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Copper(II) Coordinated in an Unusual Manner by a N_6-donor Chelating Ligand

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Introduction

As part of a research program on the synthesis and complex formation of polydentate ligands containing imidazole groups, we recently synthesized the potentially hexadentate chelate ligand N,N,N′,N′-tetrakis(2′-benzimidazolylmethyl)1,2-ethane diamine (abbreviated EDTB) [1]. From spectroscopic and magnetic data (UV–VIS, IR, ESR, NMR) it was deduced that this chelating ligand is hexadentate towards transition-metal ions, such as Co(II), Ni(II) and Cd(II) [1]. The spectroscopic parameters of the Cu(II) compounds suggested that the metal ion does not possess a regular octahedral coordination geometry. Therefore, a crystal structure determination of a Cu(II) compound containing EDTB was carried out and the results of this study are presented here. A full paper describing the detailed structure and the magnetic and spectroscopic properties will be published later [2].

Experimental

Crystals containing the Cu(EDTB) ion were prepared from an ethanolic solution of the ligand and $Cu(H_2O)_6(BF_4)_2$. The crystals are monoclinic, space group $C2/c$, with $a = 14.402(2)$, $b = 14.955(2)$, $c = 18.846(4)$, $\beta = 101.17(1)°$, $Z = 4$, $d = 1.42(2)$ g/cm³.

The intensities of 3645 independent reflections were measured on a crystal of dimensions 0.30 × 0.15 × 0.12 mm, using Mo-Kα radiation on a Nonius CAD-4 diffractometer. From these 1727 with $I > 2\sigma(I)$ were used for structure solution (heavy-atom method) and refinements (block-diagonal least-squares procedures).

The structure of the negative counter ions in the crystal has not yet been completely clarified at the present stage of the refinement (conventional R-value amounts to 0.074). The electron density maps indicate that part of the BF_4^- ions are solvolysed to $(C_2H_5OBF_3)^-$. This would also explain the results of the elemental analyses, which indicate the presence of about one molecule of ethanol per Cu, whereas no separate ethanol molecule could be found in the crystal structure.

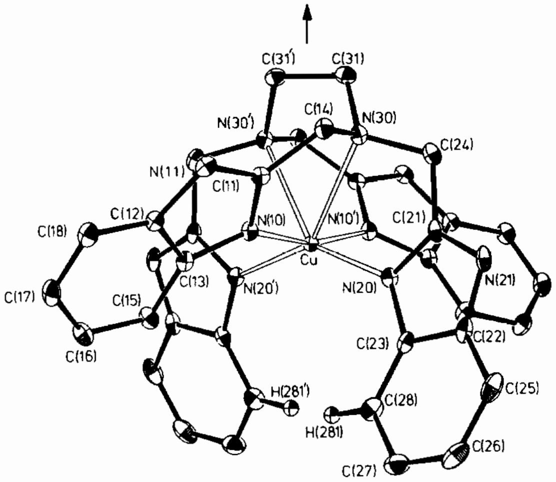

Fig. 1. ORTEP drawing of the $Cu(EDTB)^{2+}$ cation showing the anisotropic vibration ellipsoids (probability 11%). Hydrogen atoms have been omitted for clarity, except the two H atoms in close contact, H(281) and H(281′). Bond distances and angles are given in Table I.

TABLE I. Angles (degrees) and Distances (Angstrom) in $Cu(EDTB)^{2+}$.

Cu–N(10)	1.99(1)	N(30)–C(24)	1.46(1)
Cu–N(20)	2.03(1)	N(30)–C(31)	1.46(1)
Cu–N(30)	2.50(1)	C(31)–C(31′)	1.49(2)
N(10)–C(11)	1.31(1)	N(20)–C(21)	1.32(1)
N(10)–C(13)	1.41(1)	C(21)–C(24)	1.50(2)
C(11)–C(14)	1.48(1)	C(21)–N(21)	1.35(1)
C(11)–N(11)	1.35(1)	N(21)–C(22)	1.37(1)
N(11)–C(12)	1.39(1)	C(22)–C(23)	1.39(1)
C(12)–C(13)	1.40(1)	C(22)–C(25)	1.41(2)
C(13)–C(15)	1.37(1)	C(25)–C(26)	1.39(2)
C(15)–C(16)	1.38(1)	C(26)–C(27)	1.38(2)
C(16)–C(17)	1.38(2)	C(27)–C(28)	1.36(2)
C(17)–C(18)	1.37(2)	C(28)–C(23)	1.38(2)
C(18)–C(12)	1.35(1)	H(281)- - -H(281′)	2.50
N(30)–C(14)	1.47(1)	Cu- - -H(281)	3.45

N(20)–Cu–N(20′)	142.9(5)
N(20)–Cu–N(30′)	142.7(3)
N(30)–Cu–N(30′)	70.3(4)
N(10)–Cu–N(10′)	165.6(5)
N(10)–Cu–N(30′)	91.4(3)
N(30)–Cu–N(10)	76.7(3)
N(10)–Cu–N(20′)	93.6(3)
N(20)–Cu–N(10)	90.9(3)
N(20)–Cu–N(30)	74.1(3)

Description of the Structure

An ORTEP drawing of the Cu(EDTB)$^{2+}$ cation is given in Fig. 1. Selected bond distances and angles are given in Table I. As is seen from the Figure and the Table, the copper atom indeed is hexa-coordinated by the chelating ligand, as predicted from spectral and magnetic data. However, the geometry of the coordination polyhedron around Cu(II) is unusual, even for a versatile cation like Cu(II). In fact the structure can be described as derived from distorted octahedral, tetrahedral or square pyramidal coordination geometries. Using the octahedral description, the unusual features are:

a) Two elongated Cu–N bonds in a *cis*-geometry, rather than in the usual *trans* orientation as observed in almost all other known CuN$_6$ species.

b) A severe distortion from 90° of the N–Cu–N angles in the plane of the atoms N(20)–N(30)–N(30)′–N(20)′. The angle N(20)–Cu–N(20)′ of 143° is very large indeed.

The origin of this unusual coordination geometry most probably lies in the steric constraints imposed by the ligand. Due to the close H(281)....H(281′) contacts of 2.50 Å, the angle N(20)–Cu–N(20)′ of 143° – in fact the major distortion from octahedral – cannot be smaller, with the present ligand conformation. The volume of the space below Cu, however, is too small to accommodate a small ligand like *e.g.* F$^-$.

A final comment is made about the counter ion. Both elemental analyses and the X-ray refinement have shown that part of the BF$_4^-$ ions (*viz.* 40%) is decomposed into the (C$_2$H$_5$OBF$_3$)$^-$ ions, most probably by solvolysis of the BF$_4^-$ ion during the formation of the compound.

Decomposition reactions of metal tetrafluoroborates during the synthesis of coordination compounds with azole ligands have been reported [3–5]. So far, invariably fluoride anions have been found in the solid products. This is the first example where the decomposition product containing borium cocrystallizes.

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