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Five-coordinate Copper(II) with Branched-chain Quinquedentate Ligand N,N-bis(2-aminoethyl)diethylenetriamine (trenen). The Crystal Structure of Cu(trenen)Br_2

M. CANNAS, A. CRISTINI and G. MARONGIU
Istituto Chimico, Via Ospedale 72, 09100 Cagliari, Italy
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The crystal structure of N,N-bis(2-aminoethyl)diethylenetriaminecopper(II) bromide $C_8H_{23}N_5CuBr_2$ has been determined by three-dimensional X-ray data. Crystals are orthorhombic, space group $P2_12_12_1$, with $Z = 4$ in a unit cell of dimensions: $a = 8.75(1)$, $b = 13.19(2)$, $c = 12.90(2)$ Å. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to $R = 0.10$ for 1475 refined reflections measured by diffractometer. The coordination polyhedron is a distorted trigonal bipyramid, with the apices occupied by the ligand nitrogen atoms; its geometry is compared with that of analogous copper(II) and zinc(II) complexes.

Introduction

Tetraethylenepentamine has been widely used in the chemistry of coordination compounds mainly to investigate the geometric and optical isomers which may occur in its complexes.

The commercially available product, which is generally the starting material in the synthesis of the compounds, is known to be a complex mixture of amines; House and Garner[1] detected at least eight species in the chromatographic analyses of a sample, which contained both tetraethylenepentamine (tetren, 20%) and its branched chain isomer, N,N-bis(2-aminoethyl)diethylenetriamine (trenen, 30%). This fact poses the problem of deciding which isomer is actually present in the complexes, unless an accurate preliminary purification of the commercial product is carried out.

Recently the preparation of several complexes obtained by reaction of the commercial amine with different copper(II) salts has been reported[2]; the X-ray structure determination of the copper bromide derivative, which, among those prepared, gives the most suitable crystals for an X-ray analysis, was undertaken and is reported in this paper.

Experimental

The compound, supplied by Dr. Ponticelli, forms blue prismatic crystals by evaporation of a concentrated methyl alcohol solution, containing a few drops of water.

Crystal Data

$C_8H_{23}N_5CuBr_2$: M = 412.67, orthorhombic, $a = 8.75(1)$; $b = 13.19(2)$; $c = 12.90(2)$ Å; U = 1488 Å^3; Dm(flotation) = 1.83 g cm^{-3}; Z = 4, Dc = 1.84 g cm^{-3}, F(000) = 820. Space group $P2_12_12_1$ from systematic absences (h00, 0k0, 00l for h, k, l = 2n + 1). Mo-Kα radiation, $\lambda = 0.7107$ Å; μ(MoKα) 72.2 cm^{-1}. Unit cell parameters and their estimated standard deviations were determined by a least-squares fit to 13 values of Θ, χ, Φ accurately measured by use of a very narrow counter aperture.

Intensity Measurements

A crystal of dimensions 0.026 × 0.013 × 0.050 cm was mounted with its longest dimension (the $\vec{a} + \vec{c}$ diagonal of the unit cell) nearly coincident with the polar Φ axis of the goniostat. The procedure was similar to that previously described[3]. The Θ–2Θ scan technique with a five-value measuring procedure was used. The intensities of three standard reflections were measured after every 200 reflections and their net counts did not vary noticeably during the data collection. A total of 2720 intensities (two octants of the reciprocal lattice) up to $2\Theta \leqq 50°$ was recorded, which after correction for Lorentz-polarization effects were reduced to a set of 1518 independent reflections; 43 having $I/\sigma(I) < 2$ were considered unobserved and were not used in the analysis.

Solution and Refinement of the Structure

The positions of the copper and two bromine atoms were determined by a three-dimensional Patterson synthesis; a three-dimensional Fourier map gave the positions of all non-hydrogen atoms. The R factor, ob-

TABLE I. Atomic Coordinates (× 10^4) and Thermal Parameters.

	x/a	y/b	z/c	B
Br(1)	−1811(2)	3684(1)	1139(2)	a
Br(2)	1628(3)	4399(2)	4309(2)	a
Cu	1603(2)	1521(1)	2156(1)	a
N(1)	−686(20)	1412(14)	2178(12)	3.73(32)
N(2)	1355(17)	1925(12)	3648(11)	3.02(28)
N(3)	3901(16)	1586(12)	2416(10)	2.47(26)
N(4)	2076(20)	2684(14)	1104(14)	4.30(37)
N(5)	2008(19)	77(14)	1550(14)	4.21(35)
C(1)	−1285(23)	1577(17)	3213(16)	3.93(40)
C(2)	−59(22)	1415(16)	4002(15)	3.68(38)
C(3)	2817(19)	1602(13)	4173(13)	2.51(31)
C(4)	4112(24)	1971(17)	3550(16)	3.63(40)
C(5)	4597(27)	2275(20)	1685(19)	4.99(50)
C(6)	3522(28)	3140(19)	1398(18)	4.93(48)
C(7)	4428(24)	515(17)	2371(15)	3.59(40)
C(8)	3736(21)	−24(16)	1471(15)	3.48(38)

[a] Anisotropic thermal parameters in the form:
$\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}hlb^*c^*)$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	3.55(9)	2.64(7)	4.46(7)	0.28(9)	0.32(9)	0.34(7)
Br(2)	4.47(9)	2.99(7)	5.65(7)	0.60(9)	−0.77(9)	0.20(7)
Cu	1.81(9)	1.60(7)	2.66(7)	0.00(9)	0.18(9)	−0.07(7)

tained using the overall temperature and scale factors derived from a Wilson plot was 0.22 for 1475 observed reflections. Both positional and isotropic thermal parameters were then refined by the block diagonal least-squares method; the quantity minimized was $\Sigma w(\Delta F)^2$, where w = $4\ F_o^2/[\sigma^2(F_o^2)+(0.06\ F_o^2)^2]$. Four cycles of refinement reduced the R factor to 0.14. Three more cycles by use of anisotropic thermal parameters for copper and bromine atoms reduced R to 0.10 and R′ to 0.11 [R′ = $\Sigma w(\Delta F^2)/\Sigma wF_o^2$] for 1475 observed reflections. The final R value for all 1518 measured reflections is 0.11. Atomic scattering factors were interpolated from the values given in Ref. 4. Final atomic parameters, with estimated standard deviations, are given in Table I. Observed and calculated structure factors are listed in a Table available from the Editor.

Discussion

A perspective view of the complex is given in Figure 1. Clearly the ligand is not the linear form "tetren" but the branched chain isomer "trenen", which has been previously found in two octahedral structures of cobalt(III)[5,6].

The geometry of the coordination polyhedron, shown in the Figure, is close to a trigonal bipyramid, with N(2), N(4) and N(5) in the equatorial plane; the copper atom lies 0.17 Å below this plane toward N(1). Intramolecular bond lengths and angles are shown in Table II. Distortions of the coordination polyhedron from exact D_{3h} symmetry are very similar to those found in the case of $[Cu(tren)NCS]^+$ [7], where tren = tris(2-aminoethyl)amine. Thus the intrachelate N–Cu–N bond angles are equal to the mean value of 84.9° and one of the N–Cu–N angles in the equatorial plane has a value about 10° higher than that of the other two. The values in $[Cu(tren)NCS]^+$ are 84.1° for intrachelate angles and 112.9, 114.3 and 129.6° for N–Cu–N angles in the equatorial plane.

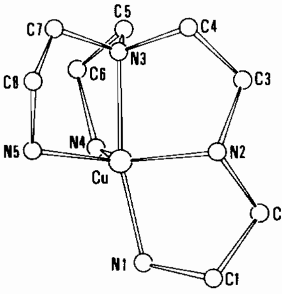

Figure 1. Perspective view of the complex.

TABLE II. Bond Distances and Angles in Cu(trenen)Br_2 with Estimated Standard Deviations.

Cu–N(1)	2.01(2) Å	N(3)–C(5)	1.44(3) Å
Cu–N(2)	2.01(2)	N(3)–C(7)	1.49(3)
Cu–N(3)	2.04(2)	N(4)–C(6)	1.45(3)
Cu–N(4)	2.09(2)	N(5)–C(8)	1.52(3)
Cu–N(5)	2.09(2)	C(1)–C(2)	1.49(3)
N(1)–C(1)	1.45(3)	C(3)–C(4)	1.47(3)
N(2)–C(2)	1.48(3)	C(5)–C(6)	1.49(3)
N(2)–C(3)	1.51(3)	C(7)–C(8)	1.52(4)
N(3)–C(4)	1.56(3)		
N(1)–Cu–N(2)	84.1(6)°	Cu–N(3)–C(7)	105.1(11)°
N(1)–Cu–N(3)	169.6(6)	Cu–N(4)–C(6)	107.9(14)
N(1)–Cu–N(4)	105.0(7)	Cu–N(5)–C(8)	105.9(12)
N(1)–Cu–N(5)	96.3(7)	N(1)–C(1)–C(2)	110.3(16)
N(2)–Cu–N(3)	86.4(6)	N(2)–C(2)–C(1)	109.0(16)
N(2)–Cu–N(4)	116.7(7)	N(2)–C(3)–C(4)	108.3(14)
N(2)–Cu–N(5)	128.2(7)	N(3)–C(4)–C(3)	108.3(16)
N(3)–Cu–N(4)	83.2(6)	N(3)–C(5)–C(6)	111.7(19)
N(3)–Cu–N(5)	86.1(6)	N(3)–C(7)–C(8)	110.9(16)
N(4)–Cu–N(5)	113.2(7)	N(4)–C(6)–C(5)	107.0(20)
Cu–N(1)–C(1)	111.2(12)	N(5)–C(8)–C(7)	108.1(16)
Cu–N(2)–C(2)	105.4(11)	C(2)–N(2)–C(3)	116.3(14)
Cu–N(2)–C(3)	105.3(10)	C(4)–N(3)–C(5)	110.9(16)
Cu–N(3)–C(4)	106.5(11)	C(4)–N(3)–C(7)	108.0(14)
Cu–N(3)–C(5)	109.6(12)	C(5)–N(3)–C(7)	116.3(16)

In the case of [Zn(tren)NCS]$^+$ [8] and [Zn(tren)Cl]$^+$ [9] cations, which also have a trigonal bipyramidal geometry, the values of N–Zn–N intrachelate angles are still around 84–85°, while N–Zn–N angles in the equatorial plane have values which are much closer one to the other (116, 118 and 118° in Ref. 8 and 113, 117, 119° in Ref. 9). Distortions of the coordination polyhedron from exact D_{3h} symmetry are therefore higher for copper than for zinc ion, and the mentioned structures seem to confirm that they are a consequence of the tendency of copper toward square-pyramidal five-coordination rather than of the constraints of the ligands.

TABLE III. Equations of Molecular Planes, Referred to *a*, *b* and *c* Axes, with Deviations (Å) of Atoms from the Planes Given in Square Brackets.

Plane (a)	N(2), N(4), N(5) $8.585\,x + 0.203\,y + 2.493\,z = 2.112$ [Cu –0.17; N(1) –2.13; N(3) 1.87]
Plane (b)	Cu, N(1), N(2) $-0.637\,x + 12.65\,y - 3.526\,z = 1.062$ [C(1) –0.12; C(2) –0.68]
Plane (c)	Cu, N(2), N(3) $0.032\,x + 12.713\,y - 3.432\,z = 1.199$ [C(3) –0.59; C(4) 0.10]
Plane (d)	Cu, N(3), N(4) $-1.303\,x + 8.930\,y + 9.294\,z = 3.153$ [C(5) –0.154; C(6) 0.491]
Plane (e)	Cu, N(3), N(5) $-1.178\,x - 5.242\,y + 11.706\,z = 1.537$ [C(7) 0.447; C(8) –0.243]

All bond lengths and angles in the ligand are close to the expected values. Atomic distances from least-squares planes, given in Table III, show that all the chelate rings have the *gauche* unsymmetrical configuration; the conformation is K′ for the rings sharing the Cu–N(3) bond and K for the remaining one.

The crystal structure consists of discrete [Cu(trenen)]$^{2+}$ cations and Br^- anions held together by a combination of electrostatic forces and some hydrogen bonds involving bromine atoms: $Br(1)^{I}$–$N(1)^{I}$ = 3.43 Å, $Br(1)^{I}$–$N(5)^{II}$ = 3.51 Å, $Br(2)^{I}$–$N(1)^{II}$ = 3.38 Å, $Br(2)^{I}$–$N(2)^{I}$ = 3.38 Å, $Br(2)^{I}$–$N(5)^{II}$ = 3.49 Å (I = x, y, z; II = $\bar{x}$, $^1/_2+y$, $^1/_2-z$).

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