the respective H atoms then effectively locks the dithizone residues in *anti, s-trans* configurations. These configurations of the N—N—C—N—N chains are the same as those found in other $M(Hdz)_x$ complexes and in crystals of the free ligand itself.

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Bis(3-aminopyridine)copper Cyanate Monohydrate*

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Abstract

The structure of $Cu(NCO)_2(3\text{-ampy})_2(H_2O)$ (3-ampy: 3-aminopyridine, $C_5H_6N_2$), $C_{12}H_{14}CuN_6O_3$, $M_r = 353.8$, was determined from 2029 independent reflec-tions using a single crystal and Mo $K\alpha$ radiation. Crystals are triclinic, space group $P\bar{1}$, with $a = 8.487$ (3), $b = 8.349$ (3), $c = 12.346$ (4) Å, $\alpha = 102.44$ (3), $\beta = 82.69$ (3), $\gamma = 120.84$ (3)°, $V = 733.3$ Å^3, $Z = 2$, $D_m = 1.61$, $D_x = 1.60$ g cm^{-3}. The structure was refined by block-diagonal least-squares techniques to $R = 0.054$ and $R_w = 0.040$ for 2029 independent reflections. It consists of infinite chains mutually linked by hydrogen bonds. One half of the

NCO groups are bonded through their N atoms to Cu atoms. The other half are bidentate and, in comparison with the monodentate groups, show a slight deviation from linearity. Bond angles N—C—O are 177 (1), 179 (1)° and the bond lengths N—C and C—O are 1·15 (1), 1·14 (1) and 1·22 (1), 1·21 (1) Å.

Introduction

In the crystal structure of $Cu(NCO)_2(pyridine)_2$ (Valach, Dunaj-Jurčo & Handlovič, 1980) the NCO group forms a bridge between two Cu^{II} atoms through its terminal atoms, while in $Cu(NCO)_2(2,4-lutidine)$ (Valach, Dunaj-Jurčo, Garaj & Hvastijová, 1974) it bridges only through the N atom and its O atom remains uncoordinated. In the structures of the series of cyanatocopper(II) complexes with the neutral ligands 2-dimethylaminoethanol (Mergehenn & Haase, 1977a), 2-dibutylaminoethanol (Mergehenn & Haase, 1977b), 2-dipropylaminoethanol (Merz & Haase, 1978a) and N,N-diethylaminoethanol (Merz & Haase, 1978b) the NCO groups are end-bonded to the Cu^{II} atoms through their N atoms. To investigate further the bonding properties of the NCO group in cyanatocopper(II) complexes with nitrogen-containing organic ligands (Kohout, Hvastijová & Gažo, 1978) the crystal structure of another cyanate complex of this group of compounds was determined.

Experimental

Dark-blue needle-shaped crystals of $Cu(NCO)_2(3-ampy)_2(H_2O)$ were prepared as already described (Kohout, Hvastijová & Gažo, 1978).

Weissenberg photographs indicated the possible space groups $P1$ and $P\bar{1}$. Cell parameters were refined on the Syntex $P2_1$ diffractometer by the least-squares method from the angles of 15 selected reflections. The orientation matrix obtained was employed for further intensity measurements, carried out within the range $0 \leq 2\theta \leq 55°$ using the θ–2θ scan technique with a variable scan rate ranging from 4·88 to 29·3° min^{-1}. The scan range for each reflection was from $2\theta(Mo\ K\alpha_1) - 1°$ to $2\theta(Mo\ K\alpha_2) + 1°$. Two standard reflections were remeasured after every 98 reflections. The original total of 3218 reflections was reduced to 2029 by rejecting reflections with $I < 1\cdot96\sigma(I)$. Intensities were corrected for Lorentz–polarization and experimental absorption effects.

Structure determination

The Cu atoms were located on Patterson-function maps and space group $P\bar{1}$ (No. 2) was chosen. Other

Table 1. *Fractional coordinates* ($\times 10^4$) *with equivalent isotropic thermal parameters for nonhydrogen atoms*

The isotropic temperature factor $T = \exp(-B_{eq} \sin^2 \theta/\lambda^2)$. Standard deviations are in parentheses.

	x	y	z	B_{eq} (Å^2)
Cu(1)	0	0	0	2·08 (6)
Cu(2)	0	0	5000	2·86 (6)
N(1)	532 (8)	623 (8)	8512 (5)	2·6 (3)
N(2)	2472 (8)	457 (9)	4560 (6)	2·7 (4)
N(3)	2700 (7)	1656 (8)	369 (5)	2·7 (3)
N(4)	565 (8)	2305 (8)	4389 (5)	2·6 (3)
N(5)	7218 (8)	2865 (9)	9050 (5)	3·6 (4)
N(6)	8226 (8)	3694 (9)	2821 (5)	3·3 (3)
C(1)	779 (10)	1395 (10)	7783 (6)	3·0 (4)
C(2)	3478 (10)	351 (10)	3876 (7)	4·6 (5)
C(3)	3187 (10)	2923 (10)	1308 (6)	3·0 (4)
C(4)	5018 (10)	4297 (10)	1530 (7)	3·4 (4)
C(5)	6364 (10)	4303 (10)	774 (7)	3·6 (4)
C(6)	5867 (9)	2943 (10)	9813 (6)	3·1 (3)
C(7)	4002 (9)	1644 (10)	9633 (6)	2·6 (4)
C(8)	9285 (10)	2285 (10)	3850 (6)	2·3 (4)
C(9)	9574 (10)	3832 (10)	3430 (6)	1·9 (4)
C(10)	8719 (10)	4521 (10)	6405 (6)	2·7 (4)
C(11)	7413 (10)	4502 (10)	5849 (7)	3·5 (4)
C(12)	2210 (10)	3902 (10)	4531 (7)	3·5 (4)
O(1)	1082 (8)	2164 (7)	6988 (5)	3·6 (3)
O(2)	4543 (8)	214 (9)	3162 (6)	6·4 (4)
O(3)	9588 (7)	2886 (7)	619 (4)	3·5 (3)

Table 2. *Fractional coordinates* ($\times 10^3$) *with isotropic thermal parameters for hydrogen atoms*

The isotropic temperature factor $T = \exp(-B \sin^2 \theta/\lambda^2)$. Standard deviations are in parentheses.

	x	y	z	B (Å^2)
H(1)	889 (8)	262 (8)	125 (5)	5 (2)
H(2)	887 (8)	262 (8)	2 (5)	5 (2)
H(3)	818 (8)	420 (8)	892 (5)	4 (2)
H(4)	689 (8)	211 (8)	831 (5)	6 (2)
H(5)	823 (8)	478 (8)	288 (5)	3 (1)
H(6)	690 (8)	268 (8)	290 (5)	3 (1)
H(7)	199 (8)	286 (7)	183 (4)	2 (1)
H(8)	466 (7)	452 (7)	779 (5)	3 (1)
H(9)	235 (7)	470 (7)	914 (5)	3 (1)
H(10)	354 (7)	62 (8)	889 (5)	2 (1)
H(11)	803 (7)	104 (7)	370 (4)	3 (1)
H(12)	311 (7)	381 (7)	496 (5)	4 (1)
H(13)	622 (7)	348 (7)	575 (5)	3 (1)
H(14)	835 (8)	315 (8)	662 (5)	5 (2)

non-hydrogen atoms were located by Fourier syntheses. The structure was refined by the least-squares method with anisotropic thermal-vibration coefficients to an R value of 0·067. H atoms were located from difference Fourier syntheses. After several further cycles of refinement on F^2 the final values for 2029 observed structure factors with weights $w = 1/\sigma(F)$ were as follows: $R = 0·054$ and $R_w = 0·040$. Atomic scattering factors were taken from Cromer & Waber (1965). The final atomic parameters are summarized in

Tables 1 and 2.* All calculations were performed by means of the *XTL* program (Ahmed *et al.*, 1976).

Results and discussion

Fig. 1 shows part of the structure with bond angles. The bond lengths are given in Table 3. Cu atoms occupy centrosymmetric positions. An approximately square-planar *trans* coordination of one half of the Cu atoms, formed by two N atoms of the bidentate NCO groups and two N atoms from the 3-aminopyridine molecules, is completed by two O atoms from water molecules to form an approximately tetragonal bipyramidal coordination with coordination number 4 + 2. The other half of the Cu atoms have an identical type of coordination, the equatorial plane of which is formed by two N atoms from the monodentate NCO groups and two N atoms from the 3-aminopyridine molecules. Two O atoms from the bidentate NCO groups are in axial positions. The bidentate NCO groups link the Cu atoms into infinite chains. The interatomic distance Cu—Cu is 6·17 (4) Å and does not indicate any direct intermetallic interaction.

The bidentate NCO groups show a significant deviation from linearity. The angle N(1)—C(1)—O(1), 177 (1)°, and the lengths N(1)—C(1), 1·15 (1), and

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* Lists of structure factors, anisotropic thermal parameters of nonhydrogen atoms, parameters of least-squares planes and interplanar angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36794 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
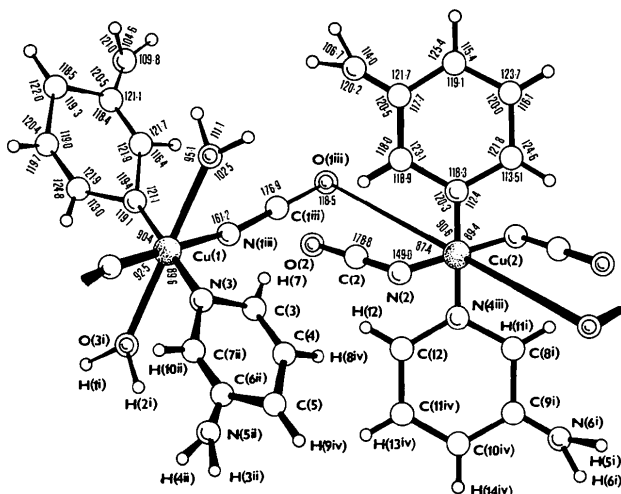

Fig. 1. Bond angles (°) in the chain structure of Cu(NCO)$_2$-(3-ampy)$_2$(H$_2$O). The standard deviations are in the range 0·2–5·9°. Symmetry code: (i) $x - 1$, y, z; (ii) x, y, $z - 1$; (iii) $-x, -y, 1 - z$; (iv) $1 - x, 1 - y, 1 - z$.

Table 3. *Bond distances* (Å) *with standard deviations in parentheses*

Cu(1)—N(3)	2·029 (5)	C(2)—O(2)	1·21 (1)
Cu(1)—O(3^i)	2·552 (7)	C(3)—C(4)	1·397 (9)
Cu(1)—N(1)	1·952 (7)	C(3)—H(7)	1·12 (6)
Cu(2)—N(2)	1·955 (7)	C(4)—C(5)	1·38 (1)
Cu(2)—N(4)	2·022 (7)	C(4)—H(8)	1·08 (5)
Cu(2)—O(1)	2·663 (6)	C(5)—C(6)	1·39 (1)
N(1)—C(1)	1·15 (1)	C(5)—H(9)	0·98 (4)
N(2)—C(2)	1·14 (1)	C(6)—C(7)	1·40 (8)
N(3)—C(7)	1·34 (1)	C(7)—H(10)	1·06 (5)
N(3)—C(3)	1·334 (9)	C(8)—C(9)	1·39 (1)
N(4)—C(8^i)	1·34 (1)	C(8)—H(11)	1·04 (4)
N(4)—C(12)	1·346 (8)	C(9)—C(10)	1·394 (8)
N(5)—C(6)	1·41 (1)	C(10)—C(11)	1·37 (1)
N(5)—H(3)	1·02 (5)	C(10)—H(14)	1·10 (7)
N(5)—H(4)	0·98 (6)	C(11)—C(12)	1·38 (1)
N(6)—C(9)	1·39 (1)	C(11)—H(13)	0·93 (5)
N(6)—H(5)	0·89 (7)	C(12)—H(12)	1·03 (7)
N(6)—H(6)	1·01 (8)	O(3)—H(1)	0·91 (5)
C(1)—O(1)	1·22 (1)	O(3)—H(2)	0·93 (7)

C(1)—O(1), 1·22 (1) Å, are practically identical with the values 177 (1)°, 1·15 (1) and 1·18 (1) Å of the NCO groups coordinated in the same way in Cu(NCO)$_2$(pyridine)$_2$ (Valach, Dunaj-Jurčo & Handlovič, 1980). The monodentate NCO groups can be considered as linear [the angle N(2)—C(2)—O(2) is 179 (1)°] and the bond lengths N(2)—C(2), 1·14 (1), and C(2)—O(2), 1·21 (1) Å, approach the average values of the bond lengths N—C [1·090 (7)] and C—O [1·220 (7)] in the structures of cyanato(2-dimethyl-aminoethanolato)copper(II) (Mergehenn & Haase, 1977a), cyanato(2-dibutylaminoethanolato)copper(II) (Mergehenn & Haase, 1977b), monoclinic and ortho-rhombic form of cyanato(2-dipropylaminoethanolato)-copper(II) (Merz & Haase, 1978a) and tetrakis[(2-diethylaminoethanolato)isocyanatocopper(II)] (Merz & Haase, 1978b).

The 3-aminopyridine molecules show a slight deviation from planarity (χ^2_A = 50·2, χ^2_B = 51·2) and are bonded as monofunctional ligands to the Cu^{II} atoms. Deviations from the least-squares planes and interplanar angles of both 3-aminopyridine molecules have been deposited.* The angles between the plane of 3-aminopyridine and the CuN$_4$ plane about the atoms Cu(1) and Cu(2) are 47·5 and 40·5°.

The structure consists of infinite chains of the type—[Cu(3-ampy)$_2$(H$_2$O)$_2$]—N—C—O—[Cu(3-ampy)$_2$-(NCO)$_2$]—O—C—N— along the *c* axis. These are mutually bound by hydrogen bonds N(6)—H(6)-···O(2), N(6)—H(5)···O(1), N(5)—H(4)···O(2), O(3)—H(2)···N(5) and O(3)—H(1)···N(6). Lengths and angles of these bonds are given in Table 4.

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* See deposition footnote.

Table 4. *Hydrogen-bond distances and angles with estimated standard deviations in parentheses*

$D-H\cdots A$	Position of acceptor atom	Distance (Å) $D\cdots A$	$H\cdots A$	Angle (°) $D-H\cdots A$
O(3)–H(1)···N(6)	x,y,z	2·897 (8)	2·09 (5)	147 (6)
O(3)–H(2)···N(5)	$x,y,z-1$	2·96 (1)	2·07 (8)	158 (6)
N(5)–H(4)···O(2)	$1-x,y,1-z$	3·221 (8)	2·27 (5)	164 (5)
N(6)–H(5)···O(1)	$1-x,1-y,1-z$	3·16 (1)	2·28 (7)	168 (5)
N(6)–H(6)···O(2)	x,y,z	3·045 (7)	2·06 (6)	164 (7)

In $Cu(NCO)_2(3\text{-ampy})_2(H_2O)$ the NCO groups were found as functionally non-equivalent ligands. The monodentate groups which are bound to the Cu^{II} atoms through the N atom maintain linearity, and the bidentate groups, being bound to the Cu^{II} atoms by means of a bridge through the N and O atoms, show a slight deviation from linearity.

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The Structures of Chloro(diethylenetriamine)platinum(II) Chloride and (Diethylenetriamine)nitratoplatinum(II) Nitrate and Some Comments on the Existence of $Pt^{II}-OH_2$ and $Pt^{II}-OH$ Bonds in the Solid State

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Abstract

$[Pt\{NH_2(CH_2)_2NH(CH_2)_2NH_2\}Cl]Cl$, $C_4H_{13}ClN_3Pt^+$.-Cl^-, (I) is orthorhombic, $Pca2_1$, with $Z = 4$, $a = 13\cdot954\ (3)$, $b = 4\cdot828\ (1)$, $c = 13\cdot272\ (4)$ Å. $[Pt\{NH_2(CH_2)_2NH(CH_2)_2NH_2\}ONO_2]NO_3$, $C_4H_{13}N_4O_3Pt^+$.NO_3^-, (II) is orthorhombic, *Pbca*, with $Z = 8$, $a = 12\cdot777\ (4)$, $b = 9\cdot749\ (3)$, $c = 17\cdot145\ (4)$ Å. (I) is isostructural with $[Pt\{NH_2(CH_2)_2NH(CH_2)_2NH_2\}Br]Br$ and its structure was solved using the Pt position from the bromide and difference methods. The structure of (II) was solved by heavy-atom methods. Both were refined by full-matrix least squares to $R = 0\cdot031$, $R_w = 0\cdot039$ (I); $R = 0\cdot065$, $R_w = 0\cdot050$ (II), based on 1561 and 2314 reflections respectively. The basic cation units are similar for (I) and (II). Bond lengths [Pt–N, range 1·984 (8)–2·063 (10), Pt–Cl 2·312 (3), Pt–O 2·030 (8) Å] are normal. Hydrogen bonds to the chloride ion are important in determining the packing of (I) and hydrogen bonds to the uncoordinated nitrate ion and to the coordinated O atom of the bound nitrate ion determine the packing of (II). An explanation is given as to why (II) was obtained rather than the $[Pt\{NH_2(CH_2)_2NH(CH_2)_2NH_2\}OH_2]^{2+}$ cation on crystallization and conditions necessary for the isolation of the latter cation as a salt are suggested.

Introduction

For some time we have been attempting to isolate Pt^{II} amine complexes containing coordinated aqua

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