The Crystal Structure of Cu(NO₃)₂. 2.5 H₂O*

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(Received 5 June 1969 and in revised form 28 August 1969)

The room temperature crystal structure of $Cu(NO_3)_2.2.5 H_2O$ has been refined by the full-matrix least-squares method using 2338 Mo K α 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 NO₃⁻ oxygen atoms (~1.99 Å) in a near square-planar arrangement, by two more distant oxygen atoms belonging to these same NO₃⁻ groups (~2.66 Å) and by an oxygen atom (2.39 Å) of an adjacent NO₃⁻ group. The copper ions are connected via the oxygen atoms of the NO₃⁻ 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 nitrogenoxygen separations in NO₃⁻ groups appear to be correlated with chemical bonding in the structure.

This X-ray study on Cu(NO₃)₂.2.5H₂O was initially undertaken to provide detailed structural evidence to support low-temperature thermal and magnetic measurements (Berger, Friedberg & Schriempf, 1963; Friedberg & Raquet, 1968; Wittekoek & Poulis, 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, $Cu_2(CH_3COO)_4.2H_2O$, with a Cu-Cu separation of 2.64 Å. The earliest structural study on Cu(NO₃)₂. 2·5H₂O (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 $Cu(NO_3)_2 \cdot 2 \cdot 5 H_2O$.

The space group, $I_{2/a}$, 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 2θ values measured on films taken with a 115 mm diameter Weissenberg camera utilizing Straumanis film loading and Cu K α radiation (λ for $K\alpha_1 = 1.54050$ Å). With eight molecules per cell, the observed and calculated densities are 2.35 and 2.38

A C 26B - 1

g.cm⁻³ respectively. The 2335 three-dimensional Mo K α intensity data were measured with a scintillation counter employing pulse-height discrimination using the θ -2 θ 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) ($\mu_{MoK\alpha} = 15.3 \text{ cm}^{-1}$). Lorentz and polarization factors were applied and structure factors calculated using Cu2+, 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 Crystal*lography* (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 202, 602 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 $Cu(NO_3)_2 \cdot 2 \cdot 5H_2O$.

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

^{*} This work was supported by the U.S. Atomic Energy Commission.

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 $Cu(NO_3)_2$. CH_3NO_2 (Duffin & Wallwork, 1966) and $Cu(NH_3)_4SO_4$. H_2O (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 Cu(NO₃)₂. $2.5H_2O$ the copper lies in the plane.

The spread (1.22-1.31 Å) found in the nitrogenoxygen separations of the NO₃⁻ ions must be considered real. Similar spreads in N-O values have been

Table 1	. Final	atomic	coordinates	and i	thermal	factors	for '	Cu(l	NO ₃)	.2.5H ₂ O
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	X	Y	Ζ	<i>B</i> ₁₁ or <i>B</i>	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)	<i>−</i> 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)	<i>−</i> 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)	<i>−</i> 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)	<i>−</i> 0·02 (6)	<i>−</i> 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)	<i>−</i> 0·29 (4)	-0.28(5)
O(9)	$\frac{1}{2}$	0.0458 (6)	4	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 $\left(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_j^*\right)$.



Fig.1. A representation of the crystal structure of $Cu(NO_3)_2.25H_2O$ viewed along the *b* axis. Solid and dashed lines indicate chemical and hydrogen bonding respectively.

reported in several other carefully determined structures containing NO_3^- ions. Among these are the studies by Zalkin, Forrester & Templeton (1963) on

 $Ce_2Mg_3(NO_3)_{12}.24H_2O$, 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'.

L , LOF H# 0 2 23	0 10FC	L 10F	0 10FC 1 529	L 10FD	10FC 282	L 10F0	10FC -156	L 13	FO LOFO	-14	UFO 1	0FC L	10F0	10FC -135 -137	. 10 1 10	FO 10FC		612	0FC 798	L 10F	0 10FC 9 -191	-2	242 252
4 83 0 144 8 218 10 42 12 10 14 18	2 -792 4 -1495 7 2240 5 438 9 -168 4 -170	- 32 - 37 - 37 - 6 - 50 - 6 - 50 - 6 - 50	2 320 8 -370 8 -692 6 339 7 -565 -	-6 165 8 1137 -8 877 10 1316 -10 498 12 125	-149 -1131 -862 -1282 484	-22 106 H# 10 1 303 -10 00	-106 KJ 1 -295 2	-80 4 -10 1 -10 5 12 5	61 22 83 -100 52 560 24 -520	-16 18 -18 20 -20	241 - 279 - 229 309 - 358 75	245 -9 287 114 239 -11 320 134 362 -134	93 54 310 57 51	-100 -29 312 19 20	-10 30 -3 1 5 2 -50	65 17 54 2 68 170 40 255 64 47 85 -76	-6 -8 10	900 500 - 535 - 682 - 837 - 201	948 493 673 812 215	9 10 -9 21 110 0 -11 11 13 17	0 -100 2 -217 6 -100 2 179 8 -79		313 32V 427 423 116 -114 308 -311 209 -224 155 - 455
16 27 18 49 20 7 22 16 24 7	1 261 5 498 1 21 8 -172 8 -52	10 11 -10 54 12 34 -12 47 14 55	2 90 - 0 -538 7 343 - 3 -470 0 -551 -	-12 738 14 1087 -14 91 10 516 -16 607	716 1077 -100 532 -609	-3 104 5 142 -5 62 7 107 -7 435	-103 136 54 -110 -437	140 -14 2 10 2 -16 1 -18 2	78 2 60 -26 69 20 81 -17 02 20	-22•	77 3 K# 508 247 -	47 -15 17 2 -17 82 19 151 -19	53 115 81 94 73	-116 -55 -109	-7 -9• 11 -11•	90 -94 66 -31 43 -8 97 -106 68 26	12 -12 14 -14	162 500 850 81 267	162 506 861 -19 262	15 10 -15 7 170 -17 10 19 8	1 -61 7 25 2 U 6 -96 9 75	-10* -12	43 -2 216 216 20 K# 3 76 -57
HØ 2 0 13 2 135 -2 244	x 0 3 -109 3 -1355 8 2767	-14 19 10 41 -16 50 18 9 -16 7	7 202 5 -419 - 9 575 9 106 - 3 -80	18 542 -18 448 20 283 -20 330 22 173 22 173	-553 -463 -292 330 162	9 144 -94 31 41 67 -11 326 139 39	-152 -10 42 -328	-1 1 -1 1	6 K0 1 29 -112 81 -79		153 757 64 346 -	129 -214 150 59 0 155 2	10 10 298 1954	7 209 -1946	-13 1 -13 -15• -15• -17•	17 89 82 64 67 16 76 -39 63 -5	-16 18 -18 20 -20 -22	305 · 200 · 273 ·	-313 -259 -278 -206 -247	-19• 7 H# 11 0 60 2 70	KØ 3 KØ 3 -594 0 -698	- 30	71
-4 136 0 209 -6 71 8 130 -8 86	 1469 2200 -699 1287 -870 	48 16 0 65 2 7 -7 18	KJ 0 2 040 5 59 7 163	HE 4 1 88 -1 414 3 424	K# 1 - 81 440 - 434	15° 66 -15 191 17 85 -17° 70 19 117	+0 -184 -61 10 113	-5 -5 -7 1 -7 1	65 -2 70 41 47 -15 25 -10 69 -4	-9 -11 -11 +3	92 331 - 50 94	-82 4 40 0 84 -6	243 622 863 604 850	-220 623 829 -591 861	H 1	8 K# 2 68 -91 85 -702 15 527 29 -4	-1 -1 3	40 274 286	-13	- 19 - 19 - 11 - 19 - 11 - 19	2 493 5 174 1 452 6 -112 0 -191	-7• 9• -9• -11	12 -3 81 -22 77 9 110 -92
-10 61 -12 119 -12 98 -14 14	7 - 1095 7 590 0 - 1171 3 959 4 118	4 951 -4 1281 -0 261 -0 481 -0 481	-968 -1280 -254 -486 357	-30 24 5 408 -5 720 7 160 -7 84	414 728 -148 85	-19 150 210 81 -210 75	-149	-9• 11 1 -11 13 -13•	65 -21 62 -100 80 -51 95 41 72 32	-13 -15 -15 -17 -17	63 63 63 136	30 10 30 10 55 12 107 -12	269 976 197 248 297	-255 -980 170 -239 292		32 348 54 561 17 -433 27 332 74 -271	-3• -5 7 -7	37 208 135 352 -	203	-8 70 10 100 -10 11 12• 0 -12 25	0 -763 2 -1013 4 112 7 26 2 262		21 AB 3 185 -157 211 217 189 -191 95 97
40 66 -16 9 16 61 -18 39 20 63	9 680 9 -88 1 -408 6 J99 1 -440	10 7 -10 32 12 31 -12 33 14 35	5 50 328 3 -307 - 5 -339 9 -326 -	-9 845 11 193 11 59 13 149 13 360	805 203 -77 135 354	2 700 -2 168 + 695 -4 258 + 119+	-654 148 668 228 1179	-15.	77 -10 77 -10 9 10 1	-190 21 -210 -230	60 76 76	45 -14 100 16 14 -16 60 18 -18	183 372 247 199 73	-182 384 -249 -194 -24	-10 2 12 2 -12 2 14 1 -14	27 233 56 -244 16 215 93 183 63 -83	-9 -11 -13 -13	423 275 145 165	+31 288 134 104	-14 20 16 11 -16 47 16 42 -16 10	5 212 7 ¥6 5 -475 6 -423 8 -155	-0 -6 -6	153 - 155 192 - 155 76 - 61 22 - 66 - 5
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0 264 2 89 -2 31 4 79 -4 70 0 110	5 -2757 9 -925 1 -326 6 753 3 -809 9 1143	0 90 2 95 -2 37 40 40 -4 40	-77 -975 - 9 393 - 10 - 8 418 2 597	210 76 -21 84 230 63 -230 77	-58 70 -3 30	-12 534 14 949 -14 279 16 84 -16 472 18 424	530 960 279 91 -477 -431	-6 3 10 -10 12 -12	51 -45 61 -31 96 -495 70 -33 79 -34 75 146		517 504 398 - 063 -11	11 3 107 -3 100 5 108 -5 191 7 178 -7	202 53 214 120 362	-210	- 30 - 50 - 7 - 70 - 70	64 3 73 -17 68 72 78 -79 72 -14 74 -76	-21	5 NI 37	-110 38 38	-5 9 -7 7 -7 8 9 11	7 114 0 88 3 50 0 84 3 -108 3 94	H. 2 4 1	0 K0 4 •29 1•59 1•7 -150 053 -10•0 752 -700
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-12 42 14 31 -14 75 15 67 -10 7	6 428 8 310 7 741 8 -687 1 -01	-12 20 14 23 -14 17 -16 23	211 241 -108 -230	-6 1525 6 1100 -8 488 10* 45 10 1450	1554 -1074 -492 29 -1455	1 227 -1 135 3 281 -3 51 5 298	225 128 271 -44 293	-30 -5 -5 -5	72 30 67 -3 06 -6 70 -61 97 -64	-18 20 -20 22	515 - 599 - 175 104 371	25 15 09 -15 70 17 56 -17	1+3 7+ 82 72 78	-127 50 -74 13 32	H# 2 2 -2 -2	0 KB 2 52 -40C 72 39 84 -0C 90 399	-8 10 -10 12 -12	62 684 1041 222	61 671 1060 -210	-12 13	4 -96 124 7 -50	20• не -1•	76 - 55 1 49 4 227 - 200 60 - 15
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-244 7 He 6 50 2 35 -2 407	8 584 8 584 5 -371 2 -4825	-0 17 8 324 -8 21 10 24 -10 18	278 181 - 321 1 - 244 5 - 196	18 231 18 550 20 400 20 272 22 353 22 284	-237 -563 +15 -276 351 -275	-11 69 13 223 -130 64 150 69 -150 64 17 139	220 14 -84 27 120	-15* HØ 2 2 2 -2 1	-5 1 24 -221 88 300 49 -161	-3	74 10 220 289 176 176	40 -2 29 4 134 -4 198 6 185 -6	309 839 729 194 423 784	-295 808 712 189 405 -777	-10 1 -12 1 -14 1 H# 2	67 -106 60 151 37 137 1 K8 2 60 -7	-20 -20 H#	141 205 583	+00 -191 -275 586	-6 32 -8 65 -8 14 10 36 -10 55 12 46	2 323 3 -643 2 -148 9 377 7 -543 3 498	-9 11 -11 13 -13	502 -513 130 -129 374 -367 90 82 159 173 134 135
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10 11 -10 147 12 30 -12 78 14 24	98 5 - 1470 0 345 3 - 763 - 240	2 38 -2 15 -4 11 -4 11 -4 11	+08	5 222 -5 171 7 419 -74 43 94 8	-217 -167 -407 56 15	0 494 2 390 -2 506 4 554 -4 510	-477 374 -482 535 498	-10 2 -12 He 2	73 40 92 -364 97 -64 2 48 1	-150 170 -17 19 -190	61 67 178 146 71	53 -14 19 10 74 -16 13 18 19 -18	3+1 251 202 340 221	340 -260 -200 -351 -240	-7. 90 -90 -110	72 34 48 -3 62 7 60 23	-9 -11 -11 13	230 458 192 93 198	224 474 197 -97 -214	10 10 1 21 1 21	x# 3 3 35 5 259 5 140	на 2 -2	2 K8 4 289 -280 554 -933 743 790
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22. 7 -22. 7 -22. 7		0 34 2 9 -2 9 4 231 -4 19	354 -92 -92 -241 -162	170 05 170 56 19 120 19 61 210 68	69 · -113 · 77 ·	12 14 12 09 14 162 16 532 16 590 16 163	-01 150 534 -587 159	-7. 9. -9. -11.	76 -21 77 20 75 31 80 -10	-0 1	192 -1 192 -1 192 -1 192 -1 192 -1 192 -1 192 -1 192 -1	109 5 140 -5 192 7 101 -7	200 54 08 139 68	-254 -39 128 50	-6 2 -8 1 -10 1 H# 2	45 247 68 171 34 -135 3 KB 2	-21+	74 7 K 603	3	-11 14 -11 16 -13 11 -13• 5 -15 11	1 134 8 159 8 -141 7 9 1 -109	-10	1+7 138 596 -610 412 423 308 315 372 -376
-2 63 6 160 -6 105 6 85 -6 123	80 5 643 7 -1576 6 -1706 9 -826 7 -1236	-6 24; MB 0 1 18; 3 9; 5 63;	-253 - -188 -93 -673	HB 7 0 1242 2 1411	-33 55 - 1240 1346	18 143 -18 286 -20 358 -20 358 -20 358 -20 358	-143 -277 -352	-2 1 -2 1 -2 1	3 KB 1 09 189 00 190 30 -139 66 -00 57 -200	-10 -10 -12 -12	753 594 324 324 103	50 -9 574 11 519 -11 511 13 531 -13 59 15	193 05 71 174	57 192 30 24 -177 -37	-10 -3 1 -30 -7	78 -7 80 -40 16 -110 76 18 77 -57 90 -64		547 542 542 507 76	-575 -581 -368 501 91	-13* 4 -17 15 0 36 2 31	* 159 * 159 1 370 3 378	- 16 - 18 - 18 - 18 - 20 - 20	303 370 259 -264 70 -54 94 82 234 -249 198 207
8 92 -8 108 10 88 -10 80 12 7 -12 47	9 909 3 1081 0 848 7 802 5 82	7 200 9 191 11 54 13 25 154 55	187 192 -66 260 -64	-2 1204 4 703 -4 1083 6 1008 -6 637 8 188	-1220 -685 -1049 -960 628 159	-1 173 3 218 -3 205 5* 9 -5* 55 7 209	173 214 200 2 -53 206	-8 2 _10 2	48 - 151 76 84 12 223 4 48 1 81 18	-14 10 -16 18 -18	97 34 376 157 141 -	98 -15 55 17 572 -17 164 -19 135	72 124 68 78	-18 108 18 33	1 0 3 3 5 3	0 KØ 3 30 -627 69 47 41 360 73 691	-10 -10 12 -12	1082 869 108 266 536	1075 865 -103 -269 -529	-2* 0 4 21 -4 40 0 11 -0 21 0 16	1 -187 9 -294 4 -493 7 -143 1 280 0 179	H#	3 R. 4 439 -430 229 -219 254 256 235 -229
14 37 -14 84 16 45 -16 14 18 35	6 - Jo8 6 - 832 8 473 9 154 1 303	19. 61 21 114 23. 61	103 3 -	-8 1237 10 851 10 188 12 470 12 1112	1215 791 -180 -475 -1110	-7 173 9 87 -9 72 11 211 -11 265	144 73 57 201 252	-1. 3. -3. -5. 1	78 52	-20 22* -22*	76 78 7 Ki	17 -2	59 707 542 128 332	-26 691 -342 129 -335	9 2 11 1 13 15 1 17	52 -278 35 130 65 -58 83 185 89 -71	-14 16 -10 18 -18	172 110 546 356 323	-177 -109 544 356 320	-6 64 10 41 -100 1 120 1 -12 41	8 652 1 462 0 -41 6 15 2 -441	-5-799	187 -185 194 198 440 -473 287 -281 370 -575
200 -20 19 22 29 -22 32	-48 -186 -302 -324	2 167 -2 631 4 2594 -4 950 6 1144	-1798 - 622 -2797 - -992 1162	14 201 16 232 16 533 18 419 20 184	-185 -229 520 +36 194	13 79 15• 74 15 129 17• 74 17• 72	-35 37 110 26 49	0 23	85 3320 06 818 75 -2379 53 -739 56 726	- 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2	30 80 48	87 -6 -3 8 76 -8 25 10 16 -10	342 529 481 348 481	335 -533 485 349 -482	21+ 2	75 -00 1 48 3 50 -813	-20 H	157 8 K 90 158	-141	-14 14 -16 31 M# 10	8 -127 1 293 8 -246	-11 -13 -13 -15	120 -98 323 -339 132 151 205 -201 211 -205
2 140 -2 247 - 65 - 59	95 -1356 2508 -650 543	8 2021 -8 491 10 64 -10 1115 12 140	2046 483 - 40 1088 -1370	22 180 22 143 H# 8 1 509	-175 -133 K# 1 -576	Ha 13 0 363 2 441 -24 49	44 1 350 421 -90	12 5 14 2 16 18 3 20*	87 -561 48 -238 91 82 32 340	-7 -90 11 -11	84 82 93 -	69 -12 70 14 -0 -14 06 16 34 -10	402 309 162 310 452	-403 -319 147 -326 452	6 7 6 7 6 7 6 7	01 -1821 97 -681 80 764 52 -1035 64 852		191 176 14 32 421	150	-3 11	9 -202 5 126 6 142 5 -46	-17 -17 -19 -19*	48 -57 89 -68 82 -63 72 -57
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-12 34 14 60 -14 10 16 54 -16 23	-226 330 6 607 7 -120 552 1 -238	-18 476 20 302 -20 187 22 141 -22 165	-318 183 -160 -172 -	-7 140 9 523 -9 385 11• 53 11• 53 11 83 13 260	-136 -515 -385 -29 75 -280	10 409 10 77 12 136 12 640 14 641 14 151	403 66 126 -643 -446 -135	-5 1 -7 1 -7 1 9 0	18 629 19 -34 60 -164 96 183 49 146 10 -601	-19 21• -21•	109 10 17 17		125	116 -123 -5 56	16 3 -16 3 18 4 -18 2 20 2	51 -705 107 412 111 -314 58 107 34 235 53 -254	-15 17 -17• 19 -19•	252 97 59 95 72	-259 94 -14 -79 38	-15+ 0 H# 13	-16 44 3 -334	-6 8 -6 10 -10	537 542 458 -452 483 -500 428 -442 173 -108
18 10 -18• 71 20 11 -20 37 -22• 80	-112 -31 -116 302 -15	H# 2 L* 24 -1 431 3 794 -3 590 5 346	10 442 - 840 637 - 348	13 289 15 94 15 96 17 121 17 141 19• 68	-288 91 - -86 - -112 -116 -16	16 80 16 384 18 119 H9 16 1 130	-81 380 105 48 1 -129	-9 1 -11 2 -13 1 -130 15 1	66 -160 8 11 47 244 71 189 58 -47 63 169		512 1 259 5 579 -1 128 -1 589 -1	87 -9 145 11 166 -11 16 13 199 -13 158 15	72 132 70 146 92	19 30 128 -53 -137 66	-20 -22 #8 -1	2 KØ 3 117 -215 2 KØ 3 117 -308 36 -123	-210 -2	77 9 x 500 761 874	531 -751 805		-260 -260 -152 1 130 8 -299 -6 545	-12 14 -14 10 -10	108 105 364 375 463 463 171 -179 220 -220
HE 12 0 8 2 14 -2 49 4 148 -4 153	KØ 0 -145 -498 1448	-5 192 7 1029 -7 522 9 98 -9 62 11 584	205 - 1034 531 - -90 - -63 594	190 69 21 84 210 77 230 79	20 -71 -24 -23	-1 61 3* 59 -3 66 5* 61 -5 75 7* 62	38 -55 45 43 54 33	-15* 17* -17 1 19* -19* 21 1	61 55 56 - 7 91 - 184 63 - 26 70 17 09 85	-6 1 -8 1 10 -10	00 - 055 101 11 168 152 -	99 -15 41 17 89 -17 72 -19 39 86	70 127 74 74 77	-45 134 42 42	-3 3	19 224 87 176 80 592 98 312 47 454 84 81		830 625 531 947 522 238	-820 -820 529 -950 517 234	-80 L -10 4 12 2 -120 4	7 -2 8 -124 9 509 3 -208 7 18 1 -141	-18 -20* HØ	244 -251 342 -334 77 -37 326 -330
6 10 -6 37 8 680 -8 74 10 60 -10 40	160 375 -650 -65 -603	-11 300 130 50 -13 113 15 322 -15 192	345 14 119 323. 180	0 586 2 862 -2 1743 4 1181 -4 1429 6 108+	546 -831 1736 -1145 -1433 - 1005	-7 84 90 67 -9 144 110 39 110 64	-71 -62 137 -62 137 -72	-21 -23 -23 1	43 -25 42 -25 12 70 2 54 2	-12 14 -14 16 -16	140 - 155 - 137 - 160 130	38 0 34 -2 81 4 20 -4	930 72 65 454 714 330	949 -55 50 -451 -725 -336	-9 -11 1 -11 1 -13 1 -13 1	50 33 79 -65 07 98 32 122 120 329 55 265	10 -10 12 -12 -12 14 -14	241 627 699 69 180 386	-230 630 -720 45 -153 -394	HØ 11 1 24 -1 21 30 -30	4 3 2 -203 5 -203 1 0 2 11		30 -7 41 8 83 -70 96 92 557 -5/8 159 -171
12 19 -12 48 14 600 -14 452 16 27	385 490 614 449 -278	-170 50 19 133 -190 63 210 72 -210 71	-16 137 -13 37 26 -	-6 1243 8 868 -8 128 10 414 10 939	-1231 - 834 113 - 417 929 -	13 114 15* 74 15* 71 17 88 17 80	107 31 -34 -84 72	2 -2 + 12	12 -1741 39 1190 51 -457 33 1277 08 1378	-10 -20 -22	75 137 - 199 -	46 -6 86 8 19 -8 92 10 -10	422 592 401 71 308	-434 601 418 59 310	15* -15 1 17 1 -17 19 -19	53 7 19 115 17 -111 65 -55 82 -75	16 -16 -18 -20	243 71 179 224 149	249 -05 192 216 148	-5 -7 -7 -7 -7	10 -23 11 78 16 -75 19 -80 16 -154 19 -91	-7 -9 -11 -11	72 55 110 110 06 42 282 266 205 -206 05 -03
10 354 -18 174 200 76 -20 114	-360 -170 75 102	-25- 63 H8 3 0 1804 2 240 -2 1806	-2 - -1898 -190 -	12 64 14 313 14 484 16 458 16 36 18 161	-324 -324 -481 -15 106	HØ 17 0 473 2 477 -2 617 4 580	-480 -480 -480 -480	-8 9 -10 8 -12 9	92 972 58 -525 35 -820 00 77 58 -958 78 769	-1 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3	107 - 118 - 191 - 125 -	00 -12 28 14 81 -14 20 16 20 -16 29 -18	198 240 282 175 110 163	-194 -241 -278 108 103 158	-21 I	02 143 73 31 3 KØ 3 111 -781 102 -555	н -1 -3 -3 5	10 K 192 91 138 286 429	-200 -87 132 297 +31	-11+ -13 He 11	4 -18 17 -18 12 -33 14 -3 12 -304	-13 15 -15* 17* -17 19	379 - 381 208 - 207 68 40 66 8 113 113 271 228

Table 2 (cont.)

247 254 345 338 256 210 168 78 305 -10 270 65 42 232 297 583 100 139 168 81 337 123 353 353 245 245 251 148 255 153 -6 -10 -10 -12 -12 -14 -14 -14 testeretestestes arrieter errestes betreter betreter etter ere arrieter arrieter arrietere arrieteret 15 191 178 178 178 178 129 129 129 129 129 126 73 194 140 -1-3-357799111335577799111335577799111355 3227 1992 3333 461 318 174 258 49 75 108 153 111 75 HI - 13 - 5 - 7 - 9 - 1 x0 0 -193 -31 37 228 249 13 -158 -82 -35 234 9 191 71 75 225 57 145 244 57 1043 3399 13043 245 1043 3399 13043 245 191 94 16 558 340 446 340 446 340 446 340 133 114 232 145 324 145 324 145 120 73 94 206 147 73 94 122 67 88 1222 67 88 82 99 97 NON244466860012214 K4 6 -80 -381 352 -84 123 366 -249 235 -193 84 Ni 022446688 -10 H4 -10 -35 -57 -70 -11 HB -1 -3 - 3 - 5 - 7 - 9 H O 2 - 4 - 6 - 6 - 8 - 186 - 190 - 190 - 190 - 190 - 191 - 195 - 195 - 195 - 191 - 191 - 195 11 75 179 60 77 146 140 183 111 74 HO22244466880 18 707 28 275 275 275 277 170 1130 1607 1595 191 95 -270 16 -159 351 2961 104 -152 12 78 167 350 268 155 103 149 H 173755779911133 + 323 159 277 352 297 1-371 - 408 1 90 77 - 57 1 177 70 177 270 108 75 114 304 129 122 131 152 121 8 215 261 282 720 183 235 69 69 121 143 77 77 169 104 H -10 -3 -3 -5 -5 -7 13 79 70 84 215 77 147 <u>لامات المعالمة المعالمة لمواتدة المعالمة المعالم</u> 2 124 491 1361 221 3410 2830 244 1427 147 147 xy 4 -1489 -1489 7466 807 -336 607 -249 -226 -226 -216 10 209 957 738 351 594 341 465 518 229 336 175 106 175 106 246 77 9 318 281 572 370 240 357 240 298 3457 122 84 406 226 72 77 290 76 -119 259 -103 156 -205 295 133 ********** 1 334 347 113 505 105 209 13 ×111335577 x# 7 -181 -139 149 177 158 129 70 -276 -166 148 131 237 -265 2 175 140 128 105 174 145 145 84 11 140 249 132 93 122 257 197 224 93 140 139 145 205 80 10 354 128 340 101 195 299 73 235 2749 117 98 105 108 77 3 267 103 165 156 148 235 135 257 -150 -150 -144 -264 156 4 151 185 131 127 76 263 151 4 -532 -3033 -2228 -11 202 186 213 334 403 404 403 404 404 153 245 380 84 50 341 103 12 521 141 372 435 55 140 396 358 341 298 151 253 204 187 -233 19 -300 131 76 -218 106 +++++0 \$ 245 58 305 125 102 225 112 H# 0 2 -2 + + 6 - 8 - 8 - 8 - 10 - 12 - 12 + - 16 - 16 - 16 H 123 35 57 79 81113 H 0124 4 6 6 8 80 3 560 291 377 354 462 229 319 444 591 138 463 291 129 210 HI 10 -1 -3 -5 -5 285 285 -116 -97 -229 -133 6 69 291 119 118 234 144 13 136 269 215 88 263 239 130 65 48 80 49 117 235 130 102 ***** 7 116 110 301 113 191 -i 21.2 -243 -109 412 -457 -182 159 425 110 425 187 163 14 656 400 131

that the length of the N-O separation tends to increase with shortening of the Ag-O separation in a nearly linear relationship. In Fig. 3 we have plotted the metal-oxygen separation vs. the adjacent N-O separation for the previously mentioned studies. The longer metal-oxygen separation for any particular ion always appears to be associated with the shorter N-O separation. If we assume the 'effective' ionic radii of Shannon & Prewitt (1969) in order to subtract the metal ion contribution and, hence, normalize the separation, we find the iron group members to be situated on a line with a slope identical to that obtained by the Ag-O separations. Unfortunately 'effective' ionic radii of 1.15 and 1.25 Å rather than values of 1.30 and 1.29 Å for Ag⁺ and Ce³⁺ respectively, as well as a 1.13 Å 'radius' for the UO_2^{+} ion would be required to place all these data on a common straight line. [The 1.13 Å UO_2^{2+} ion 'radius' is reasonable considering Shannon & Prewitt's 1.36 Å oxygen radius and the 2.49 Å U-O (equatorial) separation in sodium uranyl acetate and uranyl carbonate (Zachariasen & Plettinger, 1959).] In Fig. 4 we have plotted values of the N-O separation vs. the O-H \cdots O separation for N-O bonds which are influenced only by hydrogen bond interactions. In cases where more than one interaction is involved, we have simply averaged the values. We find in sulfate



(1965) on AgCN.2AgNO₃, by Taylor & Mueller (1965) on $UO_2(H_2O)_6(NO_3)_2$, and by Sass, Vidale & Donohue (1957) on NaNO₃; all will hereafter be denoted by their initials. It has been previously noted by BD

Fig. 2. A schematic drawing of the crooked chains which link the copper ions in $Cu(NO_3)_2 \cdot 2 \cdot 5H_2O$. The two water oxygen atoms about the lower copper atom have not been included.

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 $O-H\cdots O$ 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 Ti(NO₃)₄ (GW) involves no hydrogen bond interactions and the 1.218(4) value in NaNO₃ (SVD) involved in the Na polyhedra are the only accurate NO₃⁻ 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 $Cu(NO_3)_2.2.5H_2O$ 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 $Cu(NO_3)_2.2.5H_2O$ 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 Cu(NO₃)₂. 2.5 H₂O

(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)	98·3 7
		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 involv	e nitrate ions		
N(1)-O(3)	1·238 (3) Å	O(3) - N(1) - O(1)	$122 \cdot 1 (1)^{\circ}$
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 i	iyarogen-bond inte	ractions	
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. $O-H\cdots O$ 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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