The Crystal Structure of Bis(glutaronitrilo)copper(I) Nitrate

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In a previous paper[1)] the authors have reported the crystal structure of bis(succinonitrilo)copper(I) nitrate. As a continuation of our crystallographic study of a series of complexes prepared from nitriles of aliphatic dibasic acids and univalent copper, the present paper reports the determination of the crystal structure of bis(glutaronitrilo)copper(I) nitrate, $[Cu(NC-CH_2-CH_2-CH_2-CN)_2]NO_3$. This work was undertaken to elucidate the mechanism of cuprous ion dyeing of polyacrylonitrile fibers[2)], and the structure of bis(glutaronitrilo)copper(I) nitrate may be particularly interesting in this complex series, because, as Rath et al.[3)] have suggested, it is considered to be most suitable as the model substance of the polyacrylonitrile fibers dyed with cuprous ion technique.

Experimental

Bis(glutaronitrilo)copper(I) nitrate was prepared according to the directions of Rath et al.[3)] similar to those described in the previous paper[1)].

Anal. Found: C, 38.15; H, 4.08; N, 22.12; Cu, 20.27. Calcd. for $C_{10}H_{12}N_5O_3Cu$: C, 38.28; H, 3.86; N, 22.32; Cu, 20.25%.

Minute prismatic crystals were chosen for X-ray study in order to minimize the effects of absorption.

Rotation and Weissenberg photographs, taken with Cu $K\alpha$ radiation ($\lambda=1.542$ Å), showed the crystals to be tetragonal with $a=8.25\pm0.01$ Å, and $c=9.71\pm0.01$ Å.

The observed extinction, $(h\,h\,l)$ with $l=2n+1$ and $(h\,0\,0)$ with $h=2n+1$, is characteristic of the space group $P\bar{4}2_1c-D_{2d}^4$.

The observed density of the crystals, measured by flotation, is 1.587 g./cc., while the density calculated on the basis of two formula units in each unit cell is 1.577 g./cc.

Complete intensity data for the $(h\,k\,0)$ and $(0\,k\,l)$ zones were obtained from Weissenberg photographs in conjunction with the multiple film technique. The $(h\,k\,0)$ data comprise 41 different reflections out of a total of 48 that are accessible, and the $(0\,k\,l)$ data represent 95 forms out of all 106 forms available.

All intensities were estimated visually. After being corrected for the Lorentz and polarization factors, the intensities were reduced to relative F_o values which were later converted into absolute values by comparison with calculated ones.

Determination of Atomic Positions

In the space group $P\bar{4}2_1c$ there are two independent sets of twofold positions: 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $00\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$. Since there are two formula units of $[Cu(NC-CH_2-CH_2-CH_2-CN)_2]NO_3$ in each unit cell, the copper atoms and the nitrogen atoms of nitrate ions must occupy these positions; the copper atom may be placed arbitrarily at the origin and the nitrogen atoms at $00\frac{1}{2}$. The point symmetry of these twofold positions is $\bar{4}$. This is in accordance with the expected tetrahedral coordination of a univalent copper atom. The nitrate ions thus centered at $00\frac{1}{2}$ are also required to have the same symmetry. However, trigonal nitrate ions could have the apparent symmetry $\bar{4}$ only if disorder exists in the crystal. The central carbon atom of each glutaronitrile molecule must occupy one of the two sets of fourfold positions and all other atoms probably lie on general positions. Consequently a glutaronitrile molecule must have a twofold axis of symmetry. Patterson projections upon (001) and (100) were calculated. These served to confirm the arrangement of heavy atoms. Both Patterson projections could be readily solved on the basis of the knowledge of interatomic distances and bond angles obtained for crystals of bis(succinonitrilo)copper(I) nitrate[1)], and the orientation of the glutaronitrile molecule in the crystal could be successfully deduced. In this way, all the coordinates of atoms except those of oxygen atoms were approximately fixed. It is almost evident that the phase angles of the structure factors for a complete set can be determined on the

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1) Y. Kinoshita, I. Matsubara and Y. Saito, This Bulletin, **32**, 741 (1959).

2) R. H. Blaker, S. M. Katz, J. F. Laucius, W. R. Remington and H. E. Schroeder, *Discussions Faraday Soc.*, No. **16**, 210 (1954).

3) H. Rath, H. Rehm, H. Rummler and E. Specht, *Melliand Textilber.*, **38**, 431, 538 (1957).

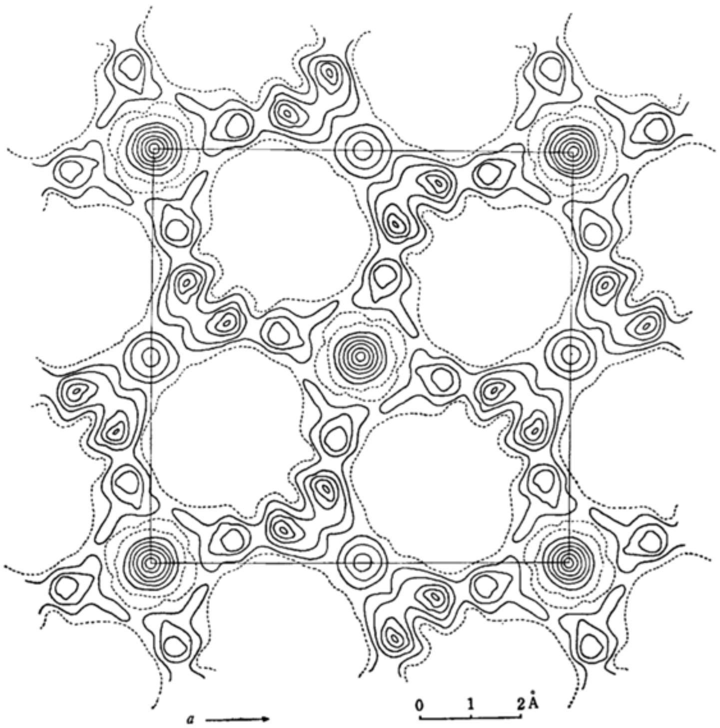

Fig. 1. Final Fourier projection of electron density upon (001). Contours are drawn at intervals of 8e Å^{-2} for copper and those for other atoms are at intervals of 2e Å^{-2}, the lowest being 2e Å^{-2}.

basis of these parameters. Fourier projections of electron density, $\rho(xy)$ and $\rho(yz)$ were then evaluated, the phase angles of which were calculated from the above mentioned parameter values. The projections so obtained showed the heavy copper atoms as well as ligand molecules clearly resolved, together with rather faint outlines of oxygen atoms in the nitrate ions. From the distribution of peaks around the nitrogen atoms, statistical orientations of nitrate ions were deduced. Calculation of structure amplitudes including the contribution of oxygen atoms improved the agreement

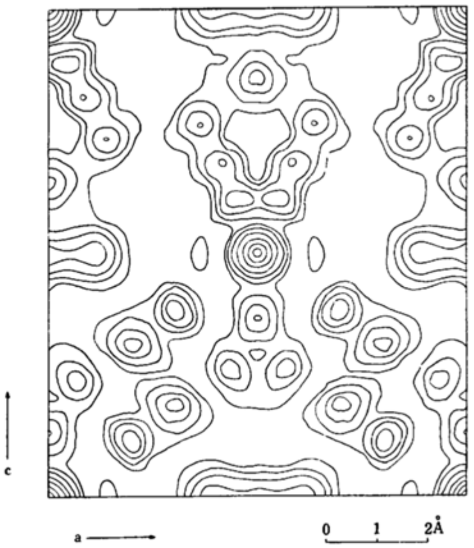

Fig. 2. Final Fourier projection of electron density upon (100). Contours are drawn at intervals of 6e Å^{-2} for copper and those for other atoms are at intervals of 2e Å^{-2}, the lowest being 2e Å^{-2}.

TABLE I. FINAL ATOMIC COORDINATES

Atom	Number of positions and Wyckoff notation	x/a	y/b	z/c
Cu	2 *a*	0.000	0.000	0.000
N_1	8 *e*	0.192	0.053	0.113
C_1	8 *e*	0.297	0.088	0.183
C_2	8 *e*	0.447	0.138	0.267
C_3	4 *d*	0.500	0.000	0.362
N_2*	2 *b*	0.000	0.000	0.500
O**	8 *e*	0.150	0.000	0.500
	8 *e*	0.130	0.075	0.500
	8 *e*	0.075	0.130	0.500

* Nitrogen atom of nitrate ion.

** Six oxygen atoms are statistically distributed on these three sets of eightfold positions with weights 1/4.

TABLE II. COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS

Index	$\lvert F_o \rvert/4$	$F_c/4$	Index	$\lvert F_o \rvert/4$	$\lvert F_c \rvert/4$	α°	Index	$\lvert F_o \rvert/4$	$\lvert F_c \rvert/4$	α°
200	22.4	+24.3	011	8.1	9.1	0	006	11.6	11.9	0
400	8.0	+ 9.9	021	5.9	6.4	90	016	< 0.3	0.2	270
600	6.8	+ 7.9	031	9.7	10.5	0	026	7.8	8.3	0
800	2.6	+ 2.6	041	4.1	5.0	270	036	2.0	1.5	270
1000	3.1	+ 2.7	051	8.3	7.6	0	046	4.9	5.8	0
			061	1.2	1.4	270	056	2.3	2.5	90
110	10.6	+12.9	071	2.1	1.9	0	066	4.0	4.0	0
210	12.0	+10.4	081	1.8	1.8	90	076	< 0.3	0.1	270
310	8.2	+ 8.7	091	1.4	1.3	0	086	3.2	3.3	0
410	6.2	+ 6.3	0101	0.8	0.7	270	096	1.1	1.3	90
510	6.9	+ 7.5								
610	1.4	+ 2.1	002	11.8	11.1	0	017	3.8	2.5	0
710	4.7	+ 4.4	012	0.6	1.1	90	027	< 0.3	0.2	90
810	0.6	− 0.1	022	13.4	14.6	0	037	3.2	3.4	0
910	2.5	+ 2.1	032	1.1	0.8	90	047	0.5	0.3	270
1010	< 0.3	− 0.3	042	9.6	10.2	0	057	4.2	4.1	0
			052	3.6	3.8	270	067	0.6	0.6	270
220	7.1	− 7.1	062	6.6	7.1	0	077	3.1	2.2	0
320	< 0.2	− 0.2	072	2.1	2.6	270	087	0.3	0.5	270
420	10.6	+ 9.7	082	4.3	4.5	0				
520	1.2	+ 0.6	092	0.4	0.8	270	008	9.6	10.7	0
620	11.6	+11.4	0102	1.4	2.2	0	018	< 0.3	0.5	90
720	< 0.4	− 0.7					028	6.9	7.5	0
820	5.3	+ 5.6	013	3.6	3.4	180	038	2.0	2.0	270
920	1.7	+ 0.9	023	7.4	7.1	90	048	4.3	4.1	0
1020	3.3	+ 2.9	033	6.7	6.6	0	058	1.1	0.2	270
			043	3.3	3.2	90	068	4.1	4.1	0
330	4.9	+ 4.6	053	8.2	8.4	0	078	0.3	0.4	270
430	1.9	− 1.4	063	2.2	1.9	270	088	1.6	2.1	0
530	6.2	+ 6.1	073	3.9	4.1	0				
630	0.7	− 0.6	083	1.4	1.3	270	019	3.7	3.0	0
730	2.6	+ 2.9	093	2.3	2.6	0	029	0.9	1.3	270
830	< 0.3	+ 0.5	0103	0.6	0.9	270	039	3.4	3.4	0
930	2.6	+ 2.1					049	0.6	0.1	90
1030	0.8	+ 0.8	004	13.7	14.0	0	059	3.6	4.0	0
			014	0.3	0.2	90	069	< 0.2	0.7	90
440	8.3	+ 7.6	024	11.0	11.9	0	079	< 0.2	0.1	180
540	0.7	+ 0.8	034	2.4	3.5	90				
640	6.7	+ 7.1	044	2.0	2.9	0	0010	5.0	5.6	0
740	2.6	− 2.0	054	1.1	0.5	90	0110	1.5	1.9	270
840	4.6	+ 4.7	064	3.0	4.4	0	0210	2.2	2.8	0
940	< 0.3	− 0.1	074	1.7	1.8	90	0310	1.5	1.0	90
			084	4.4	4.4	0	0410	2.1	2.0	0
550	6.3	+ 6.6	094	0.3	0.6	270	0510	0.6	0.6	270
650	2.4	− 2.4	0104	< 0.2	0.6	0	0610	1.1	1.5	0
750	1.8	+ 2.2								
850	< 0.3	− 0.0	015	1.8	1.2	0	0111	1.5	1.2	0
950	0.9	+ 0.9	025	4.1	4.6	270	0211	1.6	1.2	90
			035	9.5	10.0	0	0311	2.1	2.1	0
660	2.9	+ 3.6	045	< 0.3	0.9	270	0411	< 0.2	0.3	90
760	0.6	+ 0.9	055	1.8	2.1	0	0511	< 0.1	0.6	0
860	2.6	+ 2.5	065	2.5	1.9	90				
			075	2.7	2.8	0	0012	1.7	2.6	0
770	2.8	+ 2.0	085	0.4	0.2	90	0112	1.9	1.9	90
870	< 0.2	+ 0.4	095	1.7	1.8	0	0212	2.0	1.9	0
							0312	< 0.1	0.4	90

between calculated and observed intensities. The best agreement is found if the nitrate ions lie perpendicularly to the *c*-axis, taking four different azimuthal orientations in such a way that the direction of one N–O bond coincides with one of the *a*-axis. Thus the apparent symmetry of the nitrate ions becomes $\bar{4}$, in accordance with the requirement of the space group. Although structure factors were also calculated under the assumption of free rotation of nitrate ions, the result gave a slightly greater *R*-value.

By the usual method of successive approximation the final projections were obtained. The final Fourier projections upon (001) and (100) are shown in Figs. 1 and 2, respectively. The final atomic coordinates are listed in Table I. Observed and calculated structure factors as well as phase angles are listed in Table II. The agreement on the whole is quite good and values of $R=\sum||F_o|-|F_c||/\sum|F_o|$ are 0.106 and 0.117 for $(h\,k\,0)$ and $(0\,k\,l)$, respectively. In the calculation of the structure factors, the atomic scattering curves calculated by Berghuis et al.[4] were employed. A temperature correction, $\exp -B(\sin\theta/\lambda)^2$, was applied with $B=3.0\,\text{Å}^2$.

Interatomic distances and bond angles calculated on the basis of the atomic parameters listed in Table I are given in Table III.

TABLE III. INTERATOMIC DISTANCES AND BOND ANGLES

Cu–N$_1$	1.98 Å	$\angle$CuN$_1$C$_1$	176°
C$_1$–N$_1$	1.14	$\angle$N$_1$C$_1$C$_2$	176
C$_1$–C$_2$	1.54	$\angle$C$_1$C$_2$C$_3$	110
C$_2$–C$_3$	1.53	$\angle$C$_2$C$_3$C$_{2'}$	106
N$_2$–O	1.24		

Calculation of the structure factors as well as that of the electron density was carried out with a Remington Rand UNIVAC 120 electronic computer quite effectively.

Description of the Structure

The projections of the structure of bis(glutaronitrilo)copper(I) nitrate upon (001) and (100) are shown in Figs. 3 and 4, respectively. It consists of infinite two-dimensional networks of the complex ion $[\text{Cu(NC–CH}_2\text{–CH}_2\text{–CH}_2\text{–CN)}_2]^{n+}_n$ and nitrate ions. A copper atom is tetrahedrally surrounded by four nitrogen atoms at a distance of 1.98 Å. Each glutaronitrile molecule is coordinated to two different copper atoms with nitrogen atoms at both ends. As a consequence, all the copper atoms in a plane perpendicular to the *c*-axis are linked together with ligand molecules, forming a two-dimensional network of complex ions. A glutaronitrile molecule possesses a twofold axis of symmetry and takes a *gauche-gauche* configuration with respect to the C$_2$–C$_3$ and C$_3$–C$_{2'}$ bonds. The angles of internal rotation were found to be 115° with the *trans* position taken as the origin. The carbon-carbon distances and bond angles agree well with those usually found in other organic crystals. The carbon-nitrogen bond distance is 1.14 Å and the Cu–N–C–C group is close to linear, which is similar to the case of bis(succinonitrilo)copper(I) nitrate. These facts indicate that the bond character of the carbon-nitrogen bond may be expressed as C≡N. Because of the rigidity of the triple bond and the tetrahedral coordination of copper atoms, the network of the complex ion is puckered. Nevertheless, the mode of packing of each layer is considered to be satisfactory with reasonable van der Waals distances between successive sheets. At the center of each mesh of the network of the complex ion a nitrate ion is located perpendicularly to the *c*-axis. The trigonal nitrate ion seems to have statistical azimuthal orientations and its apparent symmetry becomes $\bar{4}$. Just above and below the nitrate ion lie two copper atoms of adjacent layers at a distance of 4.86 Å, which should be compared with the corresponding distance of 4.77 Å found for the crystals of bis(succinonitrilo)copper(I) nitrate. That is to say, there is a cavity in the packed layers of the two-dimensional complex ions and a nitrate ion is at the center of the cavity. The interatomic distances between oxygen atoms of nitrate ions and the carbon atoms of the nearest methylene groups in the complex ion are longer than 3.14 Å. This is to be compared with the distance of 3.12 Å found between the carbon atom of a methylene group and the oxygen atom of a water molecule in the crystals of $[\text{Co en}_3]\text{Cl}_3\cdot3\text{H}_2\text{O}$[5].

Further discussions of the structure will be made after the crystal structure of bis(adiponitrilo)copper(I) nitrate[6] has been determined.

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[4] J. Berghuis et al., *Acta Cryst.*, 8, 478 (1955).

[5] K. Nakatsu, Y. Saito and H. Kuroya, This Bulletin, **29**, 428 (1956).

[6] Y. Kinoshita, I. Matsubara, T. Higuchi and Y. Saito, ibid., **32**, 1221 (1959).

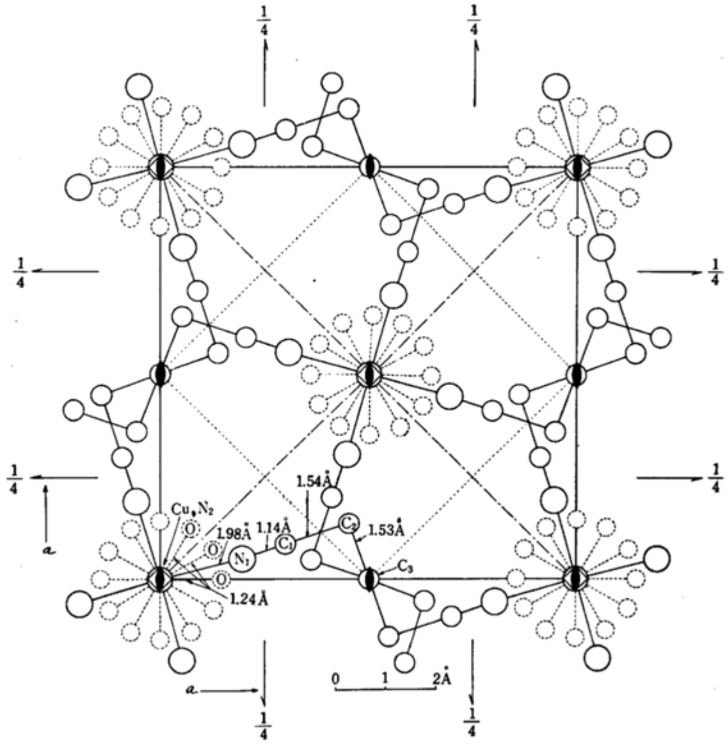

Fig. 3. Projection of the structure upon (001).

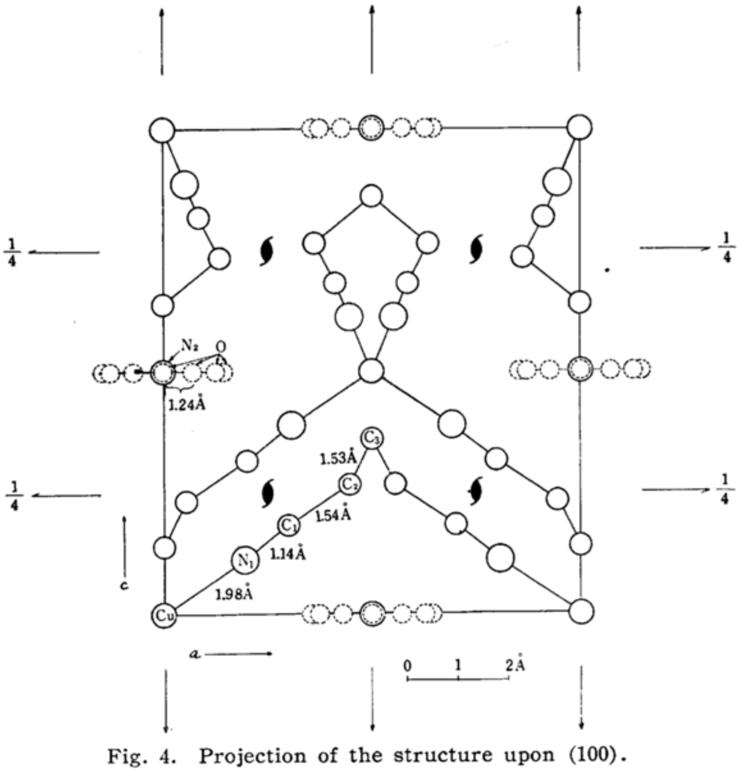

Fig. 4. Projection of the structure upon (100).

Summary

The crystal structure of bis(glutaronitrilo)copper(I) nitrate has been determined by the two-dimensional Fourier method. It is tetragonal $P\bar{4}2_1c$ with two formula units in a cell of dimensions: $a=8.25\pm0.01$ Å and $c=9.71\pm0.01$ Å.

The crystal consists of infinite two-dimensional networks of complex ion $[Cu(NC\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CN)_2]_n^{n+}$ and nitrate ions. A copper atom is tetrahedrally surrounded by four nitrogen atoms at a distance of 1.98 Å. Each glutaronitrile molecule is coordinated to two different copper atoms with nitrogen atoms at both ends and takes a *gauche-gauche* configuration with respect to the two C–C bonds. The nitrate ions lie perpendicularly to the c-axis. The trigonal nitrate ions seem to have statistical azimuthal orientations in the crystal and the apparent symmetry of the nitrate ion is $\bar{4}$.

All the atoms in the group Cu–N–C–C lie approximately on a straight line. This fact and the observed carbon-nitrogen distance of 1.14 Å suggest that the bond character in the carbon-nitrogen group may essentially be expressed as $C\equiv N$.

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