526. *The Crystal Structures of Anhydrous Nitrates and Their Complexes. Part I. The α Form of Copper*(II) *Nitrate*

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Copper(II) nitrate in the α form crystallises with four $Cu(NO_3)_2$ in each unit cell of dimensions $a = 11{\cdot}12 \pm 0{\cdot}02$, $b = 5{\cdot}05 \pm 0{\cdot}01$, $c = 8{\cdot}28 \pm 0{\cdot}02$ Å and space group $Pmn2_1$. Each copper atom is co-ordinated by six oxygen atoms from five different nitrate groups in a distorted octahedral [4 + 1 + 1] manner. Each nitrate group forms a bridge between two copper atoms and one of the nitrates forms, in addition, the moderately weak and the weak [1 + 1] bonds in opposite directions from the third oxygen atom. The refinement of the atomic positions following the preliminary report of the structure [1] has thus resulted in a different and more normal co-ordination.

UNTIL the preparation by Addison and Hathaway [2] of anhydrous copper(II) nitrate, it was considered that nitrate groups must be weak ligands. This view was disproved by the chemical stability in anhydrous conditions of copper(II) nitrate; this stability permits it, for instance, to be sublimed without dissociation of the molecules in the vapour phase. The determination of its structure was undertaken to investigate the nature of the bonding in the solid state.

At a late stage in the structure determination, it was realised that solid $Cu(NO_3)_2$ may be obtained in two crystalline forms, which are very similar in appearance. The preliminary Note [1] and this Paper are both concerned with the α form, which has only been obtained as a single phase in powder form by heating the compound $Cu(NO_3)_2{\cdot}N_2O_4$ *in vacuo* to about 100°. It is obtained as single crystals by subliming this powder slowly, *e.g.*, in dry air at moderate temperatures, but the sublimate contains a proportion of the β form, which increases on increasing the speed of sublimation. Sublimation at 200° *in vacuo* produces only the β form, and the α form is also transformed into the β form on heating (the conversion being rapid above about 150°). The characteristic features in the infrared spectra and in the powder diffraction patterns, by which the two forms may be recognised, have been reported in a separate Note.[3]

The preliminary report [1] of the structure of the α form emphasised the strong covalent bonding in chains of alternate copper atoms and nitrate groups, but drew what are now found to be incorrect conclusions about the nature of the cross-linking between the chains by further nitrate groups. More recently, an electron diffraction study [4] has shown that distinct $Cu(NO_3)_2$ units exist in the vapour phase, in which each NO_3 acts as a bidentate ligand giving either a flattened tetrahedral or a square co-ordination of the copper atom with covalent Cu–O bonds of length 2·0 Å making O–Cu–O angles of about 70°.

EXPERIMENTAL

Anhydrous copper(II) nitrate was prepared as previously described,[2] and crystals of a suitable size for *X*-ray photography were obtained by sublimation of the powdered material at approximately 180° in dry air at atmospheric pressure in a tube protected from atmospheric moisture by a guard tube containing phosphorus pentoxide. These crystals were either loaded directly into thin Pyrex capillary tubes in a dry box, or first mounted on glass fibres before being placed in the capillaries when alternative crystal orientations were required. In either case, the capillaries were sealed in a small flame within a few seconds of removal from the dry box. Because of the difficulty of handling the crystals, it was necessary to determine *X*-ray

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[1] S. C. Wallwork, *Proc. Chem. Soc.*, 1959, 311.
[2] C. C. Addison and B. J. Hathaway, *Proc. Chem. Soc.*, 1957, 19; *J.*, 1958, 3099.
[3] C. C. Addison, N. Logan, W. B. Simpson, and S. C. Wallwork, *Proc. Chem. Soc.*, 1964, 341.
[4] R. E. La Villa and S. H. Bauer, *J. Amer. Chem. Soc.*, 1963, **85**, 3597.

intensities on crystals of irregular and inconvenient shapes, for which the calculation of absorption corrections would have been too involved. At first only a- and c-axis oscillation and zero-layer Weissenberg photographs were taken and the corresponding intensities estimated. Later, oscillation and Weissenberg photographs were obtained with the crystals rotating about each of the three crystallographic axes, and intensities for the layer lines $0kl$, $h0l$ to $h2l$, and $hk0$ to $hk4$ were measured by a photometer method [5] involving the multiple film technique.[6] These intensities were corrected for Lorentz and polarisation effects and converted into F_0 values in the usual way.

The crystal data are as follows: α—$Cu(NO_3)_2$, $M = 187{\cdot}55$, orthorhombic, $a = 11{\cdot}12 \pm 0{\cdot}02$, $b = 5{\cdot}05 \pm 0{\cdot}01$, $c = 8{\cdot}28 \pm 0{\cdot}02$ Å, $U = 465$ Å^3, $D_m \simeq 2{\cdot}5$ (by displacement), $Z = 4$, $D_c = 2{\cdot}68$, $F(000) = 364$. Space group $Pmn2_1$ (No. 31) or $Pmnm$ (No. 59). Cu-K_α-radiation, $\mu = 66{\cdot}8$ cm.$^{-1}$.

STRUCTURE DETERMINATION

Examination of the Patterson projections on (100) and (001) showed that the copper atoms must be near to the positions $\frac{1}{4}\,\frac{3}{4}\,\frac{1}{4}$, $\frac{3}{4}\,\frac{3}{4}\,\frac{1}{4}$, $\frac{3}{4}\,\frac{1}{4}\,\frac{3}{4}$, $\frac{1}{4}\,\frac{1}{4}\,\frac{3}{4}$, or positions related to these by a change of origin, in either of the two possible space groups, and a number of possible positions for the nitrate groups were also indicated. The $0kl$ and $hk0$ structure factors were calculated for a number of possible trial structures with small movements of the copper atoms in various permitted directions from the special positions mentioned. Comparison with the corresponding F_0 values (which were the only ones that had been estimated at that time) showed that the space group $Pmnm$ did not allow sufficient movement of the copper atoms from the special positions to make it possible to derive any trial structure giving satisfactory agreement between F_0 and F_c. This, together with indications of a centric distribution for the $hk0$ intensities and a non-centric distribution for the $0kl$ intensities, permitted the rejection of the centrosymmetric space group $Pmnm$. A trial structure having the space group $Pmn2_1$ and derived from Fourier electron density projections on (100) and (001), phased by the copper atoms only, was refined [1] in these two projections to give $R = 0{\cdot}20$. However, attempts to refine this structure further with partial three-dimensional values uncovered difficulties arising from the false symmetry described below. It was therefore decided to make a fresh start with the structure determination using all the intensity data that were available.

Use was made of a programme named " FATAL " newly developed by Hodgson, Rollett and Stonebridge [7] for the MERCURY computer; in this the structure factors are calculated for the input atomic positions and these are used to calculate a three-dimensional Fourier electron density function, which is then scanned for peaks. The output gives the co-ordinates and approximate electron counts of all the peaks above a predetermined size. It also notes the approximate positions of all the peaks that are not locatable by a 19-point routine and gives the interatomic distances between all possible pairs of peaks. Starting only with the copper atom in the position previously determined, most of the peaks found that were above 4 eÅ^{-3} corresponded with some of the previous light-atom positions and with related false peaks generated by the two extra approximate mirror planes caused by the nearly special position of each copper atom. Several of these possible peaks could be eliminated as being too close to the copper atom. Other peaks, which were taken to be spurious owing to diffraction effects from the restriction of the intensity data, were in positions related to those of the copper atoms by translations of either $a/4$ or $b/2$. The two strongest of the remaining peaks were related by one of the false mirror planes, and each was used in turn as an input atomic position, combined with the copper atom. This use of one position from a pair partly removed the false symmetry, and resulted in two equally acceptable sets of peaks, which could correspond to light atom positions. These peaks still included some related by false symmetry elements, and, in order to find which peaks were genuine, all the possibilities in each set were included in a separate site-occupation least-squares analysis.[7] In one case, 4 cycles of least-squares reduced R from $0{\cdot}34$ to $0{\cdot}27$ and in the other case 4 cycles reduced R from $0{\cdot}33$ to $0{\cdot}20$. Structure factors and a scan of the Fourier electron-density peaks corresponding to each set of output positions were then obtained by using the " FATAL " programme. The set of peaks obtained from the

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[5] S. C. Wallwork and K. J. Standley, *Acta Cryst.*, 1954, **7**, 272.

[6] J. J. De Lange, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc.*, 1939, *A*, **171**, 398; J. M. Robertson, *J. Sci. Instr.*, 1943, **20**, 175.

[7] L. I. Hodgson, J. S. Rollett, and B. R. Stonebridge, to be published.

sites giving $R = 0{\cdot}20$ corresponded closely with the atomic positions in the previous partial refinement based on the $0kl$, $h0l$, $h1l$, $hk0$, $hk1$ and $hk2$ data, with the addition of some extra peaks, which were either too near to the copper atom or too low in electron count to be acceptable. The acceptable peaks were subjected to a normal least-squares refinement,[8] with isotropic temperature factors, using all the available structure factors, with weights $\sqrt{w} = 1$ if $|F_o| > 50$, otherwise $\sqrt{w} = 50/|F_o|$. R dropped smoothly in five cycles of refinement to 0·14. The set of peaks obtained from the application of the " FATAL " programme to the sites having $R = 0{\cdot}27$ did not correspond to a satisfactory system of interatomic distances. More prolonged attempts at refinement did not reduce R below 0·18 and still resulted in unsatisfactory interatomic distances. This set of possible atomic positions was therefore rejected in favour of the other set corresponding to $R = 0{\cdot}14$.

By contrast with the previous attempt to refine the acceptable atomic positions with mainly projection data, the temperature factors in the new least-squares output were quite reasonable. Further refinement, with the more appropriate weighting scheme $\sqrt{w} = [1 + (|F_o|/20)^2]^{-\frac{1}{2}}$ and with anisotropic temperature factors for all atoms, led to the final set of atomic positions given in Table 1 and to the structure factors of Table 4, which have an agreement index R of 0·117. In view of the rather limited data obtained from crystals of different shapes and dimensions and the lack of correction for absorption, high accuracy in atomic positions cannot be expected and no significance can be attached to the anisotropy of the temperature factors. In Table 1 an equivalent isotropic temperature factor is quoted, and was obtained by taking the mean of the magnitudes of the principal axes of each vibration ellipsoid. The standard deviations of atomic positions derived from the normal equations matrix are also represented by average isotropic values in Table 1.

TABLE 1

Final fractional atomic co-ordinates and isotropically averaged standard deviations and temperature factors

Atom	x/a	y/b	z/c	σ_{av} (Å)	B_{av} (Å^2)
Cu	0·7487	0·7692	0·2469	0·008	1·9
O(1)	0·775	0·295	0·275	0·023	1·4
O(2)	0·801	0·388	0·533	0·024	1·6
O(3)	0·782	−0·011	0·445	0·025	1·4
O(4)	0·902	0·838	0·149	0·025	1·5
O(5)	0·596	0·667	0·347	0·026	1·7
O(6)	0·000	0·655	0·341	0·043	2·5
O(7)	0·500	0·971	0·203	0·049	3·3
N(1)	0·784	0·225	0·408	0·028	1·3
N(2)	0·000	0·760	0·210	0·029	0·4
N(3)	0·500	0·784	0·278	0·055	3·0

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The atoms are shown in their final least-squares positions, together with the final Fourier electron-density projections along each of the three axes in Figure 1. A general view of the structure is shown in Figure 2, the viewpoint being the same as that for the corresponding view in the previous note, to show the changes in atomic positions that have taken place subsequently. Although these changes are small for all atoms apart from O(4) and O(6), they lead to a different interpretation of the bonding in the structure. There are still chains parallel to the *a* axis of alternate copper atoms and nitrate groups strongly bonded together, but it is now seen that these chains are also linked sideways by strong bonds between alternate copper atoms and nitrate groups. This sideways linking runs in a zig-zag manner, for example from Cu″ near $\frac{3}{4}$, $\frac{5}{4}$, $\frac{3}{4}$ to Cu near $\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{4}$ and back to the repeat of Cu′ by the *c* translation, giving rise to corrugated sheets of strongly bound copper atoms and nitrate groups with the average plane of each sheet parallel to (010). The Cu–O bonds within each corrugated sheet form the usual approximately square-planar arrangement, round each copper atom with a mean length of 1·98 Å.

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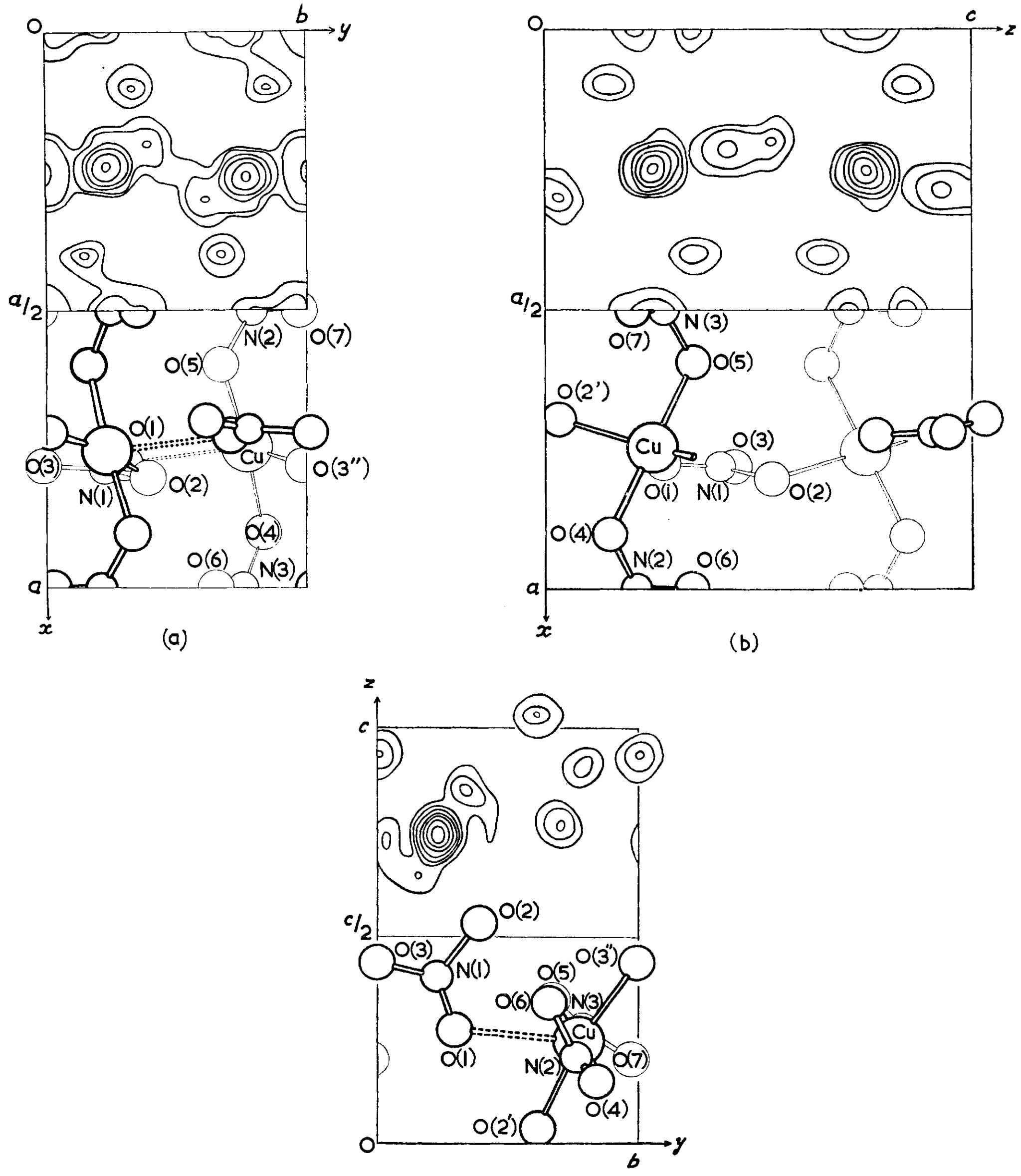
[8] R. Pepinsky, J. M. Robertson, and J. C. Speakman, " Computing Methods and the Phase Problem in *X*-ray Crystal Analysis," Pergamon Press, Oxford, London, New York, Paris, 1961, p. 107.

Between these sheets there is weaker Cu–O bonding through O(1). This atom is situated at a distance of 2·68 Å from the copper atom to which the nitrate group, of which it is part, is already linked by the Cu–O(3) bond, but it is also 2·43 Å from the adjacent copper atom in the next sheet, this copper atom being the repeat of the previous one by the *b* translation. If significant bonding properties are attributed only to the 2·43 Å bond, each copper atom has a co-ordination number of 5, better expressed by the symbol [4 + 1]. If the 2·68 Å distance is also regarded as a bond, then each copper atom has a co-ordination



(a) (b) (c)

FIGURE 1. Fourier electron density projections along each of the three crystallographic axes and projections of the atoms in their final least-squares positions. Contours for *hk*0 and *h*0*l* projections (*a*) and (*b*) at 5, 10, 20, 30, 50, 70 e.Å^{-2}; for 0*kl* projection (*c*) at 10, 20, 30, 50, 70, 90, 110 e.Å^{-2}

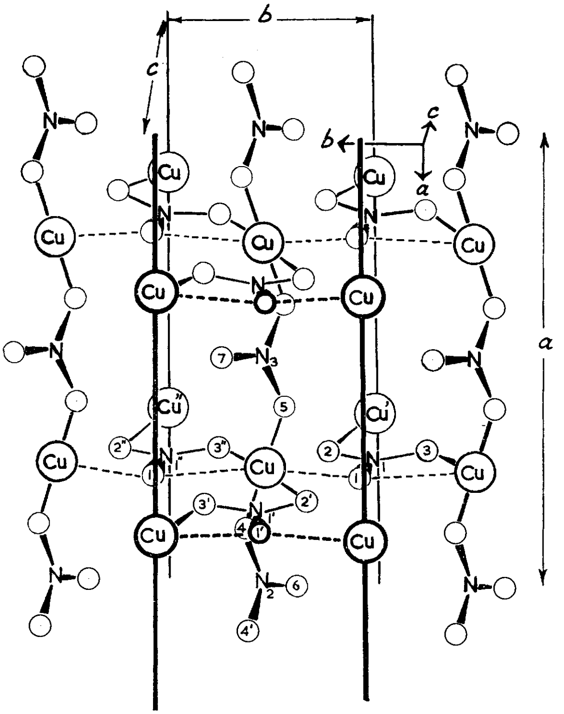


FIGURE 2. General view of the structure. Broken lines indicate the weaker Cu · · · O interactions

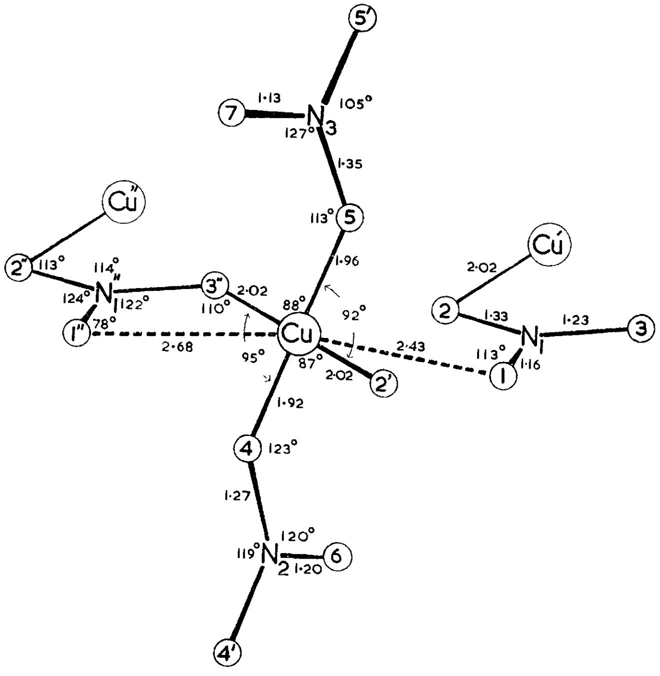


FIGURE 3. Bond lengths in (Å) and bond angles

number of 6, which differs from the more usual [4 + 2] in having unequal weak bonds, and is better expressed as [4 + 1 + 1]. In any case, the nitrate group N(1)O(1)O(2)O(3) forms a bridge between three copper atoms and, if the copper atom co-ordination is taken as being [4 + 1 + 1], then the extra weak bond Cu–O(1) together with the strong bond Cu–O(3) gives some bidentate character to the bonding of this nitrate group. This is thought to be the first example of this type of bonding by a nitrate group, and it emphasises the strong ligand properties of this group. The other nitrate groups in the structure perform the more usual function of bridging pairs of copper atoms.

The details of the environment of each copper atom and the bond distances and most of the bond angles are given in Figure 3. The bond angles that are not illustrated in this figure are given in Table 2. Average standard deviations for bonds between light atoms and for Cu–O bonds are 0·04 and 0·03 Å, respectively Since these may be underestimates, in view of the nature of the initial data, it is not appropriate to discuss the bonding

TABLE 2

Further O–Cu–O angles (degrees)

	Cu–O(1)		Cu–O(1″)
Cu–O(1″)	163		0
Cu–O(2)′	74		120
Cu–O(3″)	116		50
Cu–O(4)	96		76
Cu–O(5)	79		109
O(2′)–Cu–O(3″)		169	
O(4)–Cu–O(5)		175	

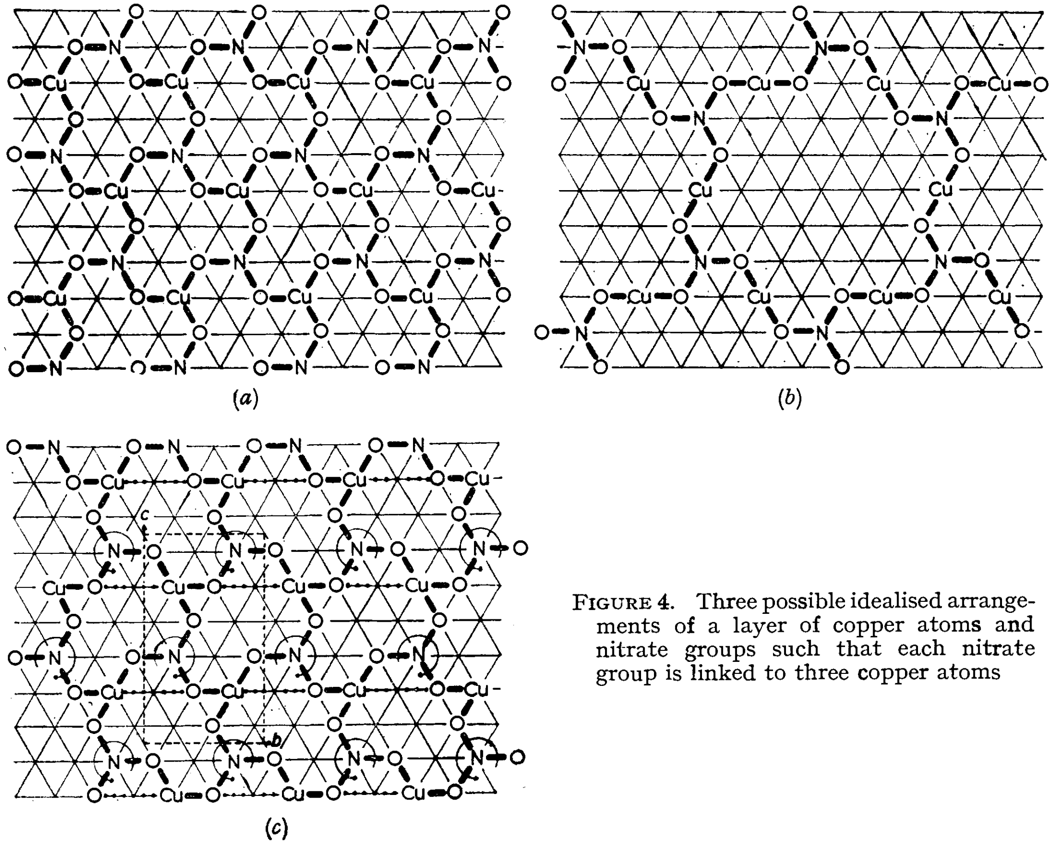


FIGURE 4. Three possible idealised arrangements of a layer of copper atoms and nitrate groups such that each nitrate group is linked to three copper atoms

in detail. However, there is no doubt that the four strong Cu–O bonds with an average length of 1·98 Å can be distinguished from the two weaker ones, and that the latter are unequal in length. Also, as might be expected, the N–O bonds to oxygen atoms that are strongly bound to copper are consistently longer than those to oxygen atoms that are not strongly bound, the average lengths for the two types of bond being 1·30 and 1·16 Å, respectively.

It is possible, by means of the following argument, to gain some insight into the way in which the structure arises. The maximum co-ordination numbers of copper atoms and nitrate groups can be taken as 6 and 3, respectively, and, if these were realised, the correct stoicheiometric ratio would be obtained. However, if the nitrate group is too bulky to permit the attachment of six different nitrate groups to each copper atom, the next-best choice is to have each copper atom attached to five different nitrate groups by allowing half the nitrates to form three Cu–O bonds and half to form only two such bonds. This is the actual situation in the structure of α-$Cu(NO_3)_2$. The layers perpendicular to the *a* axis consist of a pseudo-hexagonal array of copper atoms and nitrate groups each with a co-ordination number of 3 within the layer. The linking into chains parallel to the *a* axis through nitrate groups each with co-ordination number 2 then increases the copper co-ordination number to five.

The simplest way of building up the pseudo-hexagonal layers is shown in an idealised manner in Figure 4(*a*). This involves a trigonal arrangement round each copper atom, which would not be consistent with the usual tendency to octahedral co-ordination for copper atoms without bending the bonds so much out of the plane that the oxygen atoms would be brought too close together. Two possible arrangements involving linear O–Cu–O bonds are shown in Figures 4(*b*) and (*c*). In (*b*) an *anti*-arrangement is maintained for each pair of nitrate groups, and it can be seen that this leads to a cyclic structure that is too open in character and only permits a two-fold co-ordination within the layer for each copper atom. The corresponding structure with each pair of nitrates in a *syn*-arrangement is shown in Figure 4(*c*). This allows each copper atom to be co-ordinated by three different nitrate groups and gives a closely packed structure. Slight rotations of the nitrate groups in the directions indicated by arrows allow each copper atom to form a fourth weak bond within the layer as indicated by the dotted lines. This is the structure actually adopted in the α form of anhydrous $Cu(NO_3)_2$, as can be seen by comparing the unit cell indicated by broken lines in Figure 4(*c*) with Figure 1(*c*). This comparison also shows that the bridging nitrate groups above and below the layer take up positions such that the oxygen atoms that are bonded to each copper atom are as remote as possible from the oxygen atoms in the layer. Nevertheless, there are a number of oxygen–oxygen contacts of less than 3·0 Å, as listed in Table 3. It is presumably the repulsive forces resulting when this crystal structure is formed (in order to satisfy the bonding requirements of both the copper atoms and the nitrate groups), which cause its instability. The structure in the vapour phase [4] has the lower co-ordination numbers of 4 and 2 for the copper atoms and nitrate groups respectively. The repulsion is relieved, but the Cu–O–N angle of about 85° is less favourable than the average of 114° in the crystal structure of the α form. It is presumably for this reason that nitrate ligands are rarely bidentate in the solid state and usually perform the function of bridging groups. A determination of the crystal structure of β-$Cu(NO_3)_2$ is in progress.

TABLE 3

O · · · O contacts less than 3·0 Å between different nitrate groups

Oxygen atoms attached to the same copper				*Oxygen atoms attached to different copper*	
O(1) · · · O(2′)	2·71 Å	O(2′) · · · O(5)	2·86 Å	O(3) · · · O(4; $1\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$)	2·79 Å
O(1″) · · · O(4)	2·90	O(3″) · · · O(4)	2·90		
O(1) · · · O(5)	2·80	O(3″) · · · O(5)	2·75		
O(2′) · · · O(4)	2·71				

TABLE 4

Observed structure amplitudes compared with final calculated structure amplitudes and phases

hkl	$\|F_o\|$	$\|F_c\|$	α (deg.)	*hkl*	$\|F_o\|$	$\|F_c\|$	α (deg.)	*hkl*	$\|F_o\|$	$\|F_c\|$	α (deg.)	*hkl*	$\|F_o\|$	$\|F_c\|$	α (deg.)
002	109	130	195·7	224	59	57	3·8	503	29	24	24·7	814	9	10	357·3
004	86	75	353·7	225	18	14	256·7	507	11	9	205·4	815	31	29	354·2
006	56	47	175·8	226	49	50	174·9	509	17	15	311·8	816	6	7	132·1
008	34	32	16·4	227	15	13	341·0	510	46	32	90·0	817	28	29	167·5
00·10	35	33	166·6	228	35	35	12·9	511	24	22	264·8	818	5	6	54·5
010	20	26	0·0	229	4	5	152·7	512	22	19	169·6	820	58	55	180·0
011	97	142	244·9	22·10	12	14	189·9	513	19	20	87·4	821	19	17	319·4
012	18	15	125·8	230	10	8	0·0	514	10	11	72·7	822	52	49	358·7
013	70	70	178·4	231	34	36	352·3	515	25	28	72·7	823	8	8	168·3
014	61	50	283·2	232	24	26	191·7	516	17	18	315·8	824	41	41	179·3
015	40	34	341·6	233	48	52	167·5	517	7	8	50·5	825	17	17	347·1
016	27	25	227·1	240	52	49	180·0	518	25	28	172·8	826	29	29	354·5
017	33	27	131·6	241	28	28	351·5	519	4	4	23·2	828	23	23	170·0
019	39	41	338·0	242	40	37	26·8	520	19	16	90·0	830	22	16	180·0
01·10	3	5	194·2	243	33	29	201·8	521	17	17	276·1	831	34	40	172·9
020	89	120	180·0	244	25	23	162·9	522	22	19	295·2	833	28	30	359·8
021	23	26	342·6	250	25	23	180·0	523	17	17	160·1	840	36	36	0·0
022	89	113	5·5	251	24	21	186·6	524	31	29	285·2	842	30	31	166·8
023	60	59	130·7	253	25	21	1·7	525	13	12	151·9	844	26	31	355·8
024	55	50	192·8	254	10	12	137·1	526	14	12	63·2	851	22	22	356·0
025	16	15	42·6	260	16	17	0·0	527	11	10	21·8	852	20	18	177·8
026	49	45	349·4	261	16	15	171·5	528	7	8	3·4	853	19	18	160·5
027	24	25	214·8	262	20	16	185·7	529	4	4	67·2	901	23	15	137·2
028	34	38	186·9	263	22	23	183·2	531	26	26	124·3	903	24	18	131·3
029	7	9	70·2	301	48	38	331·9	532	23	18	159·6	907	12	12	354·4
02·10	12	15	9·0	303	36	28	4·7	540	14	12	270·0	910	19	16	90·0
030	18	13	0·0	305	16	11	316·9	543	18	16	115·2	912	17	20	341·4
031	46	44	176·6	307	28	23	150·8	544	12	12	98·5	913	12	14	104·4
032	37	36	302·7	309	12	10	42·4	553	10	11	144·0	914	11	11	139·1
033	53	65	346·7	310	57	44	270·0	600	106	84	180·0	916	7	11	284·9
034	16	16	117·9	311	24	27	267·8	602	72	63	6·4	917	4	6	38·5
035	27	30	175·1	312	20	18	180·9	604	45	36	166·6	918	8	9	165·5
037	31	35	333·3	313	17	14	261·7	606	41	39	11·9	920	13	11	270·0
039	18	18	145·4	314	9	7	329·5	608	35	33	181·7	921	11	10	230·5
040	51	53	0·0	315	12	11	227·3	610	11	12	180·0	925	9	9	148·6
041	36	30	146·2	316	14	14	5·2	611	53	57	177·5	926	5	4	227·6
042	53	46	192·1	317	11	11	260·4	612	4	7	214·1	927	6	4	89·3
043	40	33	354·1	319	4	6	224·8	613	37	43	346·0	930	16	10	270·0
044	49	47	329·3	31·10	4	4	348·6	615	26	24	173·7	10·02	44	37	351·5
045	22	22	196·9	320	37	40	90·0	616	6	6	56·2	10·04	49	41	174·8
046	34	43	179·2	321	7	7	293·2	617	29	28	349·8	10·06	38	37	2·4
048	21	17	340·6	323	18	15	4·2	619	24	26	165·3	10·10	6	6	180·0
050	34	32	0·0	324	18	16	164·5	620	65	66	0·0	10·11	24	22	197·9
051	37	22	352·2	325	11	9	188·6	621	19	21	143·4	10·12	5	7	82·0
053	47	37	159·7	326	10	9	109·3	622	57	60	176·7	10·13	34	35	350·4
054	22	22	321·8	327	14	14	335·1	623	12	12	324·8	10·14	14	15	284·6
055	33	31	351·3	328	5	5	177·2	624	39	40	359·5	10·15	37	37	175·6
056	17	16	164·4	329	10	11	183·5	625	9	11	193·2	10·16	7	8	264·6
060	12	13	180·0	330	12	10	90·0	626	32	31	176·2	10·17	35	30	0·5
061	25	24	350·6	333	11	14	31·9	627	8	8	63·6	10·20	29	26	0·0
062	18	19	347·0	334	11	16	348·5	628	26	28	3·7	10·21	11	10	198·4
063	22	23	183·2	343	13	14	228·9	629	8	9	197·5	10·22	33	28	169·1
064	17	20	172·2	344	12	9	19·3	630	20	20	0·0	10·23	22	18	80·7
101	10	5	73·3	400	167	146	0·0	631	33	35	350·8	10·24	38	38	354·9
103	42	33	161·9	402	95	94	193·3	632	23	20	134·4	10·25	10	10	162·6
107	12	7	353·9	404	84	97	352·1	633	32	34	179·9	10·26	24	26	180·1
110	7	6	90·0	406	65	66	176·7	640	29	29	180·0	10·30	21	20	0·0
112	33	33	6·2	408	30	25	1·0	642	23	24	12·9	10·31	26	29	355·3
113	22	19	87·5	40·10	16	16	173·1	643	17	20	160·7	10·33	16	18	189·3
114	25	22	156·6	410	33	24	0·0	644	27	30	188·2	10·40	26	23	180·0
117	5	4	37·1	411	57	62	349·6	653	18	16	11·5	10·42	20	21	347·5
119	5	5	87·3	412	17	16	251·0	654	7	9	134·9	11·01	20	17	334·0
120	21	23	270·0	413	60	78	175·7	701	34	29	328·3	11·03	18	16	206·7
121	17	21	229·0	414	17	18	301·3	703	30	20	348·4	11·05	9	9	278·1
122	11	9	344·8	415	53	60	350·1	705	15	12	292·0	11·10	10	12	270·0
123	23	18	14·2	416	12	11	178·0	707	28	24	163·8	11·12	9	10	56·9
124	8	8	86·3	417	34	34	150·0	709	11	12	40·1	11·14	8	10	190·5
125	15	14	167·9	418	9	7	256·1	710	42	35	270·0	11·15	5	8	255·5
126	7	6	279·9	419	23	23	330·1	711	17	18	287·5	11·20	10	8	270·0
127	6	4	7·4	41·10	2	3	173·1	712	20	19	165·9	11·23	13	13	5·8
12·10	3	4	78·5	420	65	70	180·0	713	14	14	276·0	11·24	8	10	99·8
131	14	19	236·7	421	23	23	31·2	714	5	5	330·5	11·25	6	7	203·3
133	11	8	341·0	422	73	80	3·9	715	8	10	222·5	12·00	36	35	0·0
140	14	12	90·0	423	28	28	195·6	716	11	11	34·5	12·02	53	50	173·1
200	145	133	180·0	424	59	60	184·5	717	10	11	254·3	12·04	29	24	359·0
202	46	40	36·8	425	18	17	11·0	719	7	7	215·5	12·10	5	5	0·0
204	83	92	175·2	426	48	49	351·1	720	35	28	90·0	12·11	39	47	9·6
206	73	73	5·4	427	12	12	156·7	723	13	13	358·5	12·12	10	11	126·4
208	37	35	206·0	428	29	32	182·9	724	13	11	161·2	12·13	28	28	179·2
20·10	26	25	352·8	431	38	45	172·1	725	6	6	200·3	12·14	6	7	19·5
210	11	8	180·0	432	17	18	32·7	726	9	8	101·5	12·15	23	19	343·6
211	37	42	118·7	433	47	50	349·8	727	14	14	331·6	12·20	35	34	180·0
212	40	38	102·1	440	60	61	0·0	728	4	5	170·9	12·21	13	10	311·5
213	54	60	348·1	441	21	21	178·9	730	17	15	90·0	12·22	29	28	355·5
214	19	15	67·1	442	46	43	181·4	743	11	16	237·2	12·23	8	7	132·4
215	59	60	172·7	443	29	31	23·2	750	14	5	270·0	12·24	30	28	175·3
216	16	16	52·5	444	33	34	333·8	800	85	71	0·0	12·30	14	12	180·0
217	36	31	338·0	450	24	25	0·0	802	88	78	180·3	12·31	28	28	182·0
218	12	12	75·3	451	34	33	353·1	804	51	43	350·1	13·12	4	7	291·0
219	32	32	161·9	453	29	27	155·4	806	36	34	182·2	13·14	2	2	96·2
21·10	6	6	347·2	454	12	16	336·3	808	24	27	337·8	13·20	6	6	90·0
220	56	70	0·0	460	27	23	180·0	810	22	17	0·0	14·00	18	13	180·0
221	34	35	227·7	461	20	21	354·1	811	59	64	5·9	14·02	19	26	339·7
222	72	86	178·1	462	23	22	347·0	812	9	9	112·0	14·11	20	28	187·6
223	32	30	19·6	501	77	77	166·4	813	44	50	173·2				

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