.Struct.Comm., 1977, 6(2), p.171-174.
 [12]M.J.GOLDBERG and R.E.MARSH, Acta Cryst., 1979, B35(4), p.960-962.

	x/a	y/b	z/c	Beq
Cu	0.0	0.0	0.0	1.465(3)
N1	0.3920(3)	0.8104(2)	0.8191(2)	1.71(2)
N2	0.9878(3)	0.2610(3)	0.7281(2)	1.85(2)
O1	0.3574(3)	0.2444(3)	0.1120(3)	2.98(2)
O2	0.3793(4)	0.7388(3)	0.6422(2)	3.23(3)
H1	0.125	0.791	0.375	4.0(*)
H2	0.100	0.609	0.235	4.0(*)
H3	0.147	0.281	0.671	4.0(*)

TABLE I -Final atomic coordinates and equivalent isotropic temperature factors of $\alpha\text{-Cu(NO}_2)_2(\text{NH}_3)_2$.

$$B_{eq} = \frac{4}{3} \sum_{ij} \beta_{ij} a_i a_j$$

(*) Atoms which have not been refined.

	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Cu	1.435(6)	1.547(6)	1.370(6)	-0.146(5)	-0.315(5)	-0.170(5)
N1	1.51(3)	1.77(3)	1.92(3)	-0.41(3)	-0.29(3)	-0.37(3)
N2	1.89(3)	1.86(3)	1.73(3)	-0.29(3)	-0.46(3)	-0.01(3)
O1	2.10(3)	2.91(4)	4.68(5)	0.17(3)	-1.69(3)	-1.64(3)
O2	2.70(4)	4.87(6)	2.64(3)	-0.23(4)	-0.66(3)	-1.93(3)

TABLE II -Anisotropic temperature factors of non hydrogen atoms.

(2x)Cu-N1	2.056(1)	N1-Cu-N1	180.00
(2x)Cu-N2	1.977(1)	N1-Cu-N2	90.18(4)
(2x)Cu-O1	2.540(1)	N1-Cu-N2	89.82(4)
		N1-Cu-O1	90.72(4)
		N1-Cu-O1	89.29(4)
		N2-Cu-N2	180.00
		N2-Cu-O1	93.37(5)
		N2-Cu-O1	86.63(5)
		O1-Cu-O1	180.00
N1-O1	1.240(1)	O1-N1-O2	118.0(1)
N1-O2	1.236(1)		
N2-H1	1.00	H2-N2-H1	110.0
N2-H2	0.81	H2-N2-H3	106.0
N2-H3	0.72	H1-N2-H2	111.8

TABLE III -Bond lengths (Å) and Angles (°).

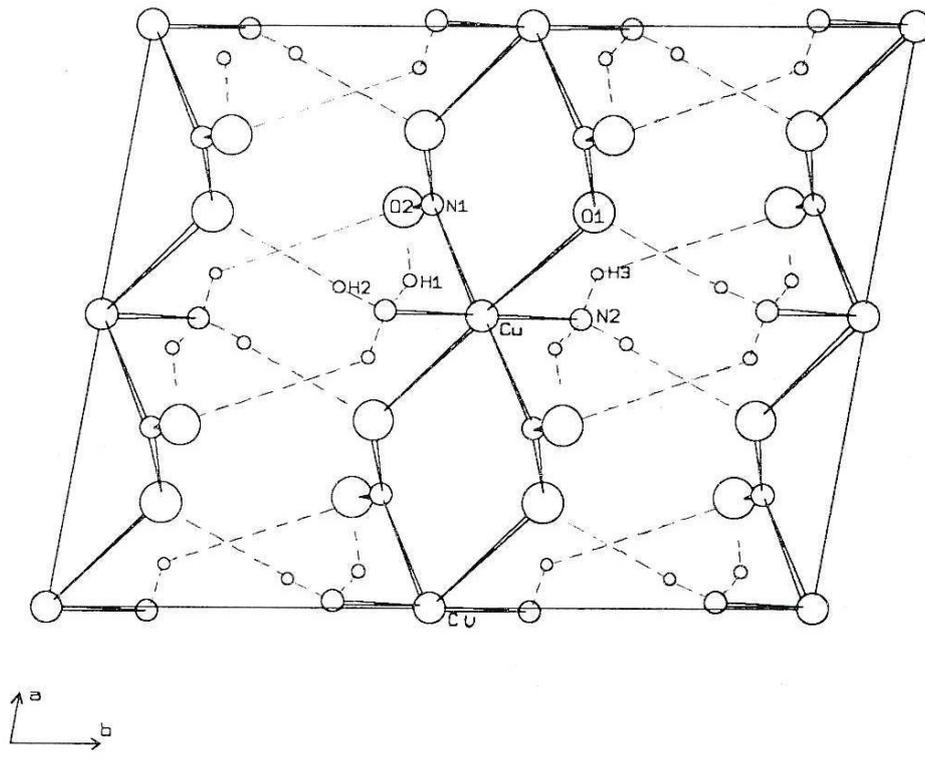


Fig 1: Projection of the structure along the c axis.