

## The Crystal Structure of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}^*$

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The room temperature crystal structure of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$  has been refined by the full-matrix least-squares method using 2338 Mo  $K\alpha$  intensity data. The space group is  $I2/a$  with lattice constants  $a_0 = 16.453$ ,  $b_0 = 4.936$ ,  $c_0 = 15.963$  Å and  $\beta = 93.765^\circ$ . The copper ion is surrounded by four oxygen atoms from two water molecules (1.959 Å) and two  $\text{NO}_3^-$  oxygen atoms ( $\sim 1.99$  Å) in a near square-planar arrangement, by two more distant oxygen atoms belonging to these same  $\text{NO}_3^-$  groups ( $\sim 2.66$  Å) and by an oxygen atom (2.39 Å) of an adjacent  $\text{NO}_3^-$  group. The copper ions are connected via the oxygen atoms of the  $\text{NO}_3^-$  groups forming a crooked chain-like arrangement, and a network of hydrogen bonds hold these chains and the water of hydration together. Differences in the nitrogen-oxygen separations in  $\text{NO}_3^-$  groups appear to be correlated with chemical bonding in the structure.

This X-ray study on  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$  was initially undertaken to provide detailed structural evidence to support low-temperature thermal and magnetic measurements (Berger, Friedberg & Schriempf, 1963; Friedberg & Raquet, 1968; Wittekoek & Poullis, 1968; Myers, Berger & Friedberg, 1969) which had been interpreted to be those of a salt in which the cupric ions were associated in pairs. A system of such pairs (or binary clusters) is found in cupric acetate and other cupric alkanoates. In cupric acetate (van Niekerk & Schoening, 1953), the cupric ions are found to be structurally paired by the acid groups forming a binuclear molecule,  $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ , with a Cu-Cu separation of 2.64 Å. The earliest structural study on  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$  (Dornberger-Schiff & Leciejewicz, 1958) contained several misprints, among which were the chemical formula, the densities and the location of a water molecule; hence Garaj (1968) did not recognize this earlier work when he reported on the crystal structure of this compound. Concurrent with the appearance of Garaj's study, we had nearly completed our more precise and detailed study; hence in this note we summarize our structure results and provide the details of the hydrogen bonding found in  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ .

The space group,  $I2/a$ , was selected on the basis of systematic extinctions ( $h+k+l$  odd for  $hkl$ , and  $h$  odd for  $h0l$  reflexions absent), absence of a piezoelectric response, and statistics of the normalized structure factors calculated from the intensity data. The lattice constants  $a_0 = 16.4539(4)$ ,  $b_0 = 4.9384(3)$ ,  $c_0 = 15.9621(3)$  Å, and  $\beta = 93.765(2)^\circ$  were obtained by a least-squares fit of 60 high  $2\theta$  values measured on films taken with a 115 mm diameter Weissenberg camera utilizing Straumanis film loading and Cu  $K\alpha$  radiation ( $\lambda$  for  $K\alpha_1 = 1.54050$  Å). With eight molecules per cell, the observed and calculated densities are 2.35 and 2.38

$\text{g.cm}^{-3}$  respectively. The 2335 three-dimensional Mo  $K\alpha$  intensity data were measured with a scintillation counter employing pulse-height discrimination using the  $\theta$ - $2\theta$  scan technique; of these data, 285 were considered to be unobserved.

No absorption corrections were included for the crystal specimen of dimensions  $0.23 \times 0.08 \times 0.12$  mm mounted along the longest direction ( $a$ ) ( $\mu_{\text{Mo}K\alpha} = 15.3 \text{ cm}^{-1}$ ). Lorentz and polarization factors were applied and structure factors calculated using  $\text{Cu}^{2+}$ , N, O and H scattering factors from Table 3.3.1A (p. 202) and dispersion corrections for copper from Table 3.3.2C (p. 215) of *International Tables for X-ray Crystallography* (1962). Positional parameters were obtained from a Patterson synthesis and subsequent Fourier syntheses. Atomic positional and thermal parameters were refined by full-matrix least-squares refinement, with the function,  $\sum w(F_o - F_c)^2$ , minimized in which weights were assigned from counting statistics or, for unobserved reflections with  $|F_o| > |F_c|$ , set equal to zero. On the basis of a three-dimensional difference synthesis calculated with the refined parameters (the reliability index,  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , is 0.037 excluding unobserved and the  $20\bar{2}$ ,  $60\bar{2}$  and  $020$  reflections), the hydrogen positions were assigned and subsequently refined using isotropic thermal parameters along with the positional and anisotropic thermal parameters for the heavy atoms. The final  $R$  value is 0.034; the final atomic positional and thermal parameters are given in Table 1. The observed and calculated structure factors are listed on Table 2. Fig. 1 shows the structural arrangement and hydrogen bonding found in  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ .

Although there are no gross structural differences between Garaj's ( $R = 0.109$ ) and this refinement, many of the  $y$  coordinates for various atoms differ significantly; this leads to interatomic separations involving the copper environment which differ by almost 0.1 Å. Our interatomic separations and angles are given in Table 3. As Garaj pointed out, the copper atom has

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an unusual coordination. Fig. 2 shows this copper environment as well as the crooked chain-like arrangement by which the copper atoms are connected. As in  $\text{Cu}(\text{NO}_3)_2 \cdot \text{CH}_3\text{NO}_2$  (Duffin & Wallwork, 1966) and  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  (Morosin, 1969), the closer five neighbors around the copper atom form a slightly distorted [4+1] tetragonal pyramid in which the base of the pyramid is formed by 4 atoms at approximately

2.0 Å and the apex by an oxygen atom at about 2.3 Å. However in those compounds the copper atom is located about 0.2 Å above the plane of the base of the pyramid, while in  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$  the copper lies in the plane.

The spread (1.22–1.31 Å) found in the nitrogen–oxygen separations of the  $\text{NO}_3^-$  ions must be considered real. Similar spreads in N–O values have been

Table 1. Final atomic coordinates and thermal factors for  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$

	X	Y	Z	$B_{11}$ or B	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Cu	0.12613 (2)	0.01352 (6)	0.11376 (2)	1.915 (9)	1.755 (9)	1.804 (9)	-0.023 (7)	-0.272 (5)	-0.142 (7)
N(1)	0.1683 (1)	-0.0243 (4)	0.2797 (1)	1.74 (5)	1.83 (6)	1.96 (7)	-0.06 (5)	-0.08 (4)	-0.25 (5)
N(2)	0.4016 (1)	0.0765 (4)	0.9888 (1)	1.73 (6)	1.84 (6)	2.12 (7)	0.06 (5)	-0.10 (4)	0.13 (5)
O(1)	0.1914 (1)	0.0299 (4)	0.3534 (1)	3.12 (6)	2.74 (7)	1.77 (5)	-0.19 (6)	-0.34 (5)	-0.19 (5)
O(2)	0.1580 (1)	0.1685 (4)	0.2264 (1)	2.71 (6)	1.79 (5)	1.96 (6)	0.09 (5)	-0.60 (5)	-0.04 (5)
O(3)	0.1557 (1)	-0.2597 (4)	0.2556 (1)	3.45 (7)	1.88 (6)	2.92 (7)	-0.46 (6)	-0.33 (6)	-0.41 (6)
O(4)	0.4235 (1)	-0.0602 (4)	0.0500 (1)	3.24 (7)	2.49 (7)	2.66 (7)	-0.02 (6)	-0.31 (5)	0.99 (6)
O(5)	0.3725 (1)	-0.0160 (4)	-0.0785 (1)	3.40 (7)	1.95 (6)	2.57 (6)	0.00 (6)	-0.76 (5)	-0.43 (5)
O(6)	0.4096 (1)	0.3393 (4)	0.9941 (1)	2.63 (6)	1.57 (5)	1.99 (6)	0.01 (5)	-0.47 (5)	0.01 (4)
O(7)	0.2407 (1)	-0.0172 (4)	0.0883 (1)	2.13 (5)	2.35 (6)	2.72 (6)	0.05 (6)	-0.20 (5)	-0.16 (5)
O(8)	0.0119 (1)	0.0457 (4)	0.1399 (1)	2.01 (5)	2.12 (7)	2.20 (6)	-0.03 (5)	-0.29 (4)	-0.28 (5)
O(9)	$\frac{1}{2}$	0.0458 (6)	$\frac{1}{2}$	2.51 (9)	2.12 (9)	3.11 (10)		0.31 (7)	
H(1)	0.267 (3)	0.11 (1)	0.120 (3)	2.4 (10)					
H(2)	0.265 (3)	-0.18 (1)	0.099 (3)	2.5 (10)					
H(3)	-0.025 (3)	0.05 (1)	0.091 (3)	2.6 (11)					
H(4)	0.000 (3)	0.20 (1)	0.175 (3)	1.5 (8)					
H(5)	0.452 (4)	-0.05 (1)	0.247 (4)	4.8 (15)					

The temperature factor is of the form  $\exp\left(-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^*\right)$ .

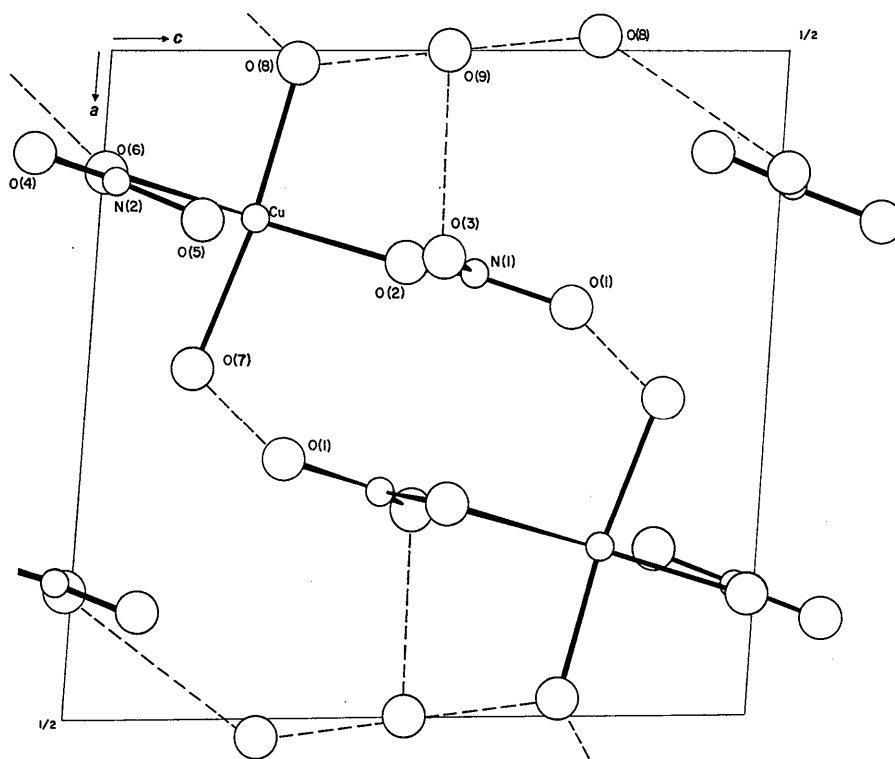


Fig. 1. A representation of the crystal structure of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$  viewed along the  $b$  axis. Solid and dashed lines indicate chemical and hydrogen bonding respectively.

reported in several other carefully determined structures containing NO3- ions. Among these are the studies by Zalkin, Forrester & Templeton (1963) on

Ce2Mg3(NO3)12.24H2O, by Garner & Wallwork (1966) on Ti(NO3)4, by Gallezot, Weigel & Prettre (1967) on Ni(NO3)2.4H2O, by Britton & Dunitz

Table 2. Observed and calculated structure factors for Cu(NO3)2.2.5H2O

\* Denotes 'less than'.

Table with multiple columns for h, k, l, Fo, Fc, and various indices. The table lists observed and calculated structure factors for Cu(NO3)2.2.5H2O. It includes a header row with column labels and a large body of numerical data. Asterisks indicate values 'less than' a certain threshold.



compounds, where a much larger number of reliable bond separations are available, that this averaging procedure may be questionable. In such sulfate compounds, the average O-H...O separations appear to be consistently longer whenever three, rather than two, hydrogen-bond interactions are involved. Since the

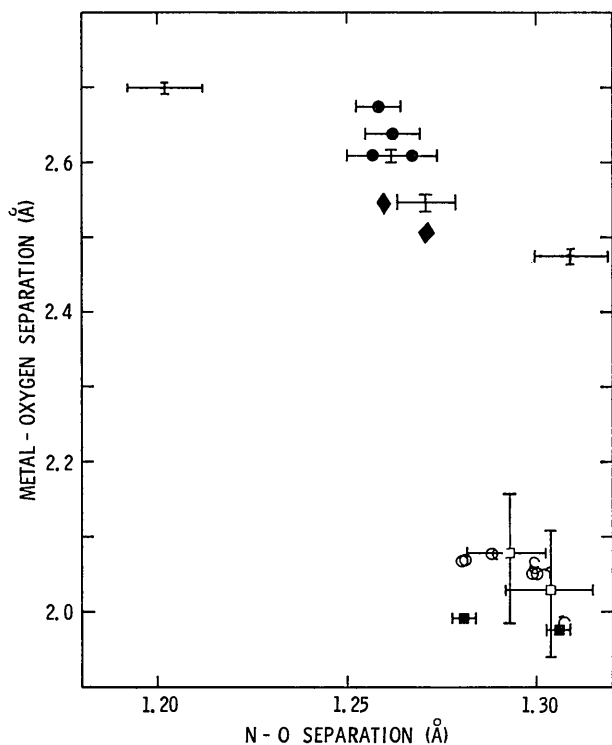


Fig. 3. The N-O bond lengths *vs.* metal-oxygen separations. The values shown are for the following ions: Ti (open circle, GW), U (solid diamond, TM), Ce (solid circle, ZFT), Ni (open square, GWP), Ag (crosses, BD), and Cu (solid squares, this work). (Initials are defined in the text.)

number of carefully determined structures containing nitrate ions is limited, we are unable to make a more detailed comparison in this case. However, we find a reasonably linear relationship for N-O separation *vs.* O-H...O separation in these nitrate compounds. (The average N-O separation of 1.185(6) found in  $\text{Ti}(\text{NO}_3)_4$  (GW) involves no hydrogen bond interactions and the 1.218(4) value in  $\text{NaNO}_3$  (SVD) involved in the Na polyhedra are the only accurate  $\text{NO}_3^-$  ion non-hydrogen bonded separations available for comparison with those given in Fig. 4.) It appears the ionic interactions and bonding associated with the hydrogen atoms in the lattice have a well characterized influence upon interatomic separation in anions. Our results on sulfate ions will be reported elsewhere.

Since our room-temperature structure results on  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  indicate a chain-like arrangement rather than isolated binary clusters as suggested by the low-temperature thermal and magnetic data, we have also examined crystals at liquid nitrogen temperatures. No gross changes in the intensity data, recorded by precession photographs, were found, suggesting that there is no structural phase transition upon cooling. Evidently long-range magnetic ordering requires favorable chain geometry (more linear as found in the copper tetrammine compound; Morosin, 1969) and, hence, the crooked chain system in  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  is favorable only to short-range exchange. The latter would yield properties very similar to binary clusters.

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Table 3. *Interatomic separations and angles in*  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$

(a) Those which involve the copper environment

Cu-O(8)	1.959 (2) Å	O(8)-Cu-O(6)	91.20 (8)°
Cu-O(7)	1.959	O(8)-Cu-O(5')	81.91
Cu-O(6)	1.978	O(8)-Cu-O(3)	90.72
Cu-O(2)	1.992	O(8)-Cu-O(2)	90.99
Cu-O(5)	2.391	O(8)-Cu-O(5)	90.14
Cu-O(3)	2.653	O(6)-Cu-O(5)	102.99
Cu-O(5')	2.675	O(6)-Cu-O(7)	89.18
		O(5')-Cu-O(7)	98.37
		O(3)-Cu-O(7)	89.11
		O(2)-Cu-O(5)	80.40
		O(2)-Cu-O(7)	88.63
		O(5)-Cu-O(7)	89.73

(b) Those which involve nitrate ions

N(1)-O(3)	1.238 (3) Å	O(3)-N(1)-O(1)	122.1 (1)°
N(1)-O(1)	1.241	O(3)-N(1)-O(2)	118.6
N(1)-O(2)	1.281	O(1)-N(1)-O(2)	119.2
N(2)-O(4)	1.222	O(4)-N(2)-O(5)	124.6
N(2)-O(5)	1.235	O(4)-N(2)-O(6)	118.3
N(2)-O(6)	1.306	O(5)-N(2)-O(6)	117.0

Table 3 (cont.)

(c) Those which involve hydrogen-bond interactions

O(9)-O(3)	2.922 (3) Å	O(3)-O(9)-O(3')	122.2 (1)°
O(7)-O(1)	2.787	O(1)-O(7)-O(1)	120.7
O(7)-O(1)	2.896		
O(8)-O(6)	2.838	O(6)-O(8)-O(9)	108.7
O(8)-O(9)	2.692		

(d) Those which involve hydrogen atoms

O(7)-H(1)	0.91 (8) Å	O(1)-H(1)	1.94 (8) Å
O(9)-H(5)	0.92	O(3)-H(5)	2.00
O(7)-H(2)	0.92	O(1)-H(2)	1.99
O(8)-H(3)	0.96	O(6)-H(3)	1.90
O(8)-H(4)	0.98	O(9)-H(4)	1.73
H(1)-O(7)-H(2)	108°	O(7)-H(1)-O(1)	155°
H(3)-O(8)-H(4)	107	O(7)-H(2)-O(1)	168
H(5)-O(9)-H(5)	119	O(8)-H(3)-O(6)	166
		O(8)-H(4)-O(9)	166
		O(9)-H(5)-O(3)	177

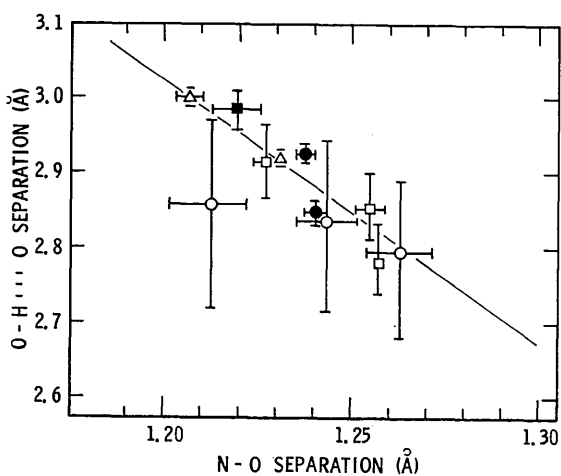


Fig. 4. The N-O bond lengths vs. O-H...O separation. The values shown are from GWP (open circles), TM (triangles), FBLT (squares), ZFT (solid squares), and this work (solid circles). (Initials are defined in the text.)

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