

Crystal and Molecular Structure of the Red Form of Bis(*N,N*-diethylethylenediamine)copper(II) Perchlorate

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The investigation of the structure of red thermochromic bis(*N,N*-diethylethylenediamine)copper(II) perchlorate is the first of two studies for explaining its 46°C transition to a violet form. The crystals are triclinic at room temperature, space group $C\bar{1}$, $a=17.868$ (1), $b=8.104$ (1), $c=10.039$ (1) Å, $\alpha=90.40$ (1), $\beta=131.63$ (1), $\gamma=90.45$ (2)°, $d=1.511$ g cm⁻³, $V(\text{unit cell})=1086$ Å³, and $Z=2$. The structure was determined by the heavy-atom technique. Intensities were obtained from θ - 2θ scans with a four-circle automatic diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The 1306 reflections were refined to $R=0.040$ by full-matrix least squares. The crystal is composed of $\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NEt}_2)_2^{2+}$ cations and ClO_4^- anions. The Cu^{II} is coordinated to two molecules of *N,N*-diethylethylenediamine through the N atoms resulting in a square-planar CuN_4 stoichiometry. The five-membered Cu-diamine rings adopt a symmetrical-skew conformation with the ring C atoms lying 0.322 and 0.329 Å above and below the CuN_4 plane. The bond distances are Cu-N(primary) 2.003 (4), Cu-N(tertiary) 2.060 (4), N-C (mean) 1.485, C-C (mean) 1.497 Å. The N(1)-Cu-N(2) angle is 84.4 (2)°. The ClO_4^- anion is tetrahedral, Cl-O distance (mean) 1.405 Å and O-Cl-O angle 109.4°. The oxygens, O(3), nearest to Cu are 3.649 (5) Å away. The vector O(3)-Cu-O(3') intersects the CuN_4 plane at 59.5°.

Introduction

The thermochromic substance $\text{Cu}(\text{Et}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{ClO}_4)_2$, hereafter called compound I, changes color from brick red to violet near 46°C. The vibrational, electronic and magnetic properties of this compound have been extensively studied at various temperatures. The crystal structures of several related bis(ethylenediamine)-copper complexes have been determined (Pajunen, 1967, 1969; Nasanen, Virtamo & Myllymaki, 1966) together with their electronic and far-infrared spectra (Lever & Mantovani, 1971). Two extreme structures were recognized: a square-planar complex with an in-plane CuN_4 stoichiometry and with the anionic X groups beyond bonding distance, and a tetragonally distorted octahedral complex with axially coordinating X groups. The position of the $d-d$ absorption bands has been taken as an indication of the degree of tetragonal distortion. A correlation was made between these bands and the highest energy Cu-N stretching mode. It was postulated that an increase in the in-plane field strength due to a tightening up of the in-plane bond when the axial interaction weakens has an effect on the in-plane Cu-N stretching frequency. Both the electronic transition and the metal-ligand stretching frequencies increase as the structure becomes more tetragonally distorted. The decrease in the electronic band maximum of compound I from 20 700 to 19 305 cm⁻¹ and the de-

crease in the Cu-N stretching frequency from 405 to 403 cm⁻¹ as the temperature increases from 22 to 78°C was taken as the result of a decrease in the tetragonality of the complex, which explains the changes that accompany the transition observed at 46°C (Lever, Mantovani & Donini, 1971). It was also seen that the weak band appearing at 933 cm⁻¹ and which was assigned to a symmetric stretching vibration ν_1 allowed in a C_{3v} symmetry intensifies by about 40% at 78°C. This was assumed to be an increased ion perturbation arising through coordination of one O to Cu^{2+} . The variation in the frequency of the $d-d$ band with temperature has also been observed to correlate well with the transition temperature observed by differential scanning calorimetry (Fabbri, Micheloni & Paoletti, 1974; Andino, 1974).

ESR studies of compound I in the polycrystalline state at -196, 22 and 80°C, and in the magnetically-dilute state in $\text{Ni}(\text{as-Et}_2\text{en})_2(\text{ClO}_4)_2$ powder at -196, 22 and 120°C were performed by Yokoi, Sai & Isobe (1969). Assuming compound I to be *trans*-square coplanar with the two perchlorate anions located at the axial positions and knowing the relations between the ESR data and the covalency parameters, it was concluded that the difference in structure of compound I in the magnetically-dilute state at the three temperatures lies mainly in the axial coordination and that the axial ligand field is strengthened as the temperature increases. The behavior of compound I in the polycrystalline state at 22 and 80°C was different, which led them to believe that this phase transition was of a

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different kind and possibly accompanies a structural change in the equatorial coordination.

It seemed obvious that structural information on these complexes would be useful in understanding the mechanism of the thermochromism. This paper describes the structure of the low-temperature form of compound I.

Experimental

Preparation and identification

Brick-red crystals of compound I were prepared by Pfeiffer & Glaser's (1938) method and purified by recrystallization from water. The IR spectrum of the compound was the same as that reported by Lever & Mantovani (1971). The spectrum was recorded from Nujol mulls on NaCl plates with a Perkin-Elmer 237B spectrophotometer. The percent Cu was determined by emission spectroscopy. The experimental value, 13.0%, agrees with the calculated value of 12.8%.

X-ray data collection

Two crystals of similar habit and dimensions were mounted on thin glass fibers with Aremco Crystalbond 509 adhesive. Oscillation and Weissenberg photographs of both crystals, differing in orientation by *ca* 90° from each other, were taken with Cu *K* α ($\lambda = 1.5418 \text{ \AA}$) radiation.

The photographs seemed to indicate a monoclinic cell. Weissenberg photographs of eight levels with the spindle axis chosen as the *b* axis showed systematic absences for (*hkl*) of $h + k = 2n + 1$ which is compatible with a *C*-centered unit cell. However, the fact that only 65% of the reflections which should be related by the mirror plane were really equivalent suggested the cell was triclinic, which was subsequently confirmed by diffractometer data.

In order to obtain intensity measurements a third crystal with dimensions 0.020 \times 0.035 \times 0.044 cm was cemented with epoxy cement to a thin glass fiber and mounted on a Nova-automated Syntex *P* $\bar{1}$ diffractometer equipped with a scintillation counter, a pulse height analyzer adjusted to admit 90% of the Mo *K* α peak [$\lambda(\alpha_1) = 0.70926$, $\lambda(\alpha_2) = 0.71354 \text{ \AA}$], and a crystal-graphite monochromator set at a Bragg 2θ angle of 12.2°. The crystal was aligned optically, and the angular coordinates $2\theta, \omega, \phi, \chi$ of 15 reflections, obtained from an oscillation photograph, were centered automatically. Once centered, the reflections were used in a least-squares refinement to determine the lattice constants and the orientation matrix from which the angle settings for all data were generated. A pseudo-monoclinic *C*-centered unit cell was chosen. The lattice parameters of $a = 17.868$ (1), $b = 8.104$ (1), $c = 10.039$ (1) \AA , $\alpha = 90.40$ (1), $\beta = 131.63$ (1) and $\gamma = 90.45$ (2)° were in accord with those calculated from the oscillation and Weissenberg photographs. The experimental density of $1.5108 \pm 0.0005 \text{ g cm}^{-3}$, measured by flotation in bromobenzene and ethylene tetrachloride, agrees with

the value of 1.513 g cm^{-3} calculated for a unit cell of volume 1086 \AA^3 containing two $\text{Cu}(\text{C}_6\text{H}_{16}\text{N}_2)_2(\text{ClO}_4)_2$ formula units. The total number of electrons per unit cell is 518. The parameters of the smaller, standard triclinic cell were determined. The values obtained are: $a = 8.76$, $b = 9.78$, $c = 8.10 \text{ \AA}$, $\alpha = 114.0$, $\beta = 116.5$, $\gamma = 65.3^\circ$. The volume of this cell is 543.1 \AA^3 . The space group is *P* $\bar{1}$.

Intensity data were collected *via* the θ - 2θ scan mode with stationary-crystal stationary-counter background measurements on each side of a peak. The ratio of total background counting time to scan time was 0.667. Variable scan speeds were used, the minimum scan speed being 2° min^{-1} . Data were collected in four octants: hkl , $h\bar{k}l$, $h\bar{k}\bar{l}$, $\bar{h}\bar{k}l$ for $3^\circ \leq 2\theta \leq 45^\circ$. Each reflection was sampled only once. Absent reflections due to *C*-centering were not scanned. Two reflections, 021 and $\bar{3}11$, were measured every 50 data reflections and used as standards to check for instrument stability, crystal alignment, and crystal decay. There was no change greater than 2.1% in the intensities of these standards during the entire experiment. There were 1335 reflections.

The intensity, *I*, of each reflection and its standard deviation, $\sigma(I)$, were calculated according to the formulae $I = S - B(T_s/T_B)$ and $\sigma(I) = \{S + [B(T_s/T_B)]^2 + \varrho(I^2)\}^{1/2}$ where *S* is the total scan count measured for time *T*_s, *B* the total background count measured for time *T*_B, and ϱ is an estimate of standard error arbitrarily assigned a value of 0.003. A linear correction was also applied to compensate for the variable scan speeds.

All the intensities were corrected for Lorentz-polarization (*Lp*) effects, for the polarization produced by the monochromator, and reduced to $|F_o|$ by the use of a data reduction program.

The data obtained from the previous program were corrected for the extinction of reflected intensities, merged, and ordered to yield 1306 independent reflections. The 129 reflections with $I < 2.5\sigma(I)$ were considered unobserved and eliminated.

The orientation of the crystal faces was found to be defined by the (11 $\bar{1}$), ($\bar{1}\bar{1}1$), (110), ($\bar{1}\bar{1}0$), (100), and ($\bar{1}00$) crystal planes. An absorption correction was made with a linear absorption coefficient, μ , of 13.34 cm^{-1} for Mo *K* α radiation. The transmission coefficients varied from 0.636 to 0.798 (*International Tables for X-ray Crystallography*, 1968, p. 166, Table 3.2.2.B).

Structure determination and refinement

The structure of compound I was determined by the heavy-atom technique. The two symmetry-related Cu atoms were arbitrarily placed in a *C*-centered unit cell at 0,0,0 and $\frac{1}{2}, \frac{1}{2}, 0$. The initial positions of all the remaining non-H atoms were then found from a Fourier difference synthesis phased on the coordinates for the two Cu atoms. The crystallographic cell contains two discrete species: one of them a Cu atom at a center of inversion

surrounded by two *N,N*-diethylethylenediamine molecules, and the other a Cl atom surrounded by four O atoms. A structure factor calculation with this model resulted in an unweighted R_1 value of 23.9% where $R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|) \times 100$. An isotopic, full-matrix least-squares refinement based on the minimization of $\sum \omega_i ||F_o| - |F_c||^2$ with the individual weights $\omega_i = 1/\sigma^2(F_o)$ lowered the R_1 value to 11.6%. The refined positional coordinates and isotropic thermal factors for all non-H atoms were used in a Fourier difference synthesis. At this point the difference map showed possible peaks due to the H atoms from the *N,N*-

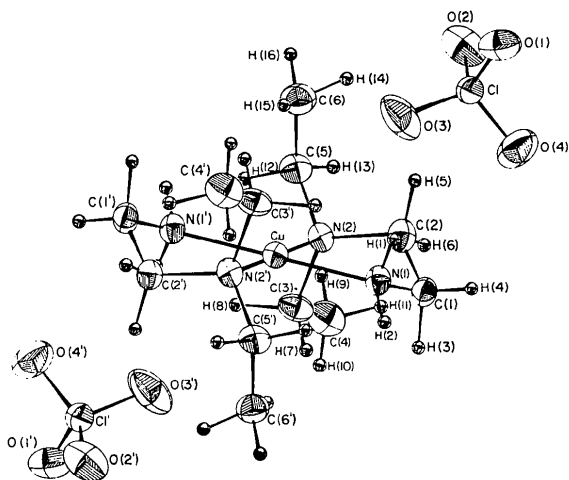


Fig. 1. View of the $[\text{Cu}(\text{Et}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$ cation lying on a crystallographic center of symmetry and two centrosymmetrically related ClO_4^- anions. All non-H atoms are represented by 50% probability thermal ellipsoids.

diethylethylenediamine molecule. A series of anisotropic, full-matrix least-squares refinements of the Cu, Cl, O, N and C atoms coupled with positional refinement for H atoms (with constant isotropic thermal parameters of 5.0) resulted in $R_1 = 0.040$ and $R_2 = 0.058$ at convergence, where R_2 is defined as $R_2 = [\sum \omega_i ||F_o| - |F_c||^2 / \sum \omega_i |F_o|^2]^{1/2}$. A final Fourier difference map revealed no residual electron density greater than $0.8 \text{ e } \text{Å}^{-3}$.

The positional and thermal parameters from the output of the final full-matrix least-squares refinement are given in Table 1. The interatomic distances and bond angles with estimated standard deviations were calculated with the Busing, Martin & Levy (1964) *ORFFE* program. The results appear in Table 2. Perpendicular distances of all non-H atoms from the CuN_4 plane are presented in Table 3. The molecular geometry and unit-cell views of compound I are given in Figs. 1, 2, and 3.*

The scattering factor tables used for all non-H atoms were those of Cromer & Mann (1968); those for hydrogen atoms are from Stewart, Davidson & Simpson (1965). Real and imaginary corrections for anomalous dispersion (*i.e.* $\Delta f' = 0.3$, $\Delta f'' = 1.3$ for Cu; $\Delta f' = 0.1$, $\Delta f'' = 0.2$ for Cl) were included in the structure factor calculations (*International Tables*, 1968, p. 215, Table 3.2.2.C). These calculations were performed either on a Univac 1108 computer (Computing Center, Univ. of

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31908 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters of $[\text{Cu}(\text{Et}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2](\text{ClO}_4)_2$*

Standard deviations in parentheses; temperature factor has the form: $\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$; B for H atoms is 5.0 Å^2 ; parameters for non-H atoms $\times 10^4$, for H atoms $\times 10^3$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	0	41.2 (5)	133 (1)	106 (2)	4.2 (5)	47 (1)	10 (1)
N(1)	1433 (2)	92 (5)	2283 (4)	47 (2)	217 (10)	117 (7)	-5 (4)	44 (4)	14 (7)
N(2)	-592 (2)	75 (4)	1202 (4)	56 (3)	159 (8)	139 (8)	-9 (3)	66 (4)	-19 (7)
C(1)	2098 (3)	-316 (6)	1961 (6)	45 (3)	181 (9)	188 (10)	9 (4)	58 (5)	18 (8)
C(2)	1667 (3)	412 (6)	209 (5)	51 (3)	191 (10)	184 (9)	-2 (4)	74 (5)	-1 (7)
C(3)	-443 (4)	1872 (5)	1751 (6)	82 (4)	138 (9)	238 (11)	-2 (4)	106 (6)	-13 (8)
C(4)	-891 (5)	2434 (8)	2501 (8)	111 (6)	207 (14)	338 (17)	-2 (7)	154 (9)	-37 (13)
C(5)	-107 (4)	-985 (5)	2789 (6)	69 (3)	188 (9)	171 (10)	0.2 (5)	80 (5)	21 (8)
C(6)	39 (4)	-2725 (6)	2493 (7)	94 (5)	186 (11)	226 (12)	9 (6)	88 (7)	40 (10)
Cl	2207 (1)	4649 (1)	2807 (1)	61 (1)	150 (2)	146 (2)	-9 (1)	57 (1)	-3 (2)
O(1)	2489 (3)	6069 (4)	3901 (4)	131 (4)	184 (7)	205 (8)	6 (4)	98 (5)	-25 (6)
O(2)	2033 (4)	5136 (5)	1279 (5)	171 (5)	327 (10)	311 (11)	-64 (6)	182 (7)	-52 (8)
O(3)	1332 (4)	3885 (6)	2230 (8)	144 (5)	315 (11)	689 (21)	-72 (6)	260 (9)	-85 (12)
O(4)	2988 (4)	3521 (5)	3715 (7)	114 (4)	240 (9)	414 (14)	51 (5)	35 (6)	-54 (9)
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>		
H(1)	154 (3)	107 (6)	252 (6)	H(9)	-71 (3)	173 (6)	338 (6)		
H(2)	162 (3)	-58 (5)	316 (6)	H(10)	-91 (3)	353 (6)	252 (6)		
H(3)	215 (3)	-159 (6)	202 (6)	H(11)	-161 (4)	197 (5)	194 (6)		
H(4)	272 (3)	1 (5)	288 (6)	H(12)	56 (3)	-45 (5)	382 (6)		
H(5)	171 (3)	172 (6)	23 (6)	H(13)	-60 (3)	-93 (5)	296 (6)		
H(6)	200 (3)	2 (5)	-13 (6)	H(14)	-56 (4)	-337 (6)	192 (6)		
H(7)	-67 (3)	253 (5)	78 (6)	H(15)	23 (3)	-248 (5)	183 (6)		
H(8)	37 (3)	208 (5)	278 (6)	H(16)	24 (3)	-349 (6)	343 (6)		

Wisconsin), or an IBM 7094 computer (Chemistry Department, Univ. of Wisconsin). The programs used

Table 2. *Interatomic distances and angles with standard deviations*

(a) Interatomic distances (Å)

Cu—N(1)	2.003 (4)	C(2)—H(5)	1.06 (5)
Cu—N(2)	2.060 (4)	C(2)—H(6)	0.91 (6)
Cu—O(3)	3.649 (5)	C(3)—C(4)	1.490 (8)
Cu—C(1)	4.747 (1)	C(3)—H(7)	0.94 (5)
N(1)—C(1)	1.462 (6)	C(3)—H(8)	1.10 (6)
N(1)—H(1)	0.81 (6)	C(4)—H(9)	0.92 (6)
N(1)—H(2)	0.90 (6)	C(4)—H(10)	0.89 (6)
N(2)—C(2)	1.478 (6)	C(4)—H(11)	1.07 (6)
N(2)—C(3)	1.510 (7)	C(5)—C(6)	1.499 (8)
N(2)—C(5)	1.491 (7)	C(5)—H(12)	1.01 (6)
C(1)—C(2)	1.503 (7)	C(5)—H(13)	1.00 (6)
C(1)—H(3)	1.04 (5)	C(6)—H(14)	0.95 (6)
C(1)—H(4)	0.89 (6)	C(6)—H(15)	0.93 (6)
Cl—O(1)	1.422 (4)	C(6)—H(16)	0.98 (6)
Cl—O(2)	1.408 (4)	O(1)—N(1')	3.091 (6)
Cl—O(3)	1.392 (5)	O(1)—H(2')	2.34 (6)
Cl—O(4)	1.399 (5)	O(3)—N(1)	3.072 (8)
		O(3)—H(1)	2.27 (6)

(b) Bond angles (°) and angles of general interest

N(2)—Cu—N(1)	84.4 (2)	O(1)—Cl—O(2)	108.3 (3)
Cu—N(1)—C(1)	110.5 (3)	O(2)—Cl—O(3)	107.7 (4)
Cu—N(2)—C(2)	106.7 (1)	O(3)—Cl—O(4)	109.8 (4)
Cu—N(2)—C(3)	101.7 (3)	O(4)—Cl—O(1)	109.9 (3)
Cu—N(2)—C(5)	116.7 (4)	O(1)—Cl—O(3)	113.0 (3)
C(2)—N(2)—C(3)	112.7 (3)	O(2)—Cl—O(4)	107.9 (3)
C(2)—N(2)—C(5)	110.1 (3)	Mean	109.4
C(3)—N(2)—C(5)	108.8 (4)		
N(1)—C(1)—C(2)	107.7 (4)	O(3)—H(1)—N(1)	162 (5)
N(2)—C(2)—C(1)	110.4 (2)	O(1)—H(2')—N(1')	173 (4)
N(2)—C(3)—C(4)	117.0 (5)	O(3)—Cu—N(1)	57.2 (2)
N(2)—C(5)—C(6)	112.7 (4)		

Table 3. *Perpendicular distances (Å) of selected atoms from the CuN₄ plane*

The equation of the plane passing through Cu, N(1), N(2), N(1'), and N(2') is $0.0041x + 0.9994y - 0.345z = 0$.

C(1)	-0.322	Cl	3.666
C(2)	0.329	O(1)	4.773
C(3)	1.447	O(2)	4.124
C(4)	1.864	O(3)	3.064
C(5)	-0.912	O(4)	2.725
C(6)	-2.311		

were those developed at the University of Wisconsin or at the Oak Ridge National Laboratory.

General description of the crystal and molecular structure

The crystal structure is composed of discrete $\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NET}_2)_2^{2+}$ cations and ClO_4^- anions. Each Cu atom is bonded to two molecules of *N,N*-diethylethylenediamine through coordination with the N atoms of the bidentate ligand molecule. The resulting stereochemistry of the Cu^{II} is square planar with the two chelating ligands related to each other by a center of symmetry. The salient structural feature of this complex which distinguishes it from other ethylenediamine Cu complexes is that in this complex the Cu^{II} is four-coordinate with the axial sites empty, rather than six-coordinate.

The two independent Cu—N bond distances are in good agreement with the values found in other *N*-alkyl substituted ethylenediamines (Luukkonen, Pajunen & Lehtonen, 1970; Pajunen, 1969; Pajunen & Luukkonen, 1969). There seems to be a significant difference

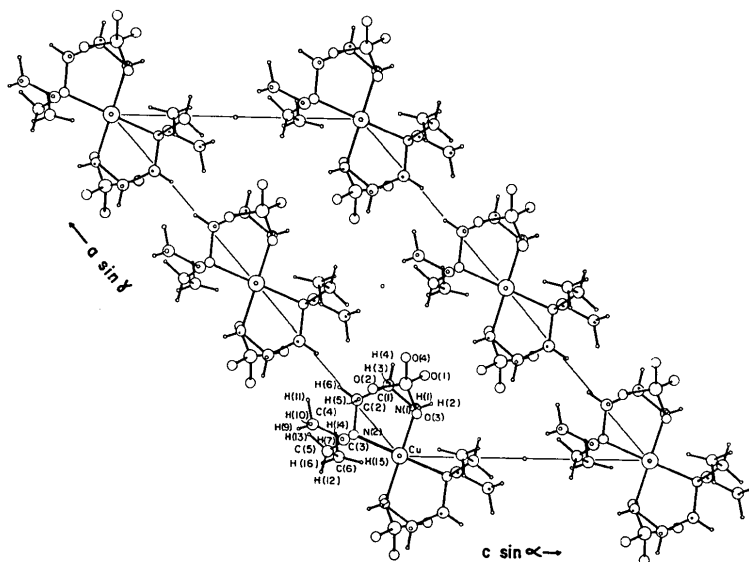


Fig. 2. [010] projection of the triclinic unit cell of symmetry C_1 containing two ionic $[\text{Cu}(\text{Et}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}(\text{ClO}_4^-)_2$ formula species.

between the primary and tertiary N atom bonding distances. The Cu–N(primary) distance is 2.003 (4) Å, while the Cu–N(tertiary) distance is 2.060 (4) Å. Similar values are observed for the Cu–N(primary) bond length of 2.004 (5) Å and Cu–N(secondary) bond length of 2.066 (5) Å in the $\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_3)_2(\text{ClO}_4)_2$ complex and with the Cu–N(secondary) bond lengths of 2.054 (mean) and 2.062 Å (mean) found in $\text{Cu}[\text{H}(\text{Me})\text{NCH}_2\text{CH}_2\text{NHMe}]_2(\text{NO}_3)_2$ and $\{\text{Cu}[\text{H}(\text{Et})\text{NCH}_2\text{CH}_2\text{NHEt}]_2(\text{H}_2\text{O})_2\}(\text{NO}_3)_2$ respectively. The N(1)–Cu–N(2) bond angle of 84.4 (2)° is near the strain-free value of 86.2° suggested by Corey & Bailar (1959).

All bond distances and angles within the ligand also agree well with the previously reported values. The average N–C and C–C distances are 1.485 and 1.497 Å respectively. The five-membered chelate ring formed by the complexing of the Cu atom with the bidentate ligand adopts a symmetrical-skew conformation with the ring C atoms lying at 0.322 and 0.329 Å above and below the CuN_4 plane.

The diethyl groups substituted on the N atoms are presumed to constitute a sufficient steric factor in preventing octahedral-like coordination of the perchlorate O atoms to Cu^{II} (Fig. 1). The nearest perchlorate O atom, O(3), is 3.649 (5) Å from Cu^{II} and the O(3)–Cu–O(3') vector makes an angle of 59.5° with the CuN_4 plane.

The ClO_4^- anion has an approximately tetrahedral configuration with the average Cl–O bond distance 1.405 Å and an average O–Cl–O angle of 109.4°. The deviation of the O(1)–Cl–O(3) angles of 113.0 (3)° from the usual tetrahedral angles might be due to hydrogen bonding of the O(1) and O(3) atoms. Each perchlorate ion is involved in two N–H...O hydrogen bonds with two neighboring complex cations. The

$\text{H}(2')\cdots\text{O}(1)$ and $\text{O}(3)\cdots\text{H}(1)$ distances of 2.34 (6) and 2.27 (6) Å, respectively, are shorter than the sum of the van der Waals radii for O and H: 2.6 Å if based on the commonly used values (Hamilton & Ibers, 1968; Pauling, 1960) or 2.4 Å if a more recent value for H is used (Baur, 1972). The observed N–O distances of 3.091 (6) and 3.072 (8) Å are reasonable. The N–H...O angles are 162 (5) and 173 (4)°.

Thus the structure observed confirms that proposed for the low-temperature form in which no coordination of the ClO_4^- anion to the square Cu complex occurs. Work on the higher-temperature form is in progress.

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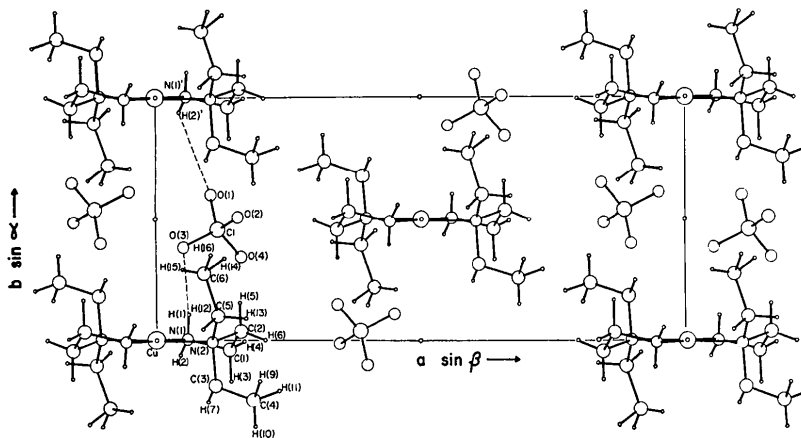


Fig. 3. [001] projection of the centrosymmetric *C*-centered triclinic unit cell. Both H atoms on the amine N(1) are hydrogen-bonded to perchlorate O atoms [viz N(1)–H(1)···O(3) and N(1')–H(2')···O(1)].

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La Structure Cristalline de $\text{Cs}_2\text{NaAl}_3\text{F}_{12}$

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$\text{Cs}_2\text{NaAl}_3\text{F}_{12}$ is rhombohedral, space group $R\bar{3}m$, with $a = 7.310$ (5) Å, $\alpha = 57.45$ (0.10)°, $Z = 1$. Single-crystal diffraction data collected on an automatic four-circle diffractometer have been refined by full-matrix least-squares calculations to a weighted R' value of 0.036 (unweighted $R = 0.028$) for 305 observed reflexions. The structure consists of trigonal $(\text{AlF}_4)_n$ layers linked by NaF_6 octahedra; it can also be considered as a pyrochlore-type structure with a $\frac{1}{3}$ order between 16(c) cationic sites.

Depuis les travaux sur les pyrochlores fluorés du type RbNiCrF_6 (Babel, Pausewang & Viebahn, 1967; Babel, 1972), l'étude des composés isotypes a été largement développée par différents auteurs (Jacoboni, 1970, 1975; Banks, Berkooz & de Luca, 1971). Pour notre part, nous avons étudié une possibilité de substitution des ions de transition qui se répartissent dans les sites 16(c) du groupe spatial $Fd\bar{3}m$ (Courbion, Jacoboni & de Pape, 1971). Ainsi, en effectuant la substitution cationique $2\text{M}^{\text{II}} \rightarrow \text{M}^{\text{I}} + \text{M}^{\text{III}}$, nous obtenons des composés du type $\text{AM}_{0,5}^{\text{I}}\text{M}_{1,5}^{\text{III}}\text{F}_6$ ou $\text{A}_2\text{M}^{\text{I}}\text{M}_3^{\text{III}}\text{F}_{12}$. Une telle formulation met en évidence une possibilité d'ordre cationique 1–3 dans les sites 16(c).

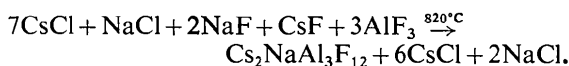
Le composé $\text{Cs}_2\text{NaAl}_3\text{F}_{12}$ présente une symétrie rhomboédrique; une étude précédente, réalisée sur le composé pulvérulent nous a permis de mettre en évidence la répartition ordonnée du sodium et de l'aluminium, la symétrie étant de ce fait abaissée au groupe spatial $R\bar{3}m$ (Courbion, Jacoboni & de Pape, 1974).

Le présent travail a pour but de préciser la structure du composé $\text{Cs}_2\text{NaAl}_3\text{F}_{12}$ par une étude cristallographique réalisée sur monocristal.

Préparation et enregistrement

La synthèse des monocristaux de $\text{Cs}_2\text{NaAl}_3\text{F}_{12}$ a été réalisée par la méthode du flux (Jacoboni 1970, 1975; Nouet, Jacoboni, Ferey, Gérard & de Pape, 1971) dans un bain de chlorures de composition $(\text{NaCl} + 3\text{CsCl})$

voisine d'un eutectique fondant vers 490°C. La réaction utilisée pour la synthèse est



Après refroidissement lent à 5°C h⁻¹, nous avons isolé du bain des cristaux transparents dont la forme générale est le rhomboèdre tronqué suivant l'axe [111].

Les clichés de Laue ainsi que l'étude optique au goniomètre à deux cercles, conduisent sans ambiguïté à la classe de symétrie $\bar{3}m$. La maille hexagonale de

Tableau 1. *Données cristallographiques de $\text{Cs}_2\text{NaAl}_3\text{F}_{12}$*

Maille rhomboédrique	Maille hexagonale
$a_R = 7,310 \pm 0,003 \text{ \AA}$	$a_H = 7,026 \pm 0,003 \text{ \AA}$
$\alpha_R = 57,45 \pm 0,10^\circ$	$c_H = 18,244 \pm 0,005 \text{ \AA}$
$Z = 1$	$Z = 3$
$\rho_{\text{exp}} = 3.7(1) \text{ g.cm}^{-3}$	$\rho_{\text{cal}} = 3.82 \text{ g.cm}^{-3}$
Groupe de Laue : $3m$	
conditions d'existence	conditions d'existence
	$-h + k + l = 3n$
	$h + 2k + l = 3n$
aucunes	$h + k + l = 3n$