*The Crystal Structure of Bis(succinonitrilo)copper(I) Nitrate**

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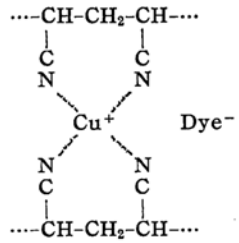
It is well known that cuprous ion plays an important role in the dyeing of polyacrylonitrile fibers with anionic dyes; cuprous ion is readily absorbed by the fibers which then acquire an almost unlimited affinity for anionic dyes, which ordinarily can not be applied to this class of fibers.

Blaker et al.[1] 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 analogous to those described by Morgan[2] for simple nitriles. These complexes, which may act as positive sites for fixation of dye anions, are considered to be of the type,



To verify this hypothesis, Rath et al.[3] have prepared similar complexes from nitriles of aliphatic dibasic acids. It would be of interest to determine the crystal structures of these compounds, since they would shed light on the mechanism of the dyeing.

The crystal structure of bis(succinonitrilo) copper (I) nitrate, $[Cu(NC-CH_2-CH_2-CN)_2]NO_3$, has been determined as a part of a program to establish the configurations of these complexes. Furthermore, the infrared spectrum of this complex has been investigated in relation to the crystal structure.

Experimental

Bis(succinonitrilo)copper(I) nitrate was prepared according to the directions of Morgan[2] by dissolving silver nitrate into succinonitrile at 60°C and adding an excess of copper powder. After black spongy silver was deposited, the mixture was filtered while warm and the filtrate was extracted with a mixture of ether and alcohol. On cooling, the clear extract deposited colorless crystals. This compound shows no definite melting point.

Anal. Found: C, 33.24; H, 2.99; N, 24.85; Cu, 22.12. Calcd. for $C_8H_8N_5O_3Cu$: C, 33.63; H, 2.82; N, 24.51; Cu, 22.24%.

Rotation and Weissenberg photograph showed the crystal to be monoclinic with

$a=11.62\pm0.03$Å, $b=5.31\pm0.01$Å, $c=9.53\pm0.03$Å, $\beta=98.8°\pm0.2°$.

Systematically absent reflections were $(h\,0\,l)$ for h odd, which indicated space groups $P2/a$ or Pa. The statistical method of Howells, Phillips and Rogers[4], when applied to the $h\,0\,l$ data, indicated the presence of a center of symmetry, which enabled us to adopt the space group $P2/a$ for the crystal. The density, determined by floatation, was found to be 1.634 g./cc., while

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

2) H. H. Morgan, *J. Chem. Soc.*, 123, 2901 (1923).

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

4) E. R. Howells, D. C. Phillips and D. Rogers, *Acta Cryst.*, 3, 210 (1950).

that calculated assuming two formula units per cell was 1.633 g./cc.

Intensity data were obtained by visual estimation of *a*-, *b*- and *c*-axis zero-layer Weissenberg photographs taken with Cu $K\alpha$ radiation. A multiple-film technique was used and the intensity was corrected for geometrical and polarization factors. The final set of data consisted of 122 ($h\,0\,l$), 66 ($h\,k\,0$) and 54 ($0\,k\,l$) terms of measurable amplitudes. Absorption corrections were not made, but errors were minimized by selecting small and as well-formed crystals as were available.

The infrared absorption spectra of bis(succinonitrilo)copper(I) nitrate and succinonitrile in the wavelength region from 2 to 15 microns were obtained with a Perkin-Elmer model 21 spectrophotometer (with NaCl optics).

Structure Determination

Space group $P2/a$ contains fourfold general point positions. Since the unit cell contains only two formula units, the copper atom and the nitrate ion must lie either on a twofold symmetry axis or on a center of symmetry. The latter can be excluded since a tetrahedral coordination of a cuprous ion and trigonal configuration of a nitrate ion are to be expected. The copper atom and the central nitrogen atom(N_1) of the nitrate ion, therefore, must lie on twofold axes. The Patterson function was computed for the *b*-axis projection, which could be solved without difficulty, because of the occurrence of the copper atoms on special positions. Approximate *x*- and *z*-coordinates of all the lighter atoms were obtained at once.

A Fourier synthesis of the electron density projected along the *b*-axis was computed and this enabled all the *x*- and *z*-coordinates to be fixed. The Patterson function for the *a*- and *c*-axis projection could be solved successfully by trial

TABLE I. FINAL ATOMIC COORDINATES

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0.250	−0.110	0.000
O_1	0.250	−0.359	0.500
O_2	0.155	−0.015	0.487
N_1	0.250	−0.123	0.500
N_2	0.340	0.108	0.143
N_3	0.153	−0.331	0.108
C_1	0.385	0.247	0.225
C_2	0.455	0.427	0.330
C_3	0.028	−0.607	0.262
C_4	0.100	−0.450	0.175

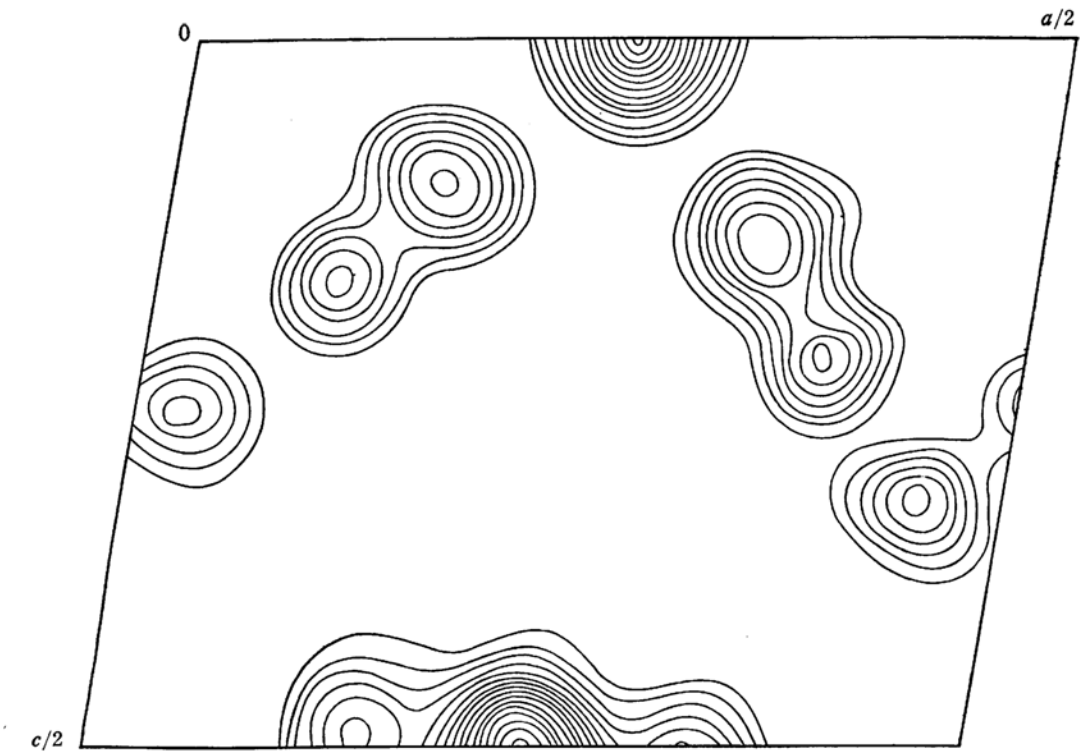


Fig. 1. Final Fourier projection of electron density along [0 1 0]. Contours are drawn at intervals of 3 eÅ^{-2} for copper and those for other atoms are at intervals of 1 eÅ^{-2}, the lowest being 2 eÅ^{-2}.

TABLE II. COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS

Index	$F_o/4$	$F_c/4$	Index	$F_o/4$	$F_c/4$	Index	$F_o/4$	$F_c/4$
200	15.7	−15.8	601	6.1	− 5.6	$40\bar{1}$	2.6	+ 3.7
400	3.7	+ 3.5	602	7.3	− 6.9	$40\bar{2}$	17.5	+17.1
600	6.1	− 4.7	603	5.0	− 3.9	$40\bar{3}$	13.5	+14.2
800	9.8	+ 8.7	604	7.2	− 6.3	$40\bar{4}$	10.6	+ 9.6
1000	6.7	− 7.4	605	10.0	− 8.8	$40\bar{5}$	5.3	+ 4.4
1200	2.9	+ 3.2	606	6.1	− 5.1	$40\bar{6}$	7.0	+ 6.1
1400	2.6	− 2.3	607	<1.2	+ 0.2	$40\bar{7}$	4.8	+ 3.8
			608	1.1	− 1.5	$40\bar{8}$	8.1	+ 6.9
010	5.1	+ 5.6	609	2.2	− 1.7	$40\bar{9}$	2.4	+ 2.2
020	7.3	+ 7.4	6010	1.5	− 1.4	$40\bar{1}\bar{0}$	<1.1	+ 1.2
030	<0.9	+ 0.6				$40\bar{1}\bar{1}$	<0.9	+ 0.9
040	7.1	− 6.2	801	5.1	+ 4.3	$40\bar{1}\bar{2}$	1.2	+ 1.7
050	2.6	− 2.1	802	6.8	+ 6.0			
060	1.4	− 1.4	803	2.4	+ 1.8	$60\bar{1}$	4.0	− 5.4
			804	5.6	+ 5.1	$60\bar{2}$	7.2	− 6.5
001	7.2	+ 8.5	805	<1.2	− 0.2	$60\bar{3}$	13.9	−12.7
002	10.3	+11.0	806	2.3	+ 3.0	$60\bar{4}$	12.6	−10.9
003	6.4	− 6.7	807	2.6	+ 2.5	$60\bar{5}$	4.4	− 5.6
004	13.1	+14.3	808	2.4	+ 3.0	$60\bar{6}$	6.7	− 5.1
005	1.2	− 0.6	809	0.6	+ 0.4	$60\bar{7}$	4.4	− 4.5
006	12.0	+11.5				$60\bar{8}$	1.2	− 0.7
007	3.6	+ 2.5	1001	1.7	− 1.8	$60\bar{9}$	<1.2	− 1.1
008	7.2	+ 7.2	1002	6.8	− 5.7	$60\bar{1}\bar{0}$	1.8	− 2.1
009	2.9	+ 2.2	1003	2.4	− 1.5	$60\bar{1}\bar{1}$	0.8	− 1.5
0010	2.5	+ 2.6	1004	2.3	− 2.6			
0011	<0.9	+ 0.5	1005	<1.1	+ 0.8	$80\bar{1}$	4.7	+ 4.3
0012	1.8	+ 2.1	1006	1.9	− 2.0	$80\bar{2}$	7.1	+ 6.2
			1007	1.2	− 0.6	$80\bar{3}$	<1.1	+ 1.5
201	7.6	− 7.0				$80\bar{4}$	10.1	+ 8.7
202	26.9	−28.7	1201	1.6	+ 1.3	$80\bar{5}$	9.7	+ 7.9
203	3.4	− 3.9	1202	2.9	+ 3.5	$80\bar{6}$	3.4	+ 2.9
204	10.4	− 9.8	1203	<1.0	+ 0.4	$80\bar{7}$	1.2	− 0.8
205	5.1	− 5.0	1204	1.2	+ 1.5	$80\bar{8}$	2.0	+ 2.1
206	7.1	− 6.4	1205	1.3	+ 0.9	$80\bar{9}$	1.1	+ 1.8
207	3.9	− 3.2				$80\bar{1}\bar{0}$	1.8	+ 1.8
208	6.1	− 4.9	1401	1.4	− 1.6	$80\bar{1}\bar{1}$	1.4	+ 1.7
209	<1.2	− 1.3	1402	<0.5	− 0.4			
2010	<1.0	− 1.3				$100\bar{1}$	2.1	− 1.5
2011	0.8	− 1.3	$20\bar{1}$	11.2	−10.1	$100\bar{2}$	6.5	− 6.2
			$20\bar{2}$	24.7	−24.7	$100\bar{3}$	2.9	− 2.2
401	0.7	+ 1.9	$20\bar{3}$	6.5	+ 5.8	$100\bar{4}$	2.7	− 3.3
402	8.6	+ 7.5	$20\bar{4}$	11.2	−11.5	$100\bar{5}$	<1.2	+ 1.0
403	18.0	+16.8	$20\bar{5}$	2.1	− 1.9	$100\bar{6}$	4.1	− 4.9
404	14.8	+13.3	$20\bar{6}$	11.8	−11.6	$100\bar{7}$	1.1	− 1.9
405	5.7	+ 4.9	$20\bar{7}$	4.0	− 3.1	$100\bar{8}$	2.0	− 2.3
406	6.0	+ 4.4	$20\bar{8}$	6.0	− 6.5	$100\bar{9}$	1.7	− 1.0
407	4.8	+ 3.8	$20\bar{9}$	3.4	− 2.3	$100\bar{1}\bar{0}$	1.9	− 2.0
408	<1.2	+ 0.5	$20\bar{1}\bar{0}$	5.7	− 5.4			
409	<1.1	+ 0.9	$20\bar{1}\bar{1}$	<0.9	+ 0.1			
4010	2.5	+ 2.0	$20\bar{1}\bar{2}$	<0.6	− 0.1			
4011	1.3	+ 1.7						

TABLE II. (continued)

Index	$F_o/4$	$F_c/4$	Index	$F_o/4$	$F_c/4$	Index	$F_o/4$	$F_c/4$
$120\bar{1}$	2.3	+ 2.6	710	6.5	− 6.4	021	4.1	− 3.9
$120\bar{2}$	3.9	+ 4.3	720	4.0	− 3.7	022	5.2	+ 4.9
$120\bar{3}$	<1.1	− 0.9	730	7.5	− 8.2	023	1.7	− 0.8
$120\bar{4}$	1.1	+ 1.8	740	<1.2	+ 0.5	024	3.6	+ 2.6
$120\bar{5}$	<1.1	+ 0.2	750	<1.0	+ 0.8	025	<0.9	− 0.8
$120\bar{6}$	1.9	+ 2.8	760	<0.5	+ 1.3	026	5.8	+ 5.2
$120\bar{7}$	2.4	+ 1.8				027	2.1	+ 0.8
$120\bar{8}$	2.5	+ 3.1	810	4.1	+ 4.0	028	<1.1	+ 0.3
			820	<1.2	− 0.4	029	<1.0	− 1.2
$140\bar{1}$	<0.8	− 0.2	830	1.8	− 1.2	0210	<0.9	+ 0.2
$140\bar{2}$	0.8	− 0.8	840	1.2	− 2.2	0211	<0.6	+ 0.4
$140\bar{3}$	1.6	− 1.4	850	1.3	− 1.5			
$140\bar{4}$	1.0	− 1.8				031	6.9	− 6.2
$140\bar{5}$	<0.6	− 0.9	910	3.5	+ 3.0	032	<0.8	+ 0.7
$140\bar{6}$	<0.4	− 1.4	920	3.8	+ 4.1	033	4.7	− 5.1
			930	1.2	+ 1.6	034	1.4	− 0.4
110	11.7	+10.7	940	1.6	+ 2.0	035	5.7	− 5.7
120	4.6	+ 4.4	950	0.8	− 1.1	036	2.6	− 2.4
130	8.5	+ 8.2				037	3.4	− 2.6
140	3.4	+ 3.1	1010	3.4	− 3.9	038	<1.0	+ 0.4
150	2.2	− 1.9	1020	1.3	− 1.4	039	<0.9	− 0.8
160	1.4	− 1.2	1030	<1.2	− 0.4	0310	<0.7	+ 0.1
			1040	2.4	+ 2.6			
210	19.2	−20.4	1050	0.5	+ 1.0	041	4.8	− 5.3
220	<0.8	− 0.3				042	4.8	− 4.1
230	2.4	+ 1.6	1110	2.9	− 3.5	043	4.4	− 3.9
240	5.0	+ 5.0	1120	<1.2	− 0.9	044	2.6	− 2.1
250	4.2	+ 4.1	1130	<1.1	− 1.3	045	<1.1	− 1.3
260	<1.0	− 0.2	1140	0.8	− 0.9	046	3.6	− 2.5
						047	2.4	− 3.1
310	15.0	−14.6	1210	2.7	+ 2.8	048	2.7	− 2.3
320	7.9	− 8.3	1220	1.1	+ 0.8	049	1.0	− 0.8
330	6.2	− 6.6	1230	0.9	− 0.3			
340	1.7	− 1.5	1240	<0.4	− 1.4	051	4.0	− 4.7
350	1.7	+ 1.3				052	3.7	− 2.9
360	<1.0	+ 1.0	1310	1.0	+ 1.3	053	1.5	− 1.7
			1320	0.9	+ 1.1	054	<1.0	− 0.3
410	4.4	+ 3.0	1330	1.1	+ 1.2	055	1.7	− 2.2
420	1.2	+ 1.1				056	1.5	− 1.5
430	3.5	− 3.9	1410	<0.7	− 0.2	057	1.8	− 1.9
440	5.9	− 6.9	1420	<0.6	− 0.2	058	<0.6	− 1.1
450	1.7	− 1.8						
460	0.9	− 1.0	011	4.2	+ 4.0	061	1.3	− 1.2
			012	20.9	+20.8	062	<0.8	+ 0.8
510	6.0	+ 6.0	013	<0.6	+ 0.8	063	1.2	− 1.4
520	12.5	+13.5	014	10.5	+ 9.1	064	<0.7	− 0.7
530	2.9	+ 3.9	015	5.3	+ 4.0	065	1.0	− 1.4
540	2.2	+ 1.7	016	7.7	+ 6.4			
550	1.2	− 1.3	017	4.2	+ 3.0			
560	<1.1	− 1.7	018	5.3	+ 4.5			
			019	1.8	+ 1.2			
610	1.3	− 1.0	0110	2.1	+ 1.8			
620	<1.0	+ 0.4	0111	<0.8	+ 0.1			
630	3.9	+ 4.9	0112	<0.3	+ 0.4			
640	3.0	+ 2.9						
650	1.6	+ 2.0						
660	<0.7	+ 1.1						

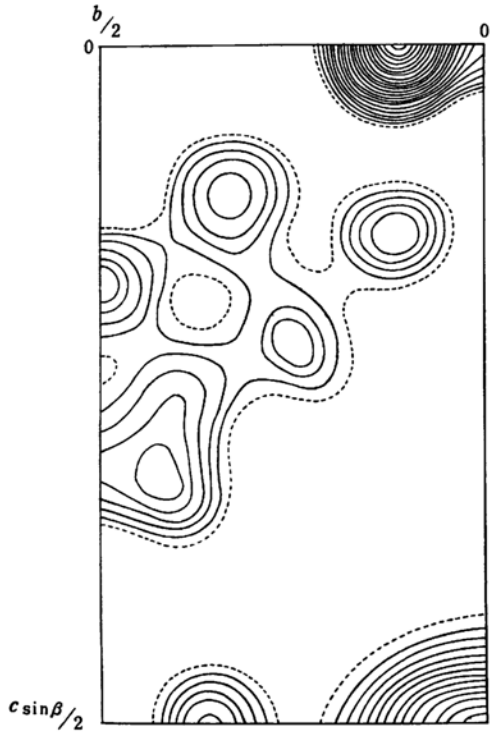


Fig. 2. Final Fourier projection of electron density along [1 0 0]. Contours are drawn at intervals of 2 eÅ^{-2} for copper and nitrate group except O_1. Those for other atoms are at intervals of 1 eÅ^{-2}, the lowest being 2 eÅ^{-2} (broken).

studies with models having suitable interatomic distances and bond angles. Approximate y-coordinates of all the atoms were thus obtained. Fourier projections of the electron density along [1 0 0] and [0 0 1] were then computed. Fourier refinements were repeated as usual. The final projections along [0 1 0] and [1 0 0] are shown in Figs. 1 and 2, respectively.

The final set of parameters is listed in Table I. This gave the reliability index $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ of 0.124, 0.106 and 0.134 for $(h\,0\,l)$, $(h\,k\,0)$ and $(0\,k\,l)$, respectively. A mean isotropic temperature factor with B=4.0 Å^2 was found to be satisfactory for the three equatorial zones. Observed and calculated structure factors are shown in Table II.

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

Description of the Structure

The interatomic distances and the bond angles calculated on the basis of the above parameter values are given in Table III. Calculation of the standard deviation of atomic coordinates by Cruickshank's

Table III. Interatomic distances and bond angles

Cu—N_2	1.96 Å	∠CuN_2C_1	175°
Cu—N_3	2.02	∠CuN_3C_4	177
C_1 —N_2	1.14	∠$N_2C_1C_2$	175
C_4 —N_3	1.14	∠$N_3C_4C_3$	180
C_1 —C_2	1.53	∠$C_1C_2C_3$	113
C_3 —C_4	1.52	∠$C_4C_3C_2$	107
C_2 —C_3	1.49	∠$O_1N_1O_2$	118
N_1—O_1	1.25	∠$O_2N_1O_2'$	125
N_1—O_2	1.23		

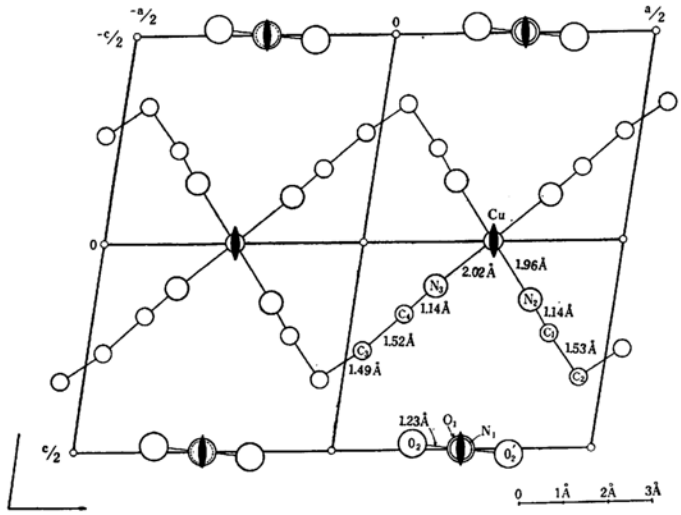


Fig. 3. Projection of the structure along [0 1 0].

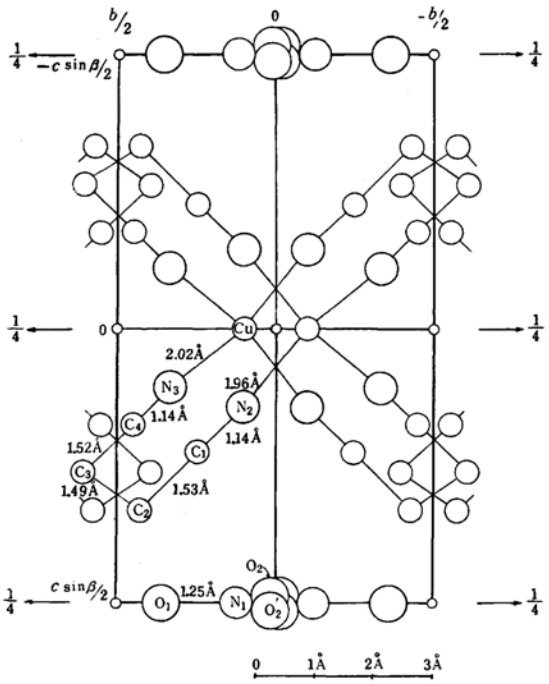
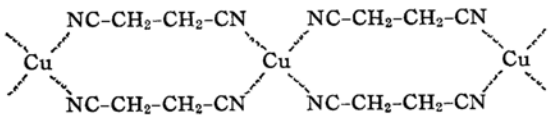


Fig. 4. Projection of the structure along [1 0 0].

method[5] for each projection gives 0.025Å for the resolved carbon and nitrogen atoms. This suggests a standard deviation of about ±0.04 Å in the Cu-N bond length determination.

The projections of the structure of bis-(succinonitrilo)copper (I) nitrate along [0 1 0] and [1 0 0] are shown in Figs. 3 and 4, respectively.

It is evident from the figures that the structure consists of nitrate ions and a polymeric chain of the composition,



which runs parallel to the *a*-axis. A copper atom is surrounded tetrahedrally by four nitrogen atoms with Cu–N distances of 1.96 and 2.02 Å. A succinonitrile molecule in the complex takes a *gauche* configuration with respect to the central C_2–C_3 bond, the azimuthal angle of internal rotation being 127° with the *trans* position taken as the origin. The observed C–N distance of 1.14 Å is, within the limits of error, close to the value expected for triple C–N bond length. The N–C–C bond as well as the Cu–N–C bond is found to be approximately linear. It is possible accordingly that the bond character in the C–N group may be expressed as C≡N.

The nitrate ion exists on a twofold symmetry axis. The shape and size of the ion is as listed in Table III. These data are in good agreement with those obtained for other crystals.

Infrared Spectrum as Related to the Configuration of the Ligand Molecule

The vibrational spectrum of the free succinonitrile molecule was investigated by Fitzgerald and Janz[6], who concluded that this molecule exists as an equilibrium mixture of two rotational isomers, *trans* and *gauche*, the latter being the more stable configuration. Nakagawa and Tokumaru[7] also studied the vibrational spectrum of this substance and reached a similar conclusion. In considering the infrared spectrum of the complex compound it was first assumed that the interaction forces between ligand molecules are so small that the main features of the spectrum may be explained from consideration of an isolated succinonitrile molecule. The infrared spectra of bis-(succinonitrilo)copper(I) nitrate and free succinonitrile are shown in Fig. 5. In Table IV are listed the vibrational frequencies and the assignments for the infrared absorption bands of these substances in the region 1300~700 cm^{-1}. In fact, all the main bands of the complex in this region may be assigned to the vibrations of the

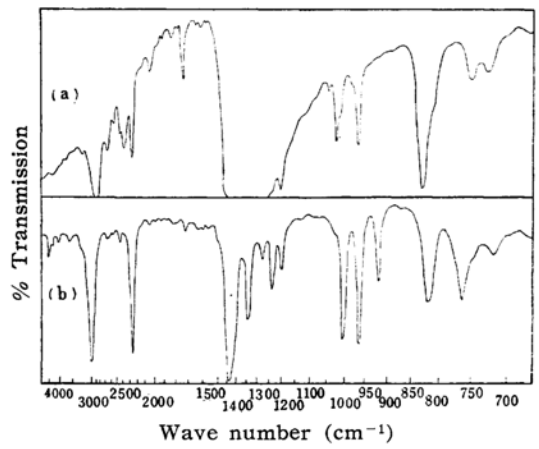


Fig. 5. Infrared spectra of (a) complex and (b) free succinonitrile.

5) D. W. J. Cruickshank, *Acta Cryst.*, 2, 65 (1949).

6) W. E. Fitzgerald and G. J. Janz, *J. Molec. Spectroscopy*, 1, 49 (1957).

7) I. Nakagawa, Private communication.

TABLE IV. INFRARED BANDS OF COMPLEX AND FREE SUCCINONITRILE

Wave numbers in cm^{-1}

Free[a]	Complex[b]	Assignments[c]			
1335	?	*gauche*	CH_2	wag	B
1271	—	*trans*	CH_2	wag	B_u
1231	1242	*gauche*	CH_2	wag	A
1198	1202	*gauche*	CH_2	twist	A
1020	1021	*gauche*	C-C	stretch	A
1001	1010	*gauche*	C-CN	stretch	B
962	965	*gauche*	CH_2	rock	A
917	—	*trans*	C-C	stretch	B_u
818	825	*gauche*	CH_2	rock	B
813	813	*gauche*	C-CN	stretch	A
761	—	*trans*	CH_2	rock	A_u

a) Solid film
b) In Nujol
c) Based on Nakagawa and Tokumaru's results

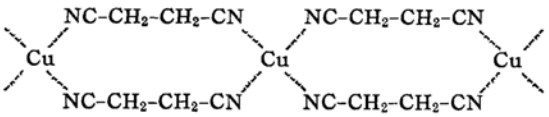
gauche configuration of succinonitrile, which is in complete agreement with the X-ray results.

The spectral features in the nitrile absorption region show strong evidence of tetrahedral coordination of the nitrile groups to the copper sp^3 orbitals; the complex compound shows two intense bands with peaks at 2278 cm^{-1} and 2381 cm^{-1}, instead of the one at 2257 cm^{-1} corresponding to the C≡N stretching vibration of the free succinonitrile. These two bands are certainly to be assigned to the C≡N stretching modes characteristic to the tetrahedral configuration of the complex compound, although the vibrational shifts towards higher frequencies with respect to the free nitrile may require further considerations.

The intense bands at 830 cm^{-1} and near 1380 cm^{-1} and a weak band at 749 cm^{-1} are assigned to the vibrations of the nitrate ion. A weak band at 1042 cm^{-1} may correspond to an infrared inactive frequency for the nitrate ion which is considered to become active because of the breakdown of the selection rule in the crystalline field.

Summary

The crystal structure of bis(succinonitrilo)copper(I) nitrate has been determined by two dimensional Fourier method. It is monoclinic $P2/a$ with two formula units in a cell of dimensions: $a=11.62\pm0.03$ Å, $b=5.31\pm0.01$ Å, $c=9.53\pm0.03$ Å and $\beta=98.8°\pm0.2°$. The crystal consists of nitrate ions and polymeric chains of the following composition:



These chains run parallel to the a-axis. A succinonitrile molecule takes a *gauche* form with respect to the central C_2–C_3 bond. A copper atom is surrounded tetrahedrally by four nitrogen atoms with Cu–N distances of 1.96 and 2.02 Å. These facts are in close agreement with infrared spectral observations.

All the atoms in the group Cu–N–C–C lie almost on a straight line. This fact and the observed C–N distance of 1.14 Å suggest that the bond character in the C–N group may essentially be expressed as C≡N.

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