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The X-Ray Structure of (N,N,N′,N′-tetra(2′-benzimidazolylmethyl)-1,2-ethanediamine)dicopper(I) bisperchlorate. A Unique Example of Copper(I) linearly Coordinated by Imidazole Ligands

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Binuclear copper sites are generally accepted as occurring as the 'EPR-silent', type III copper in proteins such as hemocyanin [1], tyrosinase [2], and laccase [3]. Imidazole groups from histidine sidechains are believed to be the donor ligands for copper in these proteins [4]. Recently we reported the synthesis and complex formation of Cu(II) compounds containing four benzimidazole groups rigidly incorporated in a chelating ligand [5] and the X-ray crystal structure [6] of one of these cationic complexes, $[\mathrm{Cu^{II}}\{(C_7H_5N_2–CH_2–)_2N–CH_2–CH_2–N(–CH_2–C_7H_5M_2)_2\}]^{2+}$. We now report the synthesis and structure of a binuclear Cu(I) derivative containing the same chelating ligand.

Experimental

The ligand (EDTB) was prepared as described previously [5]. Reaction of 1 mmol of this ligand in 500 ml of warm absolute ethanol with 2.1 mmol of $Cu(ClO_4)$ (obtained by *in situ* reduction of $Cu(ClO_4)_2$ with copper powder in 5 ml of acetonitrile) produced a colourless micro-crystalline precipitate of $Cu_2(EDTB)(ClO_4)_2$ [7]. Preparation by slow diffusion of a solution of $Cu(ClO_4)$ in acetonitrile into a solution of EDTB in acetone/dimethylsulfoxide (20:1) under a nitrogen atmosphere yielded colourless single crystals of the copper compound, together with some differently shaped colourless crystals of the free ligand; separation was carried out by hand under a microscope. The compound is quite stable when dry and turns green very slowly in contact with moist air.

The unit cell parameters* are: a = 13.849(2), b = 18,913(2) and c = 14.026(2) Å; α = 90.0°, β = 102.10°(1) and γ = 90.0°; Z = 4; d_m = 1.65(1) and d_x = 1.68 g cm^{-3}. Intensity data were collected on a Nonius CAD-4 automatic diffractometer** and the structure was solved by heavy atom methods in space group $C2/c$ and refined† (2672 reflections, 317 parameters) to a residual R value of 0.039††.

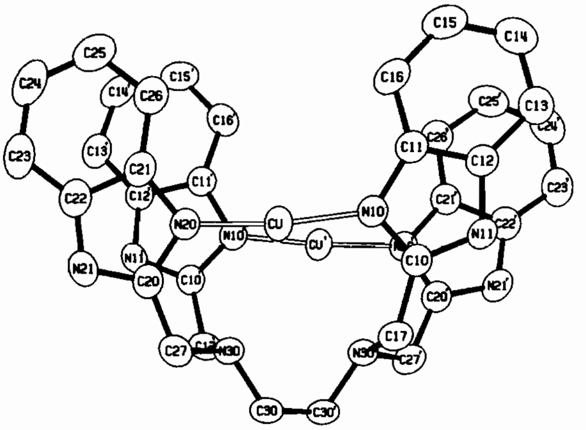

Fig. 1. ORTEP drawing of the $Cu_2(EDTB)^+$ cation, showing the anisotropic vibration ellipsoid (probability 50%). Hydrogen atoms have been omitted for clarity. Bond distances and angles are given in Table I.

Description of the Structure

An ORTEP drawing of the $Cu_2(EDTB)^{2+}$ cation is given in Fig. 1. Selected bond angles and distances are listed in Table I. As is seen from Table I and Fig. 1, the coordination around each copper(I) is nearly linear with unusually short Cu–N distances. The other contacts are Cu···N(amine) and Cu····Cu distances of 2.774(4) and 3.043(3) Å, respectively, which can hardly be considered as bonds [12]. Usual Cu(I)–N distances appear to be 1.9–2.2 Å [9, 10]. Moreover, the angles between the Cu–N(amine) vector and the other bonds around nitrogen indicate that the lone pair on the nitrogen atom N(30) does

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*Precise cell parameters were determined by least squares refinement of θ values of 24 reflections in the range 8° < θ < 13°. The density was measured by flotation in a dibromoethane–hexane mixture.

**ω–θ scans were used to collect intensity data for all reflections with 2° < θ < 26° and with h > 0.

†All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were found in a difference Fourier map and refined with isotropic thermal parameters. The ClO_4^- ions are present in a disordered way. One of the oxygen atoms is refined on two clearly different positions. For the other three oxygen atoms the disorder is reflected in the large anisotropy of their thermal parameters; they are not refined on separate positions.

††$R = \dfrac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$.

TABLE I. Bond Distances (Angströms) and Selected Angles (Degrees) in $Cu_2(EDTB)(ClO_4)_2$. Estimated Standard Deviations are in Parentheses.

Cu–N(10)	1.869(4)	N(10)–Cu–N(20)	170.9(2)
Cu–N(20)	1.876(4)		
		Cu•••N(30)–C(27)	91.8(3)
Cu•••Cu' [a]	3.043(3)	Cu•••N(30)–C(30)	121.5(3)
Cu•••N(30)	2.774(4)	Cu•••N(30)–C(17')	110.4(3)
N(10)–C(10)	1.320(6)	N(20)–C(20)	1.316(6)
N(10)–C(11)	1.392(6)	N(20)–C(21)	1.395(6)
C(10)–C(17)	1.490(7)	C(20)–C(27)	1.489(7)
C(10)–N(11)	1.340(6)	C(20)–N(21)	1.336(6)
N(11)–C(12)	1.378(6)	N(21)–C(22)	1.378(7)
C(11)–C(12)	1.389(6)	C(21)–C(22)	1.392(7)
C(12)–C(13)	1.381(7)	C(22)–C(23)	1.383(7)
C(13)–C(14)	1.367(8)	C(23)–C(24)	1.370(9)
C(14)–C(15)	1.383(8)	C(24)–C(25)	1.381(9)
C(15)–C(16)	1.367(8)	C(25)–C(26)	1.379(8)
C(16)–C(11)	1.390(7)	C(26)–C(21)	1.380(7)
N(30)–C(17')	1.479(6)	N(30)–C(27)	1.470(6)
C(30)–C(30')	1.503(10)	N(30)–C(30)	1.471(6)

[a] The primed and unprimed atoms are related by a twofold rotation axis.

not point towards the Cu^I atom (see Table I). The only comparable structure [10] which also contains Cu(I) linearly coordinated by N-donor ligands (*i.e.* diazoaminobenzenecopper(I)), has a Cu••Cu contact of 2.45 Å, which has been considered as a bonding contact. In this structure the Cu–N bond lengths amount to 1.90(2) and 1.94(2) Å, which is slightly larger than in the present compound.

The coordination geometry around the Cu(I) ions and the binuclear nature of the compound is of particular interest in view of the recent EXAFS data of Cu(I) in deoxyhemocyanin [4b]. These data indicate a Cu•••Cu distance of 3.37 Å (10% larger than in our compound) and a probable two-coordination for each Cu(I)[§]. Preliminary reactivity studies of the title compound revealed a reversible reaction with carbon monoxide in DMSO (the product is characterised by a C=O stretching frequency of 2065 cm^{-1}, which is a normal value for Cu(I)–CO adducts [11]. Even with molecular dioxygen a rapid reaction takes place in solution. The stoichiometries and the degree of reversibility of these reactions are under investigation [12].

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12 Work in progress.

[§] Although spectroscopic data [4c] may suggest a higher coordination number, the EXAFS-determined [4b] number of nearest neighbours is 1.5–2.0.