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

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We have previously reported on the crystal structures of some complexes prepared from nitriles of aliphatic dibasic acids and univalent copper[1,2], which may be of interest in relation to the mechanism of cuprous ion dyeing of polyacrylonitrile fibers. In the course of our study on crystal structures of this series of complexes, the crystal structure of bis(adiponitrilo)copper(I) nitrate, $[Cu(NC-CH_2-CH_2-CH_2-CH_2-CN)_2]NO_3$, has been determined by means of two-dimensional Fourier methods.

The crystal structure will be discussed together with those of homologues reported in the previous papers, and some remarks will be made on the mechanism of dyeing polyacrylonitrile fibers.

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

2) Y. Kinoshita, I. Matsubara and Y. Saito, ibid., **32**, 1216 (1959).

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

Experimental

Bis(adiponitrilo)copper(I) nitrate was prepared according to the method of Rath et al.[3] by dissolving silver nitrate into adiponitrile at 60°C and adding an excess of copper powder. After some black spongy silver was deposited, the mixture was filtered. On cooling, the clear filtrate deposited yellowish crystals.

Anal. Found: C, 42.05; H, 4.70; N, 20.54; Cu, 18.52. Calcd. for $C_{12}H_{16}N_5O_3Cu$: C, 42.16; H, 4.72; N, 20.49; Cu, 18.59%.

The crystals are orthorhombic and the unit cell dimensions, as determined from rotation and Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda=1.542$ Å), are $a=9.41\pm0.02$ Å, $b=13.73\pm0.02$ Å and $c=5.85\pm0.01$ Å. Systematic extinctions occur only for $(h\,k\,0)$ with $h+k$ odd, $(0\,k\,l)$ with $k+l$ odd and $(h\,0\,l)$ for $h+l$ odd. The space group is therefore $Pnnn-D_{2h}^{2}$.

Assuming two formula units in the unit cell, the calculated density is 1.502 g./cc., in good agreement with the measured density 1.516 g./cc.

The intensities of the spectra recorded on multiple-film zero-layer Weissenberg photographs were estimated visually and corrected for Lorentz and polarization factors. In view of the small size of the crystals no corrections were made

for the absorption effect. The resulting F^2's were correlated so that all observed data were on the same relative intensity scale. They were later converted into an absolute scale by comparison with calculated values.

Determination of Atomic Positions

Since the general point position in the space group *Pnnn* is eightfold, and since there are only two formula units of $[Cu(NC-CH_2-CH_2-CH_2-CH_2-CN)_2]NO_3$ in the unit cell, it follows that the copper atom must occupy one of the four sets of special positions; 0, 0, 0; 1/2, 1/2, 1/2, etc. All these positions are the intersecting points of three twofold axes which are parallel to the three principal axes respectively. Should the copper atoms occupy a set of these positions, the $(h\,k\,l)$ intensities should conform approximately to the extinction condition of body centered lattice. Equi-inclination Weissenberg photographs revealed that this condition was actually fulfilled. The positions of the copper atoms are, therefore, arbitrarily chosen as 0, 0, 0; 1/2, 1/2, 1/2.

Similarly the nitrogen atoms of nitrate ions must lie on a set of these special positions. The point symmetry of these twofold positions is 222. This is not in accordance with the trigonal symmetry of the nitrate ion. The nitrate ion could have apparent symmetry 222 only if disorder exists in the crystal.

The Patterson projections onto (001), (010) and (100) are very similar to the corresponding Fourier projections, since copper atoms at the origin and the center of the unit cell make all signs of zero-layer reflections positive and moreover the plane group symmetry of the Patterson projections are similar to that of Fourier projections. Therefore, preliminary Fourier projections were computed with all signs positive. Because the *c*-axis is as short as 5.85 Å, the extended chain form of methylene groups in the adiponitrile molecule, which apparently connects the copper atom at the origin with that at the center of the unit cell, is clearly shown on $P(uv)$ and $\rho(xy)$. Further, it has been found from $(0\,k\,l)$ data that the atoms in adiponitrile molecules are concentrated in (031) planes, because the orders of reflection from (031) are exceptionally intense and the intensity decreases through four orders according to a normal decline. Consideration of the above facts with the aid of the Patterson projection upon (100) has led to the conclusion that an adiponitrile molecule is coordinated with the nitrogen atoms of both ends to two copper atoms at 0, 0, 0 and at 1/2, 1/2, 3/2, taking a planar zigzag configuration. Thus the approximate coordinates of all the atoms in the ligand molecule could be fixed. However, from the Patterson projections and the preliminary Fourier maps of electron density only, locations of the atoms in the nitrate ions could not be fixed unequivocally. As a consequence, the approximate parameters of these atoms were determined by trial calculations of structure amplitudes. The best agreement between observed and calculated structure amplitudes was obtained when the nitrate ion was placed perpendicularly to the *a*-axis, taking four different azimuthal orientations as shown in Table I. Thus, the apparent symmetry of the nitrate ion becomes 222 in accordance with the requirement of the space group. Determination of the more precise atomic parameters was achieved by successive

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 *m*		0.129	0.076	0.200
C_1	8 *m*		0.194	0.110	0.341
C_2	8 *m*		0.292	0.164	0.509
C_3	8 *m*		0.201	0.223	0.667
N_2	2 *b*		0.000	0.500	0.500
O_1	4 *j*	(1/4)*	0.000	0.410	0.500
O_2	4 *l*	(1/4)*	0.000	0.500	0.288
O_3	8 *m*	(1/4)*	0.000	0.455	0.317
O_4	8 *m*	(1/4)*	0.000	0.422	0.394

* Oxygen atoms are statistically distributed with weights shown in parentheses.

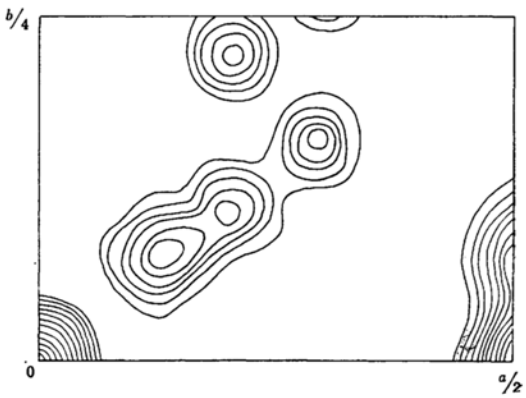


Fig. 1. Final Fourier projection of electron density upon (001). Contours are drawn at intervals of 4e $Å^{-2}$ for copper and those for other atoms are at intervals of 1e $Å^{-2}$, the lowest being 2e $Å^{-2}$.

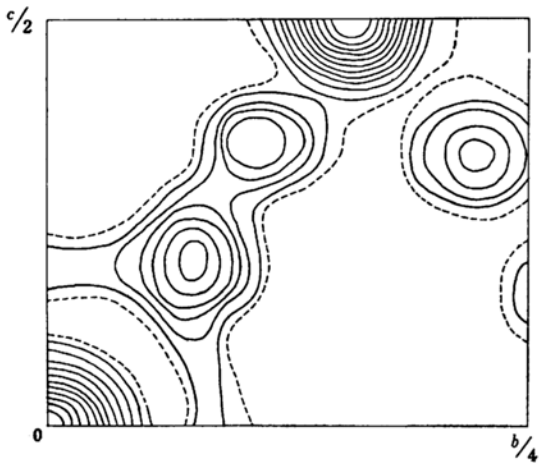


Fig. 2. Final Fourier projection of electron density upon (100). Contours are drawn at intervals of 5e Å^{-2} for copper and those for other atoms are at intervals of 1e Å^{-2}, the lowest being 2e Å^{-2} (broken).

Fourier syntheses. The final Fourier projections upon (001) and (100) are shown in Figs. 1 and 2, respectively.

The atomic parameters of the asymmetric unit are recorded in Table I and the calculated interatomic distances and bond angles are shown in Table II. The comparison of observed and calculated structure amplitudes is given in Table III, the reliability factors $R=\sum||F_o|-|F_c||/\sum|F_o|$ being 0.107, 0.116 and 0.112 for $(h\,k\,0)$, $(h\,0\,l)$ and $(0\,k\,l)$, respectively, with a weighted mean value of 0.110.

TABLE II. INTERATOMIC DISTANCES AND BOND ANGLES

$Cu-N_1$	1.98 Å	$\angle CuN_1C_1$	169°
C_1-N_1	1.13	$\angle N_1C_1C_2$	172
C_1-C_2	1.54	$\angle C_1C_2C_3$	108
C_2-C_3	1.50	$\angle C_2C_3C_{3'}$	108
$C_3-C_{3'}$	1.53		
N_2-O	1.24		

A mean isotropic temperature factor with $B=3.0$ Å^2 was found to be satisfactory for the three principal zones. Calculation of electron density as well as that of structure factors were carried out on a Remington Rand UNIVAC 120 electronic computer quite effectively.

Description of the Structure

The projections of the structure of bis-(adiponitrilo)copper(I) nitrate upon (001) and (100) are shown in Figs. 3 and 4, respectively.

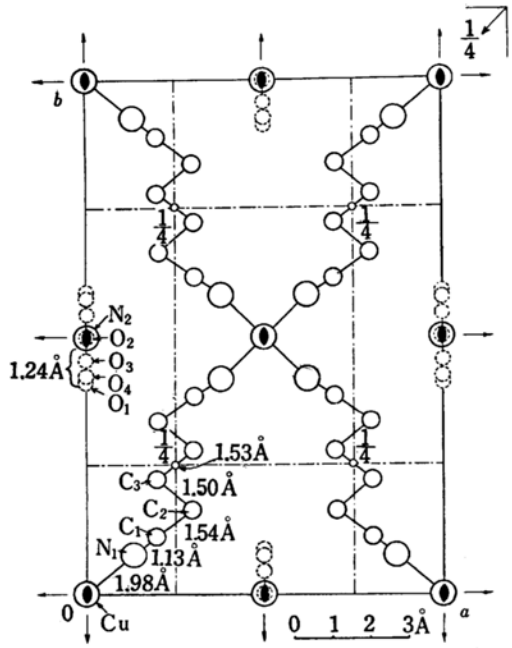


Fig. 3. Projection of the structure upon (001).

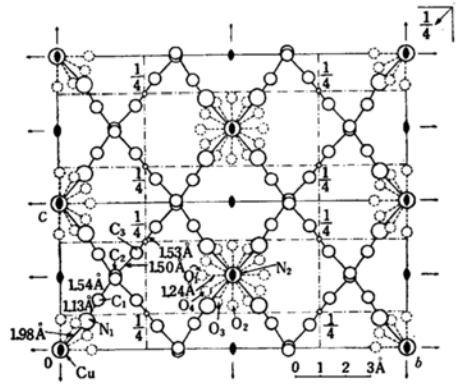


Fig. 4. Projection of the structure upon (100).

It is evident from the figures that the structure consists of infinite three-dimensional networks of the complex ion $[Cu(NC-CH_2-CH_2-CH_2-CH_2-CN)_2]_n^{n+}$ and nitrate ions. A copper atom is surrounded tetrahedrally by four nitrogen atoms at a distance of 1.98 Å, which is in good agreement with the corresponding values observed for the related compounds reported previously[1,2]. Each adiponitrile molecule is coordinated to two different copper atoms, resulting in a complicated three-dimensional network of the complex ion. A copper atom at the origin is linked to four copper atoms belonging to different unit cells at 1/2, 1/2, 3/2; −1/2, −1/2, 3/2; 1/2,

TABLE III. COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS

Index	F_o	F_c	Index	F_o	F_c	Index	F_o	F_c
200	6	7	280	22	23	705	12	9
400	72	70	480	40	35	802	14	12
600	70	64	680	22	16	804	18	16
800	26	28	880	7	3	901	14	12
1000	32	33	1080	10	11	903	17	14
1200	< 2	−1	190	41	33	905	< 2	8
020	64	69	390	< 5	−1	1002	11	12
040	22	24	590	43	47	1004	7	6
060	5	4	790	9	−6	1101	< 3	0
080	26	23	990	10	12	1103	< 2	12
0100	31	28	2100	29	25	011	54	60
0120	30	28	4100	23	20	031	102	117
0140	19	20	6100	16	14	051	28	26
0160	4	4	8100	11	9	071	18	29
002	24	23	1110	20	16	091	25	24
004	34	32	3110	14	16	0111	30	27
006	34	35	5110	< 5	1	0131	12	16
110	34	39	7110	14	17	0151	16	21
310	34	−35	9110	< 3	4	0171	< 4	4
510	< 4	3	2120	22	20	022	28	31
710	18	16	4120	13	13	042	30	31
910	13	7	6120	13	13	062	71	74
1110	< 4	2	8120	10	14	082	32	33
220	113	124	1130	14	14	0102	13	15
420	40	37	3130	9	8	0122	21	24
620	37	37	5130	< 5	0	0142	8	7
820	34	40	7130	11	12	0162	< 5	7
1020	7	9	2140	16	17	013	28	23
1220	10	15	4140	7	7	033	32	30
130	29	25	6140	7	9	053	34	32
330	19	21	1150	10	10	073	19	23
530	18	17	3150	6	6	093	51	55
730	14	13	5150	< 4	4	0113	10	8
930	12	13	2160	13	16	0133	< 7	4
1130	< 4	0	4160	< 3	5	0153	4	7
240	78	72	101	26	21	024	38	30
440	55	47	103	40	41	044	24	23
640	30	26	105	26	19	064	37	37
840	20	21	107	5	4	084	12	11
1040	8	9	202	49	44	0104	8	8
150	19	18	204	39	41	0124	17	20
350	66	61	206	< 4	0	0144	8	9
550	28	27	301	10	12	015	28	25
750	15	16	303	6	8	035	38	34
950	11	9	305	6	−2	055	12	9
1150	< 3	10	307	11	6	075	10	8
260	38	35	402	56	60	095	10	11
460	50	50	404	24	21	0115	11	13
660	15	13	406	18	15	0135	< 3	7
860	10	9	501	11	9	026	8	8
1060	10	9	503	66	64	046	8	9
170	13	14	505	7	6	066	9	9
370	68	64	602	23	20	086	11	10
570	16	19	604	18	14	0106	7	8
770	22	20	606	13	13	017	< 5	0
970	< 5	2	701	14	13	037	13	13
1170	< 2	10	703	17	12	057	10	9

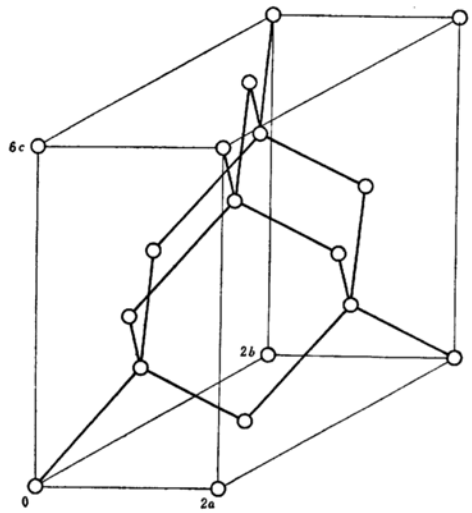


Fig. 5. Schematic diagram of a single 4-connected network in the crystal of bis(adiponitrilo)copper(I) nitrate.

$-1/2, -3/2; -1/2, 1/2, -3/2$. In this way the copper atoms and the ligand molecules form a three-dimensional 4-connected network[4], in which all the copper atoms are arranged on a distorted diamond lattice and are linked by the ligand molecules with each other. Fig. 5 schematically illustrates the constitution of the network. The figure shows a single 4-connected network. For simplicity, adiponitrile molecules are drawn as straight lines connecting two copper atoms. The structure of bis(adiponitrilo)copper(I) nitrate consists of a superposition of six sets of this 4-connected network displaced through *c* with respect to each other.

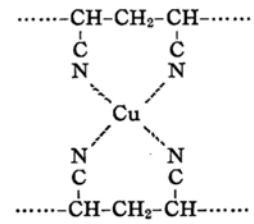
Each adiponitrile molecule has a center of symmetry between the two central carbon atoms. All the carbon atoms of the adiponitrile molecule are less than 0.06 Å from the plane (031) and constitute a planar zigzag chain configuration, while the nitrogen atoms of nitrile groups are 0.10 Å distant from that plane. All the carbon-carbon bond lengths and bond angles in the methylene groups are close to normal values. The carbon-nitrogen bond distance is 1.13 Å and the Cu–N–C–C group is close to linear as in the cases of the related compounds reported previously[1,2]. These facts indicate that the bond character of the carbon-nitrogen bond may be expressed as C≡N.

The nitrate ions lie perpendicularly to the *a*-axis. The trigonal nitrate ion seems to have statistical azimuthal orientations in the crystal and its apparent symmetry becomes 222. The interatomic distances between the oxygen atoms of the nitrate ions and the carbon atoms of the nearest methylene groups in the complex ion are longer than 3.19 Å. This is to be compared with the corresponding value of 3.14 Å found in the crystals of bis(glutaronitrilo)-copper(I) nitrate[2].

4) For the definition of the term, see A. F. Wells, *Acta Cryst.*, 7, 545 (1954).

Remarks on the Mechanism of Cuprous Ion Dyeing of Polyacrylonitrile Fibers

As pointed out in the previous paper[1], cuprous ion is readily absorbed by polyacrylonitrile fibers which then acquire an almost unlimited affinity for anionic dyes, which ordinarily can not be applied to this class of fibers. Blaker et al.[5] and Rath et al.[3] have suggested that the high affinity of cuprous ion for polyacrylonitrile is due to the inherent capability of nitrile groups in the fibers to absorb cuprous ion through formation of complexes, which may act as positive sites for fixation of dye anions. It has been established by the present investigations that, in the complexes prepared from univalent copper and nitriles of aliphatic dibasic acids, four nitrogen atoms of nitrile groups enter into combination with a cuprous ion, forming a stable tetrahedral complex. This fact strongly indicates that there may exist a strong interaction of the same kind between cuprous ions and nitrile groups of polyacrylonitrile molecules in the dyeing of fibers with cuprous ion technique. However, by analogy with the structures of these complexes it is very unlikely that stable chelate rings of the type,



are formed between cuprous ions and polyacrylonitrile molecules. In fact, it can easily be understood that such a chelate ring with reasonable bond distances and bond angles can never be obtained, owing to the rigidity of the Cu–N–C–C

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

group. Therefore, Blaker and Rath's suggestion is only valid in the sense that the nitrile groups of polyacrylonitrile molecules are involved in the formation of complexes similar to those of simple nitriles as described in this and the preceding papers.

In the structures of these complexes, nitrate ions are located in cavities which are formed in the polymeric chain or network of complex ions owing to the rigidity of the Cu–NC–CH_2– group and the tetrahedral nature of the Cu–N bonds. This fact may suggest that in the polyacrylonitrile-Cu(I) complex the dye anions are trapped in cavities analogous to those mentioned above and are fixed by electrostatic interactions with the positive cuprous ions.

Summary

The crystal structure of bis(adiponitrilo)-copper(I) nitrate has been determined by the two-dimensional Fourier method. It is orthorhombic *Pnnn* with two formula units in a cell of dimensions: $a=9.41\pm0.02$ Å, $b=13.73\pm0.02$ Å and $c=5.85\pm0.01$ Å.

The crystal consists of infinite three-dimensional networks of complex ion $[Cu(NC-CH_2-CH_2-CH_2-CH_2-CN)_2]_n^{n+}$ and nitrate ions. A copper atom is tetrahedrally surrounded by four nitrogen atoms at a distance of 1.98 Å. Each adiponitrile molecule is coordinated to two different copper atoms with nitrogen atoms of both ends, forming a planar zigzag configuration of methylene groups. Thus the copper atoms and the ligand molecules form a complicated three-dimensional 4-connected network. The nitrate ions lie perpendicularly to the *a*-axis. The trigonal nitrate ion seems to have statistical azimuthal orientations in the crystal and its apparent symmetry becomes 222.

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 1.13 Å suggest that the bond character in the carbon-nitrogen group may essentially be expressed as C≡N.

On the basis of the structures of this and the other related complexes, some remarks have been made on the mechanism of cuprous ion dyeing of polyacrylonitrile fibers.

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