By means of a small furnace-sample holder kindly loaned by Dr Robert S. Roth of the National Bureau of Standards, samples of both the monoclinic and triclinic forms were heated for varying periods of time ($\frac{1}{2}$ hour to about 16 hours) while the furnace was mounted on an X-ray diffractometer. Patterns could be taken at any temperature. No change from one polymorphic form to another could be detected. Only dehydration occurred, at temperatures as low as 50 °C if the sample was heated 12 or more hours and at 75 °C after 1 hour of heating. A transition in the solid state seems unlikely from a comparison of the two structures. Although the structures have similarities, major shifts in the relative positions of the anions, and in the sodium coordination would have to occur.

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The Crystal Structure of Bisethylenediaminecopper(II) Nitrate

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The crystal structure of bisethylenediaminecopper(II) nitrate, $Cu(C_2N_2H_8)_2(NO_3)_2$, has been determined from three-dimensional X-ray diffraction data. The dimensions of the monoclinic ($P2_1/c$) cell are $a_0=8{\cdot}30$, $b_0=10{\cdot}05$, $c_0=8{\cdot}07$ Å, $\beta=111°\ 6'$, $z=2$. The structure was refined by three-dimensional difference syntheses to $R=0{\cdot}097$.

The copper ion has the usual distorted octahedral coordination with four N atoms at 2·03 Å and two O atoms at 2·59 Å. The ethylenediamine molecule is in the *gauche* configuration, with one C atom 0·39 Å from the CuN_4 plane and the other −0·19 Å

Introduction

As a part of a study of the coordination configuration of Cu^{2+}, we have determined the crystal structure of bisethylenediaminecopper(II) nitrate, $Cu(C_2N_2H_8)_2(NO_3)_2$, which was originally prepared and described as a dihydrate by Grossman & Schuck (1906), but later shown to be anhydrous by Johnson & Bryant (1934). A short report of preliminary work on this structure was reported by Watanabe & Atoji (1951). They report the cell to have dimensions $a=8{\cdot}00$, $b=10{\cdot}00$, $c=15{\cdot}53$ Å, $\beta=97°\ 25'$, $Z=4$ molecules, space group $B2_1/a$. In *Structure Reports* (1951) it is erroneously suggested that this space group symbol is a misprint for $P2_1/a$. However, transformation of their cell to a primitive cell gives $a=8{\cdot}00$, $b=10{\cdot}00$, $c=8{\cdot}27$ Å, $\beta=111°\ 19'$, in quite satisfactory agreement with our results.

Experimental

Bisethylenediaminecopper(II) nitrate was prepared by the method described by Grossman & Schuck (1906)

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and crystallized from water. The violet-colored crystals are six-sided holohedral monoclinic plates on {100}, bounded by {010} and {011}.

Cell dimensions were calculated from measurements on rotation and Weissenberg photographs, calibrated with NaCl ($a_0=5{\cdot}6387$ Å) using Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). The results are $a_0=8{\cdot}302\pm0{\cdot}01$; $b_0=10{\cdot}052\pm0{\cdot}004$; $c_0=8{\cdot}065\pm0{\cdot}01$ Å; $\beta=111°\,6'\pm12'$. The cell contains two molecules, density calculated: 1·630 g.cm^{-3}; measured: 1·622 g.cm^{-3}. Systematic absence of $h0l$ for $l\neq2n$ and of $0k0$ for $k\neq2n$ indicate the space group to be $P2_1/c$.

Relative intensities were obtained from equi-inclination Weissenberg photographs taken on a Nonius integrating camera with Cu radiation using multiple films and a range of exposure times.

The crystal was a rod of dimensions $0{\cdot}02\times0{\cdot}09\times0{\cdot}45$ mm, rotated about its long dimension, the b axis. The camera integration was carried out in one direction only, and each spot in the linear response range on each film was scanned in the other direction with a Moll-type densitometer feeding into a Leeds & Northrup amplifier and recorder with a logarithmic slide wire. The area under each spot tracing was measured with a planimeter and used directly as relative intensity. The several films for each level were placed on a common scale for that level by correlation of spots appearing on more than one film. The range of relative intensities was 1 to 2000. 565 reflections fell within this range, while 491 others could have been recorded on the films and were therefore listed as 'less-than-1'.

Data were collected for all levels from $h0l$ through $h7l$. Lorentz and polarization factors were applied, but no corrections were made for absorption nor dispersion. The structure factors on the several levels were placed on a common scale by comparison of observed and calculated structure factors at each stage of the refinement of the structure.

Determination of the structure

The presence of two molecules in a unit cell of space group $P2_1/c$ requires the copper ions to occupy one of the sets of twofold positions. They could be placed at 000 and $0\frac{1}{2}\frac{1}{2}$ without loss of generality.

In order to determine the positions of the light atoms, two calculations were made, a three-dimensional Patterson function and the electron-density projection, $\varrho(x, z)$, using all phase angles zero due to the special positions of the copper atoms. It was possible to locate all atoms in this manner.

The structure was then refined by three-dimensional difference syntheses. For structure factor calculations, scattering factors were obtained from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen, nitrogen, carbon and hydrogen and from Thomas & Umeda (1957) for copper. In calculating the difference syntheses, ΔF was included for all measured reflections and for those 'less-thans' for which $F_c>F_{\min}$. All calculations were carried out on an IBM 650 computer. The final value of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0{\cdot}097$. Hydrogen atoms were placed in calculated positions, but not refined. Atomic anisotropic temperature factors of the form

$$\exp[-2\pi^2(a^{*2}h^2U_{11}+b^{*2}k^2U_{22}+c^{*2}l^2U_{33}+2a^*b^*hkU_{12}+2a^*c^*hlU_{13}+2b^*c^*klU_{23})]$$

were applied.

The final atomic positions and their estimated standard deviations (Cruickshank, 1949) are given in Table 1 and the temperature factor parameters in Table 2. Table 3 gives the comparison of observed and calculated structure factors.

Table 1. *Final coordinates and standard deviations*

Atom	x/a	y/b	z/c
Cu	0·0000	0·0000	0·0000
C(1)	0·3271	0·1318	0·1770
C(2)	0·3601	−0·0195	0·2007
N(1)	0·1639	0·1567	0·0245
N(2)	0·2000	−0·0904	0·1865
N(3)	0·1687	0·5571	0·1658
O(1)	0·2282	0·6279	0·0743
O(2)	0·2023	0·4338	0·1817
O(3)	0·0960	0·6117	0·2608
σ(C)	0·012	0·009	0·012
σ(N)	0·009	0·007	0·009
σ(O)	0·008	0·006	0·008

Table 2. *Final temperature factor parameters*

(× 100)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	5·37	4·50	5·72	0·06	2·41	−0·08
C(1)	6·73	6·46	7·14	0·09	2·36	−0·01
C(2)	6·46	6·59	7·27	0·09	2·33	0·00
N(1)	5·56	5·19	5·60	0·06	2·14	0·03
N(2)	5·36	5·26	5·33	0·05	2·03	0·01
N(3)	5·41	5·19	5·40	0·08	1·99	0·04
O(1)	6·50	5·83	6·23	0·08	2·52	0·05
O(2)	6·57	6·08	6·59	0·09	2·57	0·01
O(3)	6·45	6·08	6·23	0·04	2·56	0·00

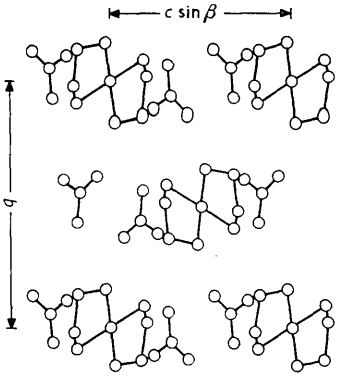

Fig. 1. Projection of structure along [100].

Table 3. *Calculated and observed structure factors*

Columns are h, $F_o \times 10$, $F_c \times 10$. Unobserved marked by *

Discussion

The arrangement of the atoms is illustrated in Fig. 1, which depicts the projection along [100]. Bond distances and angles and their standard deviations are given in Table 4.

Table 4. *Bond distances and angles*

Cu–N(1)	2·044 Å	(0·013) Å	N(1)–Cu–N(2)	86·2°
Cu–N(2)	2·012	(0·013)	Cu–N(1)–C(1)	109·1
Cu–O(3′)	2·593	(0·012)		
N(1)–C(1)	1·487	(0·025)	Cu–N(2)–C(2)	108·5
N(2)–C(2)	1·476	(0·025)	N(1)–C(1)–C(2)	109·6
C(1)–C(2)	1·545	(0·027)	N(2)–C(2)–C(1)	110·6
N(3)–O(1)	1·248	(0·020)	O(1)–N(3)–O(2)	119·9
N(3)–O(2)	1·267	(0·020)	O(2)–N(3)–O(3)	120·1
N(3)–O(3)	1·259	(0·020)	O(1)–N(3)–O(3)	119·3

N(2)–H · · · O(1′)	3·007	[O(1′) at $x, -1+y, z$]
N(1)–H · · · O(2″)	3·029	[O(2′) at $x, \frac{1}{2}-y, -\frac{1}{2}+z$]
N(1)–H · · · O(2)	3·035	
N(2)–H · · · O(1″)	3·075	[O(1′) at $x, \frac{1}{2}-y, \frac{1}{2}+z$]

The copper ion is surrounded by a tetragonally distorted octahedron, with four nitrogen atoms, from the two ethylenediamine molecules, at 2·03 Å and two oxygen atoms, from the nitrate ions, at 2·59 Å. The bond angles in the coordination polyhedron deviate only slightly from 90°. The intrachelate N–Cu–N angle is 86·2°, and the angle between the Cu–O bond and the CuN_4 plane is 87·0°. These values may be compared with corresponding values from other copper compounds. Copper–amine nitrogen 'short' distances: 1·99, 2·02 Å in $Cu(en)_2(SCN)_2$ (Brown & Lingafelter, 1964); 1·98, 1·99 Å in $[Cu(en)_2(H_2O)Cl]Cl$ and 1·97, 1·98 Å in $[Cu(en)_2(H_2O)Br]Br$ (Mazzi, 1953); 1·99 Å in $Cu(C_5H_8O_2N)_2.2H_2O$ (Mathieson & Welsh, 1952); 2·04, 2·06 Å in $Cu(NH_3)_4SO_4.H_2O$ (Mazzi, 1955); and 2·05 Å in $NH_4Cu(NH_3)_4(ClO_4)_2.NH_3$ (Bukovska & Porai-Koshits, 1960). Copper–oxygen 'long' distances: 2·68 Å in $[Cu(en)_2(H_2O)Cl]Cl$ and 2·78 Å in $[Cu(en)_2(H_2O)Br]Br$ (Mazzi, 1953); 2·53 Å in bis-(salicylaldehydeisopropylenediimine)copper monohydrate (Waters, Hall & Llewellyn, 1958); 2·89 Å in copper(II) salicylate tetrahydrate (Hanic, 1958).

The asymmetry of the ethylenediamine molecule with respect to the CuN_4 coordination plane is quite similar to that found in $Cu(en)_2(SCN)_2$ (Brown & Lingafelter, 1964), $Cu(en)_2Hg(SCN)_4$ (Scouloudi, 1953) and $[Cu(en)_2(H_2O)Cl]Cl$ (Mazzi, 1953). The ethylenediamine molecule is in the *gauche* configuration with one carbon atom 0·39 Å above the coordination plane and the other 0·19 Å below the plane.

The bond distances in the ethylenediamine molecule appear to be normal and may be compared with values from other molecules: C–C, 1·50 Å and C–N, 1·50 Å in $Ni(en)_3(NO_3)_2$ (Swink & Atoji, 1960); C–C, 1·50 Å and C–N, 1·46 and 1·50 Å in $Ni(en)_2(SCN)_2$ (Brown & Lingafelter, 1963); C–C, 1·56 Å and C–N, 1·46 and 1·49 Å in $Cu(en)_2(SCN)_2$ (Brown & Lingafelter, 1964); C–C, 1·51 Å and C–N, 1·50 Å in $[Cu(en)_2(H_2O)Cl]Cl$ (Mazzi, 1953).

The deviation of the nitrate ion from planarity is slight (the nitrogen atom is 0·062 Å from the oxygen plane) but significant ($\sigma_N \sim 0{\cdot}009$ Å). The N–O distances are not significantly different from one another and the mean value 1·258 Å may be compared to the values reported in other nitrates: 1·243 Å in N_2O_5 (Grison, Eriks & deVries, 1950), 1·24 Å in $(C_2H_8N_3)NO_3$ (Curtis & Pasternak, 1955), 1·21 Å in $Ni(en)_3(NO_3)_2$ (Swink & Atoji, 1960).

Considering the crystal to be formed from $Cu(en)_2^{2+}$ and NO_3^- ions, these ions are bound together in sheets parallel to (100) by the coordination of O(3) to Cu and by a network of NH · · · O hydrogen bonds of lengths 3·01 to 3·08 Å. This arrangement leads to the thinness of the crystals on {100} and to the easy cleavage parallel to (100).

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