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The Crystal Structure of Bis(succinodinitrile)copper(I) Perchlorate

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Bis(succinonitrile)copper(I) perchlorate crystallizes in the space group $P4_2/nmc$ with two formula units $Cu(NCCH_2CH_2CN)_2ClO_4$ in a unit cell of dimensions $a=7{\cdot}68_0\pm0{\cdot}01$, $c=10{\cdot}18_8\pm0{\cdot}01_5$ Å ($D_m=1{\cdot}78\pm0{\cdot}01$ g.cm^{-3}, $D_c=1{\cdot}786$ g.cm^{-3}). 288 independent intensities above background were collected on a diffractometer by an ω-scan technique. The structure was refined by full-matrix least squares to a conventional unweighted R index of 3·8% for all data. The structure consists of infinite puckered sheets of composition $[Cu(NCCH_2CH_2CN)_2^+]_\infty$ normal to **c**, with ClO_4^- ions lying in the planes of the sheets. The succinonitrile molecules are statistically disordered about the ⟨100⟩ mirror planes. Each Cu atom is tetrahedrally surrounded by four nitrogen atoms at a Cu–N distance of 1·987 ± 0·005 Å. Each succinonitrile is coordinated to two Cu atoms. The $Cu{-}N{\equiv}C{-}C$ segment is nearly linear with a Cu–N–C angle of 169·7 ± 0·5° and N–C–C angle of 178·3 ± 0·4°.

Introduction

Among the rapidly growing number of precise crystal structure analyses of copper complexes, those dealing with Cu(I) complexes form a small minority compared with those in which the metal is Cu(II). This is unfortunate, since accurate and precise geometrical information concerning copper in both its oxidation states is essential, for instance, for an understanding of the redox behaviour of coordinated copper which, in turn, has important biological implications (Hemmerich, 1966; Freeman, 1966). The present study is a contribution to the stereochemistry of tetrahedral Cu(I).

Experimental

$Cu(CH_3CN)_4ClO_4$ [2g, prepared by the method of Hemmerich & Sigwart (1963)] was dissolved under nitrogen in a solution of succinodinitrile§ (10 g) and absolute dimethylformamide (2 g). The mixture was heated to 140 °C for three hours, and was then allowed to cool to room temperature. $Cu(NCCH_2CH_2CN)_2ClO_4$ (1·35 g) was precipitated in the form of pale grey-brown crystals, approximately cubic in shape and detonating at 298 °C. Titration with $KMnO_4$ showed the molecular weight to be 323 ± 6 (calc. 323·2).

Neither visual nor X-ray examination showed any change in the crystals as a result of exposure to air, even after a period of weeks. The density was determined by the flotation method with mixed solvents, $BrCH_2CH_2BR$ and CCl_4. The space group was determined from $hk0$, $hk1$, $hk2$ and hhl precession photographs of a crystal mounted about its [110] axis. The lattice constants were fitted by least squares to $\sin^2\theta/\lambda^2$ for 24 reflexions ($12\alpha_1,\alpha_2$ pairs) measured on an $0kl$ Weissenberg photograph calibrated with Al powder lines ($a=4{\cdot}0489$ Å; Cu $K\alpha_1=1{\cdot}54051$ Å; $K\alpha_2=1{\cdot}54433$ Å). A variant of Cohen's analytical extrapola-

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[§] 'Succinonitrile' is the common name of the compound more properly named 'succinodinitrile'. Herein we use the two terms interchangeably.

tion procedure (Buerger, 1942) was used, parameters being introduced to correct for absorption and eccentricity errors (Freeman & Taylor, 1965). Three-dimensional intensity data were measured on a Supper diffractometer (equi-inclination Weissenberg geometry). The crystal was mounted about the *a* axis and all accessible reflexions on levels 0*kl* through 8*kl* (k, $l \geq 0$) were recorded using Ni filtered Cu $K\alpha$ radiation and a scintillation counter with pulse height discrimination. An ω-scan technique was used. Background measurements were taken at each end of the scan. Intense reflexions, for which the peak counting rate was greater than 10,000 c.p.s., were measured with attenuators. Reflexions of medium intensity were measured both with and without attenuation and used to scale the intense reflexions. The raw data were corrected for Lorentz and polarization effects. Preliminary standard deviations were calculated assuming only random counting errors. An absorption correction, calculated by the method of Coppens, Leiserowitz & Rabinovich (1965), was applied. Then the data were reindexed so that $k \geq h$ and were placed on a single scale by the method described by Rae (1965). After a preliminary refinement, the data were corrected for extinction (Zachariasen, 1963), using $\beta(2\theta)$ values which had been calculated concurrently with the absorption correction. The crystal had well defined $\langle 110 \rangle$ and $\langle 001 \rangle$ faces and had dimensions 0·10 × 0·10 mm in the plane normal to **c** and 0·14 mm parallel to **c**.

The structure amplitudes $F(hkl)$ were assigned standard deviations

$$\sigma_{F(hkl)} = \sigma_{CS(hkl)} + 0{\cdot}03\ F(hkl)$$

where $\sigma_{CS(hkl)}$ is the standard deviation for the given reflexion based on counting statistics, and $0{\cdot}03\ F(hkl)$ was added to take account of instrumental errors.*

A reflexion was defined as being 'observed' when $I > 2\sigma(I)$. The intensities and standard deviations of the 'unobserved' data were estimated from the relations given by Hamilton (1955), where the minimum intensity for a given reflexion was taken as $I_{\min} = 2\sigma(I)$. In placing the data on a single scale, only observed data were used to form an average value for a reflexion, and for reflexions for which there were no observed data, the average value was taken as the smallest of the estimated unobserved values. In this manner 343 independent data were obtained (two were later discarded as unreliable) of which 53 were unobserved; both the observed and the unobserved data were used in the refinement.

The calculations were done on CDC 3200, CDC 3600 and CDC 1604 computers. The Fourier calculations were performed with the programs *FOURIER* and *PREFOUR* (Blount, 1965). The full matrix, least-squares refinement cycles were carried out with a local version of the program *ORFLS* (Busing, Martin & Levy, 1963). Bond lengths and angles, together with their estimated standard deviations calculated from the full inverse matrix (and including estimated errors in lattice constants), were obtained with the program *ORFFE* (Busing, Martin & Levy, 1964).

Results

Unit cell and space group

The unit cell is tetragonal and contains two $Cu(NCCH_2CH_2CN)_2ClO_4$ units (formula weight 323·18): $a = 7{\cdot}68_0 \pm 0{\cdot}01$, $c = 10{\cdot}18_8 \pm 0{\cdot}01$ Å, $V = 600{\cdot}9$ Å^3, $D_c = 1{\cdot}786$ for $Z = 2$, $D_m = 1{\cdot}78 \pm 0{\cdot}01$ g.cm^{-3}. Systematic absences for $hk0$ with $h + k = 2n + 1$ and hhl with $l = 2n + 1$ ($00l$ with $l = 2n + 1$ only) are characteristic of the space group $P4_2/nmc$; the first setting, with the origin at $\bar{4}m2$, $\frac{\bar{1}}{4}\ \frac{1}{4}\ \frac{\bar{1}}{4}$ from (i), was used (*International Tables for X-ray Crystallography*, 1952).

Determination of the structure

The structure solution requires the determination of the positions of one copper, one chlorine, one oxygen one nitrogen, two carbon and, ideally, two hydrogen

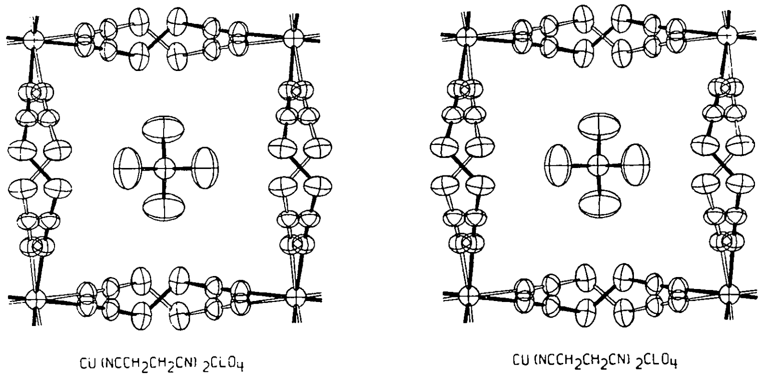

Fig. 1. View down the [001] direction of a part of a $[Cu(NCCH_2CH_2CN)_2{}^+]_\infty$ sheet and a perchlorate ion in its plane. The ligand molecules generated by the disorder are shown with unshaded bonds. Thermal ellipsoids are scaled to contain 50% probability.

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* The value of the instrumental factor was obtained by comparing plots of $\overline{\Delta F}$ *versus* F and of $\overline{\sigma_{CS}}$ *versus* F (where $\overline{\Delta F}$ and $\overline{\sigma_{CS}}$ are averages for ranges of F values) for a similarly recorded set of 3000 data for another compound. The ratio $\overline{\Delta F}/\overline{\sigma F}$ remained approximately constant over the entire range of F for these data when a value of 3% was used for the instrumental factor.

atoms. Because there are only two formula units per unit cell, all atoms except hydrogens must lie on special positions for an ordered structure. If Cu is placed in 2(*a*), then Cl is in 2(*b*) and O is in 8(*g*). Simple chemical considerations show that it is impossible for a succinonitrile molecule to have both ends coordinated to the same Cu atom, and that the succinonitrile molecules may join only Cu atoms which are separated by one unit-cell translation along **a** or **b**. Hence the independent N and C atoms of the $NCCH_2$ fragments should lie in special positions 8(*g*). If this were so, however, the succinonitrile molecules would be severely strained. A simple disordered model which reduces the bond angle distortions can be constructed by placing the N and C atoms in general positions 16(*h*) with occupancy factors 0·5. A succinonitrile molecule joining a Cu atom at (0,0,0) to one at (0,1,0) is then no longer required to be in the $x=0$ plane. If one half of the molecules lies on one side of this plane, and the other half lies on the other side, the disorder is satisfied (see Fig. 1). In this manner the distortion from tetrahedral coordination at both Cu and C(2) can be reduced.

An electron density map, based on the trial positions obtained assuming reasonable bond lengths and the ordered model, clearly showed the disorder in the succinonitrile moiety. The scattering curves of Cromer & Waber (1965) were used for Cu^+, Cl^-, O, N, C, and that of Stewart, Davidson & Simpson (1965) for H. Dispersion corrections (both $\Delta f'$ and $\Delta f''$) were applied to the Cu and Cl scattering factors (Cromer, 1965).

The structure was refined by the full-matrix least-squares method. The quantity $\sum_{hkl} w(hkl)||F_o(hkl)|-|F_c(hkl)||^2$ was minimized, where $w=\sigma^{-2}$. In the first few least-squares cycles the *x* coordinates of N and C(1) were not adjusted but were reset after each cycle on the basis of $x_{C(2)}$, according to the relation $x_A=d_A.(x_{C(2)}/d_{C(2)})$ where $d_i=(y_i^2+z_i^2)$ and $A=\mathrm{N,C(1)}$. When this restriction on the *x*-coordinates of N and C(1) was removed, and all parameters not constrained by symmetry were adjusted by least-squares, N and C(1) remained out of the $x=0$ plane. At this point the hydrogen atoms were introduced; their positions were calculated assuming a tetrahedral arrangement about C(2) and a carbon–hydrogen distance of 1·07 Å. Only the temperature factors of the hydrogen atoms were varied in the refinements because of the overlap of the hydrogen atoms due to the disorder; the positions of the hydrogen atoms were recalculated after each least-squares cycle. When all non-hydrogen atoms were treated anisotropically, N and C(1) still refined in a normal manner. After a preliminary refinement, the data were corrected for extinction. Two reflexions, for which spurious counts had apparently been recorded, were deleted from the data. The refinement was concluded when shifts in all parameters were all less than one-tenth of the corresponding estimated standard

Table 1. *Observed and calculated structure factors*

The F_o and F_c values have been scaled by 10 so that $F(000)=3240$. Reflexions tagged by an * were considered unobserved; those tagged by an X were considered incorrect and were not used.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	0	2	456	471	1	4	7	58	60	2	6	8	132	133
0	0	4	214	213	1	4	8*	13	10	2	6	9	17	14
0	0	6	338	350	1	4	9	52	54	3	6	1	44	49
0	0	8	187	181	1	4	10	21	13	3	6	2	69	65
0	0	10	383	383	1	4	11	28	33	3	6	3	36	42
0	0	12	60	63	2	4	0	284	270	3	6	4*	11	2
0	1	1	63	43	2	4	1	141	139	3	6	5	72	72
0	1	2	87	87	2	4	2	395	389	3	6	6*	11	5
0	1	3	79	74	2	4	3	108	107	3	6	7	30	25
0	1	4	166	156	2	4	4	389	397	3	6	8*	9	10
0	1	5	246	255	2	4	5	32	25	4	6	0	246	241
0	1	6	75	82	2	4	6	316	315	4	6	1*	11	10
0	1	7	197	206	2	4	7	45	52	4	6	2	186	186
0	1	8	34	30	2	4	8	213	208	4	6	3	30	29
0	1	9	121	119	2	4	9*	12	15	4	6	4	169	166
0	1	10	41	41	2	4	10	123	121	4	6	5*	11	6
0	1	11*	12	11	2	4	11	34	30	4	6	6	135	135
0	1	12	17	17	3	4	1	198	205	4	6	7*	9	5
1	1	0	748	745	3	4	2	81	71	4	6	8	95	101
1	1	2	1149	1183	3	4	3	75	75	5	6	1	52	51
1	1	4	356	367	3	4	4	29	20	5	6	2	21	21
1	1	6	221	230	3	4	5	62	65	5	6	3	23	15
1	1	8	403	411	3	4	6	48	46	5	6	4	23	18
1	1	10	150	146	3	4	7*	13	1	5	6	5*	10	18
1	1	12	151	147	3	4	8*	13	2	5	6	6*	9	0
0	2	0	1081	1167	3	4	9	30	28	5	6	7	31	31
0	2	1	378	377	3	4	10	18	16	6	6	0	174	171
0	2	2	553	581	4	4	0	326	320	6	6	2	108	111
0	2	3	56	59	4	4	2	269	268	6	6	4	115	116
0	2	4	471	486	4	4	4	264	258	0	7	1*	5	7
0	2	5	202	202	4	4	6	237	234	0	7	2	49	53
0	2	6	391	407	4	4	8	171	170	0	7	3	57	55
0	2	7	38	35	4	4	10	111	118	0	7	4	35	29
0	2	8	220	221	0	5	1	158	166	0	7	5	82	85
0	2	9*	14	4	0	5	2	109	106	0	7	6	31	25
0	2	10	244	238	0	5	3	69	60	0	7	7	32	32
0	2	11	92	90	0	5	4	101	102	0	7	8*	8	3
0	2	12	115	113	0	5	5	51	54	1	7	0	298	297
1	2	1	16	10	0	5	6	80	87	1	7	1*	6	9
1	2	2	494	494	0	5	7	120	122	1	7	2	153	151
1	2	3	353	344	0	5	8	53	46	1	7	3	79	80
1	2	4	49	36	0	5	9	82	86	1	7	4	206	205
1	2	5	123	122	0	5	10	20	17	1	7	5*	10	1
1	2	6	23	14	1	5	0	472	474	1	7	6	158	164
1	2	7	129	128	1	5	1	31	28	1	7	7	50	53
1	2	8	62	61	1	5	2	388	390	1	7	8	41	40
1	2	9	25	14	1	5	3	99	97	2	7	1	12	4
1	2	10*	13	5	1	5	4	225	228	2	7	2	18	9
1	2	11	21	17	1	5	5	36	35	2	7	3	59	60
1	2	12	38	41	1	5	6	220	222	2	7	4	30	30
2	2	0X	281	148	1	5	7	57	58	2	7	5	96	100
2	2	2	575	580	1	5	8	206	203	2	7	6*	9	4
2	2	4	617	644	1	5	9	24	18	2	7	7*	8	10
2	2	6	421	431	1	5	10	126	124	3	7	0	177	174
2	2	8	219	221	2	5	1	96	104	3	7	1*	9	2
2	2	10	143	140	2	5	2	57	60	3	7	2	157	153
0	3	1	265	251	2	5	3	124	125	3	7	3	47	48
0	3	2	431	433	2	5	4	86	88	3	7	4	187	184
0	3	3	33	22	2	5	5	24	19	3	7	5*	10	7
0	3	4	264	266	2	5	6	96	96	3	7	6	131	133
0	3	5	233	222	2	5	7	81	83	3	7	7	33	32
0	3	6	133	139	2	5	8*	12	6	4	7	1	24	16
0	3	7*	13	8	2	5	9	40	40	4	7	2*	10	6
0	3	8	68	64	2	5	10	30	33	4	7	3	37	37
0	3	9	65	65	3	5	0	285	286	4	7	4*	10	10
0	3	10	28	31	3	5	1	24	20	4	7	5	52	48
0	3	11	30	35	3	5	2	301	295	4	7	6	30	33
1	3	0	458	461	3	5	3	72	72	5	7	0	120	119
1	3	1	135	135	3	5	4	248	243	5	7	1	26	23
1	3	2	458	482	3	5	5	51	55	5	7	2	135	133
1	3	3	43	42	3	5	6	213	208	5	7	3	30	29
1	3	4	517	535	3	5	7	52	59	5	7	4	108	110
1	3	5	109	110	3	5	8	162	163	5	7	5*	8	10
1	3	6	363	375	3	5	9	37	33	6	7	1*	8	6
1	3	7	50	57	4	5	1	122	125	6	7	2*	8	3
1	3	8	242	240	4	5	2	31	26	0	8	0	78	76
1	3	9	78	83	4	5	3	43	41	0	8	1	55	56
1	3	10	170	168	4	5	4	34	26	0	8	2	212	213
1	3	11*	11	8	4	5	5	27	20	0	8	3*	7	13
2	3	1	138	134	4	5	6	29	22	0	8	4	117	120
2	3	2X	83	11	4	5	7	53	53	0	8	5	20	20
2	3	3	245	249	4	5	8*	10	1	0	8	6	74	74
2	3	4	166	164	4	5	9	45	44	1	8	1*	5	8
2	3	5	162	162	5	5	0	225	230	1	8	2	13	9
2	3	6	76	77	5	5	2	246	241	1	8	3	61	61
2	3	7	27	15	5	5	4	124	123	1	8	4*	7	5
2	3	8	23	10	5	5	6	130	128	1	8	5	35	35
2	3	9*	13	7	5	5	8	147	151	1	8	6*	7	12
2	3	10*	12	2	0	6	0	348	345	2	8	0	82	82
2	3	11	42	36	0	6	1	21	22	2	8	1	46	49
3	3	0	268	253	0	6	2	342	347	2	8	2	170	169
3	3	2	278	269	0	6	3	45	43	2	8	3*	7	3
3	3	4	543	540	0	6	4	188	193	2	8	4	134	132
3	3	6	390	378	0	6	5*	11	4	2	8	5*	7	11
3	3	8	158	156	0	6	6	136	137	3	8	1*	7	4
3	3	10	152	152	0	6	7*	11	4	3	8	2*	7	1
0	4	0	629	647	0	6	8	176	177	3	8	3	58	58
0	4	1	24	26	1	6	1	57	58	3	8	4*	7	1
0	4	2	405	428	1	6	2	70	69	3	8	5	19	23
0	4	3	128	128	1	6	3	23	20	4	8	0	99	98
0	4	4	297	313	1	6	4	46	49	4	8	1	25	26
0	4	5	67	66	1	6	5	98	94	4	8	2	117	116
0	4	6	303	309	1	6	6	69	63	4	8	3*	7	11
0	4	7	25	27	1	6	7	53	52	4	8	4	100	100
0	4	8	253	247	1	6	8	20	19	5	8	1	16	17
0	4	9	28	24	1	6	9	30	34	0	9	1	43	37
0	4	10	171	165	2	6	0	253	246	0	9	2*	10	6
0	4	11*	9	17	2	6	1	21	14	0	9	3	29	31
1	4	1	267	262	2	6	2	290	285	1	9	0	135	139
1	4	2	55	57	2	6	3*	10	12	1	9	1*	10	6
1	4	3	65	56	2	6	4	232	231	1	9	2	86	89
1	4	4	123	113	2	6	5	28	28	1	9	3	21	16
1	4	5	41	33	2	6	6	155	155	2	9	1	36	33
1	4	6	25	27	2	6	7*	11	20	2	9	2*	9	2

deviation. The weighted and unweighted discrepancy residuals were 0·052 and 0·038 for all data, and 0·051 and 0·032 for observed data, respectively.

A difference Fourier based on the final parameters and all data (except the two considered incorrect) showed only two extremes of magnitude greater than $\frac{2}{3}$ e.Å^{-3}, a maximum of 0·7 e.Å^{-3} at the Cu position and a minimum of $-1·3$ e.Å^{-3} at the Cl position. There were no other significant features in the difference Fourier.

The final observed and calculated structure factors are compared in Table 1. The final positional parameters are given in Table 2 and the final thermal parameters are given in Table 3. The standard deviations given are computed assuming that the structure factor discrepancies represent random errors.

Table 2. *Final positional parameters and their standard deviations (in parentheses)*

The standard deviations correspond to the least significant digits in the coordinates.

	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$
Cu	0	0	0
N	0·0226 (35)	0·2047 (4)	0·1180 (3)
C(1)	0·0408 (5)	0·3023 (5)	0·1982 (4)
C(2)	0·0650 (6)	0·4273 (6)	0·3076 (4)
Cl	0	0	0·5
O	0	0·1468 (4)	0·5816 (3)
H(1)	0·0536	0·3580	0·3983
H(2)	0·1926	0·4824	0·3000

Discussion

Some interatomic distances and angles for $\mathrm{Cu(NCCH_2CH_2CN)_2ClO_4}$, together with their esti-

Table 3. *Final vibrational parameters and their estimated standard deviations (in parentheses)*

Anisotropic temperature factor: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$. ($B_{\rm iso}$ values are in Å^2. The anisotropic temperature parameters have been multiplied by 10^4.)

	B	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu		133 (2)	133 (2)	66 (1)	0	0	0
N		173 (41)	116 (4)	83 (3)	−6 (8)	−3 (6)	−16 (4)
C(1)		175 (16)	108 (6)	77 (4)	0 (6)	−6 (5)	15 (4)
C(2)		226 (9)	127 (5)	65 (3)	−11 (7)	−27 (5)	3 (5)
Cl		145 (2)	145 (2)	67 (2)	0	0	0
O		560 (14)	225 (7)	164 (5)	0	0	−79 (5)
H(1)	4·9 (1·2)						
H(2)	10·0 (1·8)						

Table 4. *Interatomic distances and angles in* $\mathrm{Cu(NCCH_2CH_2CN)_2ClO_4}$

Symmetry related atoms are denoted as follows (positions x–xiii are generated by the disorder):

Superscript	Location			Superscript	Location		
–	x	y	z	viii	$\frac{1}{2}-y$	$\frac{1}{2}+x$	$-\frac{1}{2}+z$
′	$-y$	x	$-z$	ix	$-\frac{1}{2}+y$	$\frac{1}{2}-x$	$\frac{1}{2}+z$
″	$-x$	$-y$	z				
‴	y	$-x$	$-z$				
iv	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$	x	$-x$	y	z
v	$-y$	x	$1-z$	xi	y	x	$-z$
vi	$-x$	$1-y$	z	xii	x	$-y$	z
vii	y	$-x$	$1-z$	xiii	$-y$	$-x$	$-z$

Bond	Length l	$\sigma(l)$
Cu---N	1·987 Å	0·005 Å
N----C(1)	1·118	0·006
C(1) –C(2)	1·483	0·006
C(2) –C($2^{\rm vi}$)	1·498	0·012
C(2) –H(1)	1·07	
C(2) –H(2)	1·07	
Cl ---O	1·401	0·004

Angle	θ	$\sigma(\theta)$
O ----Cl–O″	107·2°	0·3°
O$^{\rm v}$ ---Cl–O$^{\rm vii}$		
O ----Cl–O$^{\rm v}$	110·6	0·2
O ----Cl–O$^{\rm vii}$		
O″---Cl–O$^{\rm v}$		
O″---Cl–O$^{\rm vii}$		

Angle	θ	$\sigma(\theta)$
Cu---N---C(1)	169·7°	0·5°
N----C(1)–C(2)	178·3	0·4
C(1) –C(2)–C($2^{\rm vi}$)	113·5	0·4
C(1) –C(2)–H(1)	108·4	
C(1) –C(2)–H(2)		
H(1)–C(2)–C($2^{\rm vi}$)		
H(2) –C(2)–C($2^{\rm vi}$)		
H(1) –C(2)–H(2)	109·5	
N---Cu---N″	105·5	0·3
N---Cu---N′	111·5	0·1
N---Cu---N‴		
N---Cu---N$^{\rm x}$	10·0	1·5
N---Cu---N$^{\rm xii}$	104·6	0·3
N---Cu---N$^{\rm xi}$	103·2	1·3
N---Cu---N$^{\rm xiii}$	120·3	1·3

mated standard deviations, are presented in Table 4. The N–Cu–N angles include both those which involve only the nitrogen atoms related to N by the $\bar{4}$ axis and those due to the disorder of the succinonitrile moiety. Short non-bonded contacts between atoms of the asymmetric unit and symmetry related units which do not involve the disorder are listed in Table 5. The molecular dimensions of $Cu[NC(CH_2)_2CN]_2ClO_4$ are compared with those of $Cu[NC(CH_2)_2CN]_2NO_3$ (Kinoshita, Matsubara & Saito, 1959*a*), $Cu[NC(CH_2)_3CN]_2NO_3$ (Kinoshita *et al.*, 1959*b*) and $Cu[NC(CH_2)_4CN]_2NO_3$ (Kinoshita, Matsubara, Higuchi & Saito, 1959) in Table 6.

If the structure were not disordered, it could be considered to belong to space group $P4_2/n$ (see Fig. 2). The apparent space group $P4_2/nmc$ is then generated by the addition of a mirror plane normal to **a**. We shall begin the description of the structure with those aspects which do not depend on the disorder.

Table 5. *Non-bonded contacts* $\leq 3{\cdot}0$ Å *involving H atoms, and* $\leq 3{\cdot}3$ Å *not involving H atoms, in* $Cu(NCCH_2CH_2CN)_2ClO_4$

Symmetry-related atoms are designated as in Table 4.

Vector	Equivalent vector	Distance
$H(1)\cdots H(1^{vi})$		2·33 Å
$H(1)\cdots H(2^{vi})$	$H(2)\cdots H(1^{vi})$	2·47
$O\cdots H(1)$		2·51
$O\cdots H(2^{ix})$	$H(2)\cdots O^{viii}$	2·55
$N\cdots H(2^{iv})$	$H(2)\cdots N^{iv}$	2·75
$O\cdots H(1^{v})$	$H(1)\cdots O^{vii}$	2·85
$Cl\cdots H(1)$ $Cl\cdots H(1'',{}^{v,vii})$	$H(1)\cdots Cl''$	2·97
$C(1)\cdots H(2^{iv})$	$H(2)\cdots C(1^{iv})$	3·00
$C(1)\cdots O^{viii}$	$O\cdots C(1^{ix})$	3·08
$C(2)\cdots O^{viii}$	$O\cdots C(2^{ix})$	3·24

The idealized structure shown in Fig. 2 consists of perchlorate ions and sheets of composition $[Cu(NCCH_2CH_2CN)_2^+]_\infty$. Each Cu atom is tetrahe-

Table 6. *Comparison of molecular dimensions of copper*(I) *complexes with nitriles of dibasic aliphatic acids*

I $Cu[NC(CH_2)_2CN]_2ClO_4$, this work
II $Cu[NC(CH_2)_2CN]_2NO_3$ (Kinoshita *et al.* 1959*a*)
III $Cu[NC(CH_2)_3CN]_2NO_3$ (Kinoshita *et al.* 1959*b*)
IV $Cu[NC(CH_2)_4CN]_2NO_3$ (Kinoshita *et al.* 1959*c*)

(*a*) Bond lengths (Å)

Bond	I	II	III	IV
Cu–N	1·99	1·96 2·02	1·98	1·98
N–C	1·12	1·14 1·14	1·14	1·13
C–C	1·48 1·50	1·53 1·52 1·49	1·54 1·53	1·54 1·50 1·53

(*b*) Bond angles (°)

Angle	I	II	III	IV
Cu–N–C	170	175 177	176	169
N–C–C	178	175 180	176	172
C–C–C	114	113 107	110 106	108 108

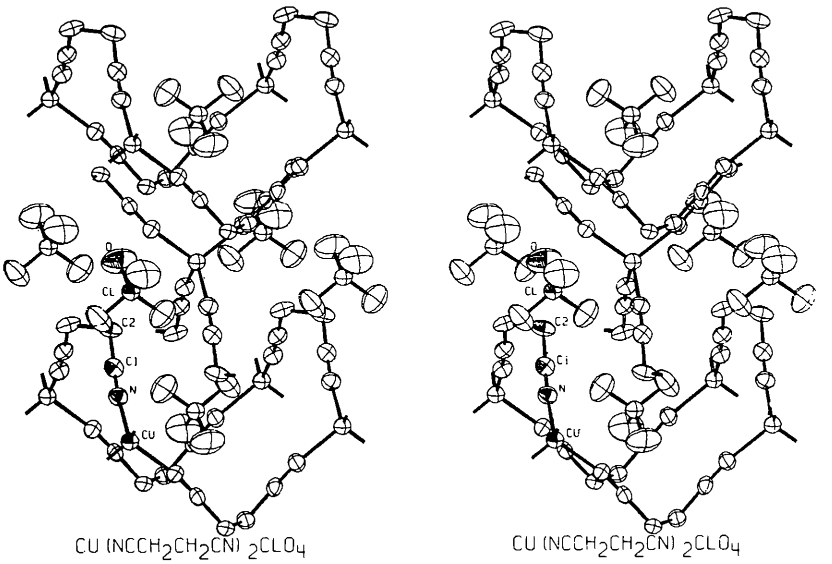

Fig. 2. A view of $Cu(NCCH_2CH_2CN)_2ClO_4$ illustrating the packing of the infinite sheets. The *c* axis is vertical, and portions of the sheets at $z=0$, $z=\frac{1}{2}$ and $z=1$ are shown. Atoms in positions generated by the disorder are not shown. Thermal ellipsoids are scaled to contain 50% probability.

drally surrounded by four N atoms, while each succinonitrile molecule is coordinated to two Cu atoms. All the Cu atoms in a given plane normal to **c** are interconnected by succinonitrile molecules which run parallel to **a** and **b** to form an infinite network; there are two such sheets per unit-cell translation along **c**. Adjacent sheets are related to one another by the *n*-glide plane between them (and by centres of symmetry which lie midway between nearest-neighbour Cu atoms in the two adjacent sheets). The perchlorate ions lie in the planes of the $[Cu(NCCH_2CH_2CN)_2^+]_\infty$ sheets, octahedrally surrounded by six Cu atoms, four from the plane in which they lie and one each from the neighbouring planes above and below.

The copper–nitrogen and nitrogen–carbon distances for $Cu(NCCH_2CH_2CN)_2ClO_4$ are in good agreement with those for the other complexes of Cu(I) with the nitriles of dibasic aliphatic acids, as shown in Table 6. These distances are also in reasonable agreement with those in $KCu(CN)_2$ (Cromer, 1967) and $KCu_2(CN)_3.H_2O$ (Cromer & Larson, 1962), where the average of four Cu–N distances is $2·002 \pm 0·017$ Å and the average of five N–C distances is $1·150 \pm 0·026$ Å. Additional Cu–N and N–C distances are $1·984 \pm 0·008$ and $1·130 \pm 0·011$ Å in $CuCN.NH_3$ (orientation II) (Cromer, Larson & Roof, 1965), $1·95 \pm 0·02$ and $1·17 \pm 0·02$ Å in $CuCN.N_2H_4$ (orientation I) (Cromer, Larson & Roof, 1966), and $1·993 \pm 0·019$ Å in $Cu_2Cl_2.N_2(CH_3)_2$ (Brown & Dunitz, 1960). The N–C–C fragment is nearly linear (angle N–C(1)–C(2) is 178°), as expected. The departure from linearity of the Cu–N–C angle (170°), and also the enlarged C–C–C angle about C(2) (114°), are presumably manifestations of crystal packing effects due in large part to the rigidity of the N–C–C fragment. A similar distortion of the Cu–N–C angle is found in $Cu[NC(CH_2)_4CN]_2NO_3$.

In $Cu(NCCH_2CH_2CN)_2ClO_4$ the succinonitrile molecule assumes a *gauche* conformation about the $C(2)–C(2^{vi})$ bond, as predicted from the infrared spectrum (Kubota, Johnston & Matsubara, 1966). Succinonitrile in the corresponding nitrate complex also takes a *gauche* conformation about the central C–C bond. The azimuthal angle about the central C–C bond, with the *trans* configuration as the origin, is 108° in the perchlorate complex and 127° in the nitrate complex.

Even if the disorder is ignored, the coordination about the Cu atom is distorted tetrahedral. The four nitrogen donors all lie 1·99 Å from the Cu atom, but two of the N–Cu–N angles are 105·5° and four are 111·5°. If we assume that the distribution of the succinonitrile molecules between the alternate positions of the disordered structure is completely random, then there are eight, instead of four, possible sites for donor atoms. Four of these will be occupied near each Cu, and only one out of eight Cu's will have local $\bar{4}$ symmetry with bond-angles of 105·5° and 111·5°. The N–Cu–N angles at other Cu atoms will range from 103° to 120°.

We consider such an additional distortion of the Cu coordination to be an improbable consequence of disorder, since the disorder is no doubt the result of a process of energy minimization. A preferable description appears to us to be one in which each sheet is completely ordered, but in which the stacking of the sheets is random.

Finally we note that, despite the disorder of nearly everything else, this structure provides one of the few examples of ClO_4^- ions which are *not* disordered.

Individual perchlorate ions are probably displaced from the equilibrium position required for $P4_2/nmc$ by small rotations about an axis parallel to **c** passing through the chlorine atom, resulting from the local arrangement of the surrounding succinonitrile ligands. In the average structure the effect of these displacements would be absorbed by the anisotropic temperature factor of the oxygen atom. This is observed, the diagonal components of the anisotropic temperature factor for O being $B_{11} = 13·2$, $B_{22} = 5·3$ and $B_{33} = 6·8$ Å^2.

It is interesting to note the variety of networks formed with copper(I) by complexes of short-chain, dibasic aliphatic acids. The linear nature of the Cu–N–C–C segment prevents both ends of such nitrile molecules from coordinating with the same Cu atom. If the tetrahedral coordination of the Cu atom is to be maintained, finite complexes of the form $Cu_m[NC(CH_2)_nCN]_{2m}^{m+}$ cannot be produced and hence infinite polymeric networks are created. The nature of the network is not determined by the ligand molecule alone, for the succinonitrile complex forms infinite chains in $Cu[NCCH_2CH_2CN]_2NO_3$, but infinite sheets in $Cu[NCCH_2CH_2CN]_2ClO_4$. Infinite two-dimensional sheets are also found in $Cu[NC(CH_2)_3CN]_2NO_3$ whereas an infinite three-dimensional network is formed in $Cu[NC(CH_2)_4CN]_2NO_3$. The stability of these complexes is possibly related to the fact that the Cu atoms are bound in an infinite network and are therefore less susceptible to attack than are Cu atoms in similar but finite complexes.

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Refinement of the Crystal Structure of Buergerite and the Absolute Orientation of Tourmalines[*]

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The crystal structure of buergerite from Mexico has been refined by least-squares by use of single-crystal X-ray intensity data collected by counter diffractometry. Buergerite, ideally $NaFe^{3+}_3B_3Al_6Si_6O_{30}F$, crystallizes in $R3m$; the hexagonal cell dimensions for the specimen used are: $a=15\cdot869\pm2$, $c=7\cdot188\pm1$ Å at 21 °C. $D_m=3\cdot30\pm1$ at 23 °C; with $Z=3$, $D_x=3\cdot29$ g.cm^{-3}. Of 3909 independent reflections measured, 3121 were observed; the residual R for the observed reflections is 0·046. The structure is very similar to the refined dravite structure of Buerger, Burnham & Peacor (*Acta Cryst.* (1962), **15**, 583) which was used as the starting model. Refinement of the (Fe^{3+}, Al) distribution shows that some ferric iron replaces octahedral aluminum in the 18(*c*) position, a substitution not required by the chemical analysis. The absolute orientation of the crystal structure with respect to the macroscopic polar properties of tourmaline was determined by anomalous dispersion, mostly due to iron, under copper radiation. The SiO_4 tetrahedra point toward the analogous pole of the *c* axis, the pole that becomes positively charged on heating.

Introduction

The extensive chemical substitution observed in tourmaline makes this mineral group a natural laboratory for the study of solid solution and the variation of structure with chemical composition. Three principal species are recognized: dravite, schorl, and elbaite, for which, in the idealized formula

$$NaX_3B_3Al_6Si_6O_{27}(OH,F)_4,$$

X stands for Mg, Fe^{2+}, and (Li,Al), respectively.

Epprecht (1953) combined cell dimensions and published chemical analyses to show that two series of tourmalines can be distinguished (Fig. 1), and by extrapolation he derived ideal cell dimensions for the three end-members (Table 1). The dravite–schorl and schorl–elbaite series are virtually immiscible, and it was later suggested that they might represent distinct sub-phases, separated by a compositional transition of first or higher order (Donnay, Wyart & Sabatier, 1959).

Table 1. *Extrapolated cell dimensions* (*Epprecht*, 1953)

End-member	*a* (Å)	*c* (Å)	*c*/*a*
Elbaite	15·842	7·099	0·4481
Schorl	16·032	7·149	0·4459
Dravite	15·942	7·225	0·4532

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