

Bolton, it is still significantly shorter than the expected minimum value of 3.1 Å corresponding to the sum of the minimum van der Waals contacts. It is to be noted that the present structure has no planar ring system, but an electronegative bromine atom is attached to the carbon atom C(24).

All the other packing distances seem to correspond to normal van der Waals separations.

As seen in Fig. 6, the gross feature of the crystal structure may be described as follows. The molecules are arranged in parallel chains along the twofold screw axes parallel to *c*. Within a chain the molecules are associated with each other head to tail, mainly through the van der Waals interactions involving the bromine and oxygen atoms O(8), O(6) and O(5) (Fig. 5). The chains are held together in the structure, as illustrated in Fig. 6, by the usual van der Waals forces and the C...O interactions described above.

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The Crystal Structure of Anhydrous Nitrates and their Complexes.

II. The 1:1 Copper(II) Nitrate-Nitromethane Complex*

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The structure of the complex $\text{Cu}(\text{NO}_3)_2 \cdot \text{CH}_3\text{NO}_2$ has been determined by two-dimensional Fourier methods. There are four molecules of complex in each orthorhombic unit cell of space group *Pnma* and dimensions $a = 12.41 \pm 0.04$, $b = 8.30 \pm 0.03$, $c = 7.08 \pm 0.03$ Å. Each copper atom has tetragonal pyramidal [4+1] coordination and the square bases of the pyramids are linked diagonally, through bridging nitrate groups at each corner, into corrugated sheets. The Cu-O distances within these sheets are all close to 1.95 Å and the fifth bond of length 2.31 Å to each copper atom is from an oxygen atom of the unidentate nitromethane. Adjacent corrugated sheets are held together in the *x* direction by van der Waals forces. The structure is compared with that of the α form of anhydrous copper(II) nitrate itself.

Experimental

Anhydrous copper(II) nitrate, prepared as described by Addison & Hathaway (1958), was dissolved in freshly distilled nitromethane at 60°C until a saturated

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solution was obtained. Blue-green crystals of the complex were deposited on standing and analysis for the copper content confirmed the 1:1 composition. The crystals were deliquescent so, for X-ray studies, they were mounted in thin-walled Pyrex capillaries in a dry box.

Oscillation and equi-inclination Weissenberg photographs showed that the crystals were orthorhombic and

* Part I, Wallwork & Addison, 1965.

Table 1. Final atomic parameters and their standard deviations

Atom	x/a	y/b	z/c	$B(\text{\AA}^2)$	$\sigma_x(\text{\AA})$	$\sigma_y(\text{\AA})$	$\sigma_z(\text{\AA})$	$\sigma_B(\text{\AA}^2)$
Cu	0.2272	0.2500	0.2016	1.6	0.005	—	0.005	0.1
C	-0.015	0.250	-0.272	4.9	0.060	—	0.082	1.4
N(1)	0.221	0.015	0.474	1.5	0.018	0.025	0.020	0.4
N(2)	0.058	0.250	-0.147	3.0	0.040	—	0.045	0.8
O(1)	0.158	0.087	0.357	1.5	0.016	0.020	0.016	0.3
O(2)	0.315	0.061	0.481	2.1	0.016	0.023	0.018	0.3
O(3)	0.180	-0.095	0.570	1.7	0.016	0.021	0.017	0.3
O(4)	0.174	0.250	-0.226	0.7	0.022	—	0.027	0.4
O(5)	0.071	0.250	0.026	1.4	0.026	—	0.029	0.5

systematic absences in the reflexions indicated that the space group was either $Pnma$ or $Pna2_1$. The former was assumed as the basis for structure determination because the crystals showed no pyroelectric effect. Intensities of the $h0l$, $hk0$ and $0kl$ reflexions were measured on zero layer Weissenberg photographs by a photometer method (Wallwork & Standley, 1954) and were converted into $|F_o|^2$ and $|F_c|$ values in the usual way. No corrections were made for X-ray absorption by the crystals ($\mu_{\text{max}} \approx 1.5$). The number of molecules per unit cell was estimated by comparing the volume of the unit cell with the value 465 \AA^3 for $\alpha\text{-Cu}(\text{NO}_3)_2$ (Wallwork & Addison, 1965).

Crystal Data

$\text{Cu}(\text{NO}_3)_2 \cdot \text{CH}_3\text{NO}_2$; $M = 248.6$.

Orthorhombic, $a = 12.41 \pm 0.04$, $b = 8.30 \pm 0.03$,

$c = 7.08 \pm 0.03 \text{ \AA}$,

$U = 729 \text{ \AA}^3$, $Z = 4$, $D_c = 2.26 \text{ g.cm}^{-3}$ $F(000) = 492$,

$\text{Cu } K\alpha$, $\lambda = 1.542 \text{ \AA}$, $\mu = 47.4 \text{ cm}^{-1}$.

Space group $Pnma$ (D_{2h}^{16} , No. 62).

Table 2. Observed and final calculated structure factors

Reflexions in parentheses were omitted from the least-squares refinement.

hkl	$ F_o $	F_c	hkl	$ F_o $	F_c
002	15	11	082	35	-37
004	57	58	084	18	20
006	30	28	091	16	-10
008	12	-13	093	22	19
(011	46	-75)	0,10,0	27	-28
013	20	-20	0,10,2	28	26
015	17	-10	101	13	15
017	41	-35	102	8	-10
019	19	18	103	23	20
020	70	-66	104	40	36
(022	86	164)	105	36	29
024	27	-22	106	48	-40
028	24	22	108	44	38
031	26	-21	(200	129	-212)
033	52	-75	201	18	-15
035	11	-4	202	13	1
037	19	18	203	18	16
040	112	117	204	44	-40
042	46	-54	205	32	31
044	50	62	206	17	-15
046	26	20	208	24	20
048	13	-11	210	74	-81
051	46	-49	220	38	-21
055	19	-11	230	99	88
057	33	-33	240	70	-56
060	135	-131	250	52	-39
062	40	43	260	77	60
071	41	41	270	39	33
073	13	-3	280	39	-32
080	62	54	290	26	-23

Table 2 (cont.)

hkl	$ F_o $	F_c	hkl	$ F_o $	F_c
2,10,0	18	16	505	45	45
301	36	39	506	23	-24
302	50	57	507	18	-18
304	73	-78	508	13	8
305	60	-56	600	33	27
306	20	16	601	38	-41
307	21	18	602	27	27
308	30	-28	603	44	37
309	7	-18	604	19	-16
400	44	52	605	12	-6
401	30	33	606	22	-17
402	38	-39	607	21	-19
403	35	-34	608	13	14
404	54	47	610	37	-43
405	51	-52	620	73	79
408	20	-20	630	81	88
410	19	15	640	77	-76
420	57	-53	650	40	-36
430	74	-67	660	10	-11
440	89	81	670	20	22
450	18	15	680	38	-35
460	18	-10	690	36	-37
470	17	-17	701	37	-35
480	41	36	702	17	19
490	26	23	703	55	60
4,10,0	23	-20	704	46	-49
501	29	-30	705	40	-34
502	48	-50	706	19	20
503	26	-28	707	8	11
504	62	63	708	7	-5

Table 2 (cont.)

hkl	$ F_o $	F_c	hkl	$ F_o $	F_c
800	48	-45	10,70	9	11
801	38	40	11,02	17	-10
802	55	-54	11,03	40	41
803	29	-26	11,04	15	16
804	10	-10	11,05	8	-9
805	40	37	11,06	13	13
807	24	22	12,00	29	24
810	52	58	12,01	50	54
820	30	-26	12,02	9	-2
830	58	-61	12,04	8	-7
840	22	18	12,05	12	15
850	50	47	12,10	54	57
860	18	18	12,20	13	-7
870	21	-22	12,50	40	46
880	15	11	12,60	17	-23
890	36	34	12,70	20	-27
903	65	-68	13,03	22	-23
904	21	18	13,04	20	-21
905	9	7	13,05	11	17
907	19	-21	14,00	10	6
10,00	9	-2	14,01	29	-32
10,01	65	-65	14,02	11	-7
10,02	25	19	14,10	34	-39
10,03	19	18	14,20	14	-13
10,04	18	13	14,30	8	14
10,05	28	-26	14,40	17	22
10,07	12	-17	14,50	25	-33
10,10	31	-33	15,03	12	21
10,20	8	9	16,00	5	-16
10,50	31	-31	16,10	7	17

Structure analysis

The general position in $Pnma$ is eightfold, so the copper atoms and the nitromethane molecules must occupy fourfold special positions in the unit cell. Only those of type (c) ($x, \frac{1}{4}, z$; $\bar{x}, \frac{3}{4}, \bar{z}$; $\frac{1}{2} - x, \frac{3}{4}, \frac{1}{2} + z$; $\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z$), which imply a molecular plane of symmetry, are possible for the nitromethane molecules. The copper atoms must also occupy special positions of type (c) because the alternative positions of types (a) and (b) would cause reflexions to be weak when $h+l$ is even and k is even, and this was not the case.

The positions of the copper atoms were derived from Patterson projections along each of the three crystal axes. The signs of the structure factors, calculated for copper atoms only, were used to calculate Fourier electron-density projections. From these most of the atoms in the structure were located. Successive F_o and $(F_o - F_c)$ Fourier summations enabled the positions of the rest of the atoms to be determined. The three sets of two-dimensional X-ray data, comprising a total of 177 independent reflexions, were put on an absolute scale by comparing F_o with F_c and they were then combined for a structure factor least-squares refinement on a MERCURY computer using Rollett's SFSL program (Mills & Rollett, 1961). The scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, Freeman (1959) for nitrogen and oxygen, and Thomas & Umeda (1957) for copper. The temperature factors B were assumed initially to be 1.0 and 2.0 \AA^2 for the copper and light atoms respectively. The program refined the over-all scale factor and the coordinates and isotropic temperature factor for each atom. At first all the reflexions were given unit weight, but after the first six cycles of refinement, when R had fallen to 0.21, the weighting scheme was revised so as to make the average $\sqrt{w(F_o - F_c)}$ approximately constant over the whole

range of F_o values. This was achieved by the weighting scheme $\sqrt{w} = \{1 + [(|F_o| - 40)/45.2]^2\}^{-1}$. After ten more cycles the refinement converged with $R = 0.13$.

The final atomic coordinates and temperature factors and their standard deviations are shown in Table 1 and the bond distances and angles calculated from these coordinates, with the use of a program written by Sparks, are shown in Fig. 1. The final Fourier electron-density projections are shown in Fig. 2 and the final values of F_o and F_c are given in Table 2.

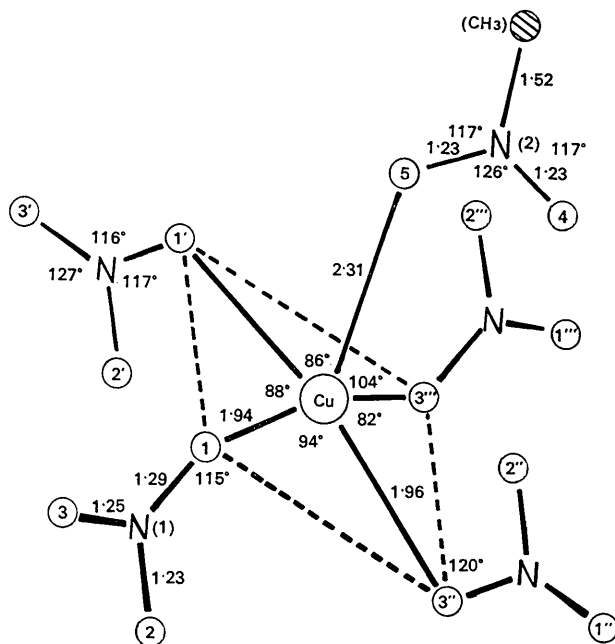


Fig. 1. The environment of each copper atom, showing approximate bond lengths and angles. The angle O(1)-Cu-O(3'') is 170° and approximate standard deviations for the bond lengths are $\sigma_{\text{Cu-O}} = 0.02$, $\sigma_{\text{N-O}} = 0.03$ (nitrate) and 0.05 (nitromethane), $\sigma_{\text{C-N}} = 0.09$ \AA .

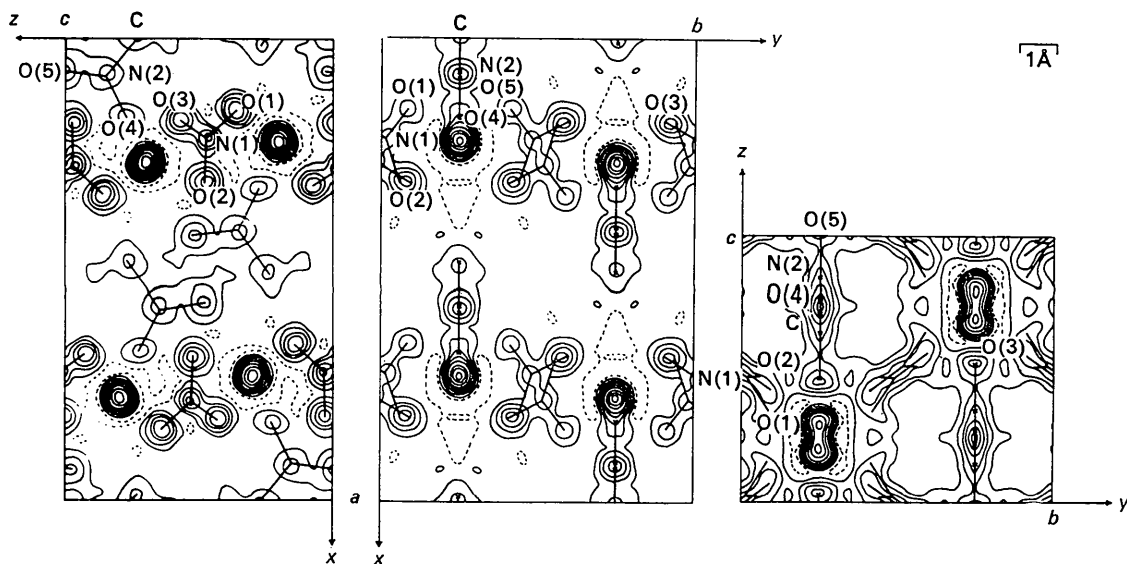


Fig. 2. Final Fourier electron-density projections, with indications of the light atom positions and the bonds joining them. Contours at 0 (broken line), 5, 10, 15, 20 $\text{e.}\text{\AA}^{-2}$ and thereafter at intervals of 5 $\text{e.}\text{\AA}^{-2}$ for light atoms and 10 $\text{e.}\text{\AA}^{-2}$ for copper atoms.

Description and discussion of the structure

Each copper atom has a slightly distorted [4+1] tetragonal pyramidal coordination in which the stronger Cu–O bonds of length about 1.95 Å in the base of the pyramid are all to nitrate groups. The weaker fifth bond, of length approximately 2.31 Å, is to an oxygen atom of the nitromethane molecule which is unidentate. The nitrate groups all act as bridging ligands. They link the square bases of the pyramids diagonally to form corrugated sheets whose mean planes are parallel to (100), as shown in Fig. 3. The sheets are then held together by van der Waals forces in such a way that oppositely tilted pyramids, related by the *a*-glide plane, are stacked above each other along the *a* axis. The nitromethane molecules protrude into the channels between the stacked pyramids. Detailed discussion of the structural dimensions would not be appropriate since they are derived entirely from projection data, but there are indications that the non-bridging oxygen of each nitrate group is the one most strongly bonded to the nitrogen atom and that each copper atom is slightly inside its oxygen pyramid, at a distance of about 0.2 Å from the plane of the base.

The only contacts less than 3.0 Å between atoms not directly bonded, apart from those along the base of each copper coordination pyramid, are Cu···N(1) and Cu···O(2), which are 2.74 and 2.75 Å respectively. These weak interactions, which are repeated for each pyramid by the mirror plane, possibly take the place of the missing sixth bond of the more usual copper coordination.

It is interesting to compare this structure with that of the α form of anhydrous copper(II) nitrate described in part I (Wallwork & Addison, 1965). Both structures exhibit essentially a [4+1] coordination of the copper atom, but this is achieved by different methods. In

α -Cu(NO₃)₂, half the nitrate groups form three approximately coplanar Cu–O bonds and half form two Cu–O bonds approximately perpendicular to the coplanar bonds. In the nitromethane complex, each of the nitrate groups forms only two Cu–O bonds and five-coordination is achieved, with less steric hindrance than in α -Cu(NO₃)₂, by making the fifth bond to a nitromethane molecule. It is probably this relief of steric hindrance, made possible by eliminating three-coordinate nitrate groups, which is responsible for the ready formation of complexes, even with such a weak ligand as nitromethane.

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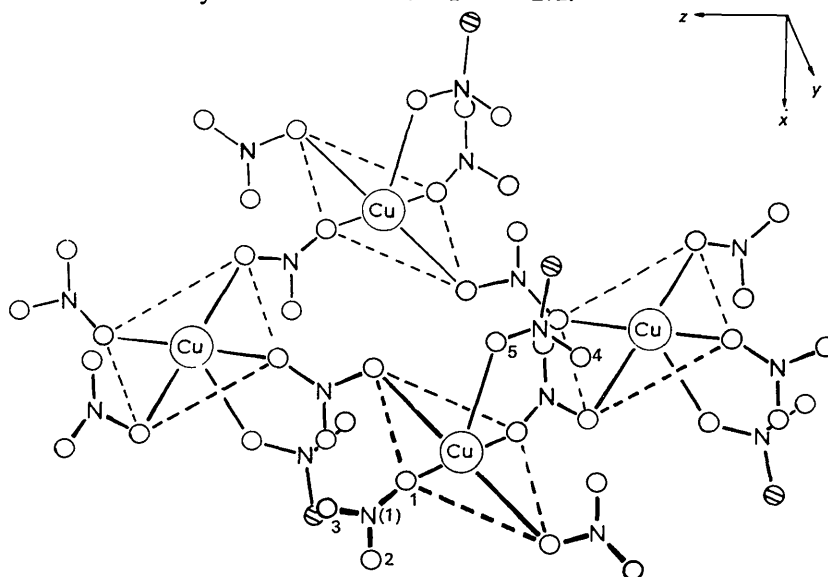


Fig. 3. Diagram of one corrugated sheet of the structure having its mean plane parallel to (100). Shaded circles indicate methyl groups.