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Synthesis and Structural Characterization of the Copper(II) Complex with *N,N'*-Bis-(1-benzimidazolylethyl)ethylenediamine

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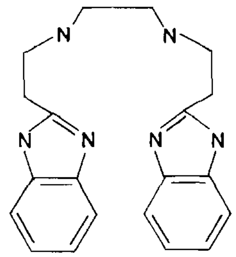
Copper proteins with spectroscopic properties characteristic of normal Cu(II) coordination compounds are considered to belong to Type II. They contain a single copper ion at the catalytic center, although in this case the ligands are coordinated via nitrogen and oxygen donor atoms with the geometry dominated by a square-planar arrangement around the copper. An importment feature of this arrangement is that there is at least one readily accessible coordination site, either in the plane or along the tetragonal axis, that binds the substrate or another ligand [1, 2]. Examples of proteins containing only this type of copper are bovine superoxide dismutase [3] and galactose oxidase [3]. Also, several multicopper proteins such as laccase and ceruloplasmin [3, 4] are known to contain at least one copper of Type II.

A large variety of copper(I) and copper(II) imidazole coordination compounds have been described [5]. The oldest study of a chelating ligand containing two imidazole groups and two other donors atoms is IMEDA (*N,N'*-bis(4-(5)-imidazolylmethyl)ethylenediamine) [6]. Later studies were of 4-IMDIEN (1,9-bis-(4-imidazolyl)-2,5,8-triazanonane) and 4-IMDPT (1,11-bis(4-imidazolyl)-2,6,10-triazaundecane) [7]. Finally, we want to mention the quenquedentate ligand IMEP (2,6-bis(1-(2-imidazole-4-ylethylimino)-ethyl)pyridine) for which Wilson *et al.* have described a $Cu^I(IMEP)^+$ complex which serves as a synthetic Cu^I oxygen carrier [8]. We report the synthesis of a new tetradentate ligand, *N,N'*-bis(2-benzimidazolylethyl)ethylenediamine (BEEDA) and the determination of the crystal structure of $(Cu(BEEDA)(ClO_4))ClO_4$ by the X-ray method.

Experimental

The ligand *N,N'*-bis(2-benzimidazolylethyl)ethylenediamine (BEEDA) was prepared by the reaction of 2.05 g (0.01 mol) ethylenediamine-*N,N'*-dipropionic acid and 2.2 g (0.02 mol) *o*-phenylenediamine in 60 cm^3 4 mol dm^{-3} hydrochloric acid solution. The solution was refluxed for 24 h. After cooling, a blue solid was obtained. The blue solid was dissolved in hot water and the solution was made alkaline with ammonium hydroxide and a yellow solid was precipitated. Recrystallization from a mixed solvent (MeOH: H_2O = 1:1) gave a colorless solid, i.e. *N,N'*-bis(2-benzimidazolylethyl)ethylenediamine (BEEDA).



The complex $Cu(BEEDA)ClO_4$ was isolated as a pale yellow powder by reaction of $Cu(CH_3CN)_4ClO_4$ dissolved in CH_3CN and BEEDA dissolved in MeOH under a nitrogen atmosphere. The above solution was stirred in air overnight, and the copper(I) complex was oxidized to a blue copper(II) complex. After filtration, the blue precipitate was washed with MeOH and ether. Recrystallization from MeOH afforded a crystalline complex $(Cu(BEEDA)(ClO_4))ClO_4$.

Results and Discussion

$(Cu(BEEDA)(ClO_4))ClO_4$ crystallizes in the monoclinic space group $P2_1/C$ with $a = 10.985(4)$, $b = 24.497(6)$, $c = 9.784(4)$ Å; $\beta = 112.89(3)$, $V = 2914.5$ $Å^3$, and $Z = 4$. The final residue value of R was 0.051 for 1043 reflections ($I \geqslant 3\sigma(I)$). Positional parameters are given in Table 1 and bond lengths and bond angles are given in Tables 2 and 3 respectively. The structure and unit cell of $(Cu(BEEDA)(ClO_4))ClO_4$ are given in Figs. 1 and 2.

The two benzimidazole rings are in different least-squares planes respectively. The CuN_4 unit is not rigorously planar. The Cu(II) ion is in the least-squares plane, N_1 and N_{21} are 0.4–0.5 Å above the plane and N_2 and N_{11} are 0.4–0.5 Å below the plane. The coordination geometry around Cu(II) is best described as distorted square-based pyramidal with N_1, N_2 from the amine and N_{11}, N_{21} from the benzimidazole comprising the nearly square plane; one of the perchlorate oxygen atoms (O_{12}) is in the axial position.

The bond lengths of Cu–N_1 and Cu–N_2 are the same, 2.03(2) Å; Cu–N_{11} and Cu–N_{21} are shorter than the above two bonds and equal to 1.94(3) and

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TABLE 1. Position parameters and their estimated standard deviations

Atoms	x	y	z	B (Å^2)
Cu	0.27(1)	0.879(2)	0.682(1)	3.12(9)
Cl(1)	0.25(2)	1.026(1)	0.7419(9)	3.5(2)
Cl(2)	−0.4227(5)	0.7771(2)	0.3588(5)	4.8(3)
O(11)	0.207(2)	1.063(1)	0.8180(2)	6.0(7)
O(12)	0.36823(9)	0.9996(2)	0.843(1)	8(1)
O(13)	0.2727(5)	1.0531(2)	0.6278(5)	6.9(8)
O(14)	0.161(1)	0.985(1)	0.6815(5)	7.8(9)
O(21)	−0.332(1)	0.739(2)	0.3527(7)	11(1)
O(22)	−0.385(2)	0.831(1)	0.35(2)	9(1)
O(23)	−0.437(2)	0.7576(6)	0.485(2)	8(2)
O(24)	−0.543(1)	0.76(3)	0.238(3)	11(2)
N(1)	0.456(1)	0.863(1)	0.846(1)	3.6(8)
N(2)	0.2046(6)	0.879(2)	0.844(1)	4.1(8)
N(11)	0.352(1)	0.9107(6)	0.549(2)	2.6(7)
N(12)	0.498(1)	0.929(1)	0.4515(6)	3.7(8)
N(21)	0.119(2)	0.851(1)	0.530(1)	3.3(7)
N(22)	−0.1055(5)	0.839(1)	0.406(1)	3.4(8)
C(1)	0.586(1)	0.8812(8)	0.696(2)	5.2(5)
C(2)	0.570(2)	0.8905(9)	0.837(2)	6.0(6)
C(3)	0.440(2)	0.9722(9)	0.990(2)	5.9(6)
C(4)	0.305(1)	0.8535(8)	0.975(2)	3.9(5)
C(5)	0.072(1)	0.8584(7)	0.818(1)	2.8(4)
C(6)	−0.031(1)	0.8801(9)	0.661(1)	4.8(5)
C(11)	0.298(1)	0.9373(6)	0.412(2)	2.4(4)
C(12)	0.158(2)	0.9537(8)	0.338(2)	4.0(5)
C(13)	0.121(2)	0.9789(7)	0.201(2)	5.5(6)
C(14)	0.219(2)	0.9875(8)	0.143(2)	5.1(6)
C(15)	0.350(1)	0.9709(7)	0.218(2)	3.2(4)
C(16)	0.377(2)	0.9466(7)	0.374(2)	3.6(5)
C(17)	0.480(2)	0.9054(7)	0.567(2)	3.8(5)
C(21)	0.090(1)	0.8277(6)	0.402(2)	3.1(4)
C(22)	0.180(1)	0.9093(7)	0.337(2)	3.7(5)
C(23)	0.133(1)	0.7853(7)	0.200(2)	3.8(5)
C(24)	0.000(2)	0.7793(9)	0.119(2)	6.2(5)
C(25)	−0.096(2)	0.7976(7)	0.173(2)	4.1(5)
C(26)	−0.041(1)	0.8198(6)	0.317(2)	2.4(4)
C(27)	−0.011(1)	0.8557(7)	0.534(1)	3.0(4)

TABLE 2. Bond distances (Å)

Cu–N(1)	2.03(2)	N(21)–C(21)	1.29(2)
Cu–N(2)	2.03(2)	N(21)–C(27)	1.44(2)
Cu–N(11)	1.94(3)	N(22)–C(26)	1.40(2)
Cu–N(21)	1.93(3)	N(22)–C(27)	1.34(2)
Cl(1)–O(11)	1.38(2)	C(1)–C(2)	1.47(3)
Cl(1)–O(12)	1.44(2)	C(1)–C(17)	1.47(2)
Cl(1)–O(13)	1.40(2)	C(6)–C(27)	1.46(2)
Cl(1)–O(14)	1.37(2)	C(11)–C(12)	1.39(2)
Cl(2)–O(21)	1.38(3)	C(11)–C(16)	1.37(3)
Cl(2)–O(22)	1.39(5)	C(12)–C(13)	1.39(2)
Cl(2)–O(23)	1.38(2)	C(13)–C(14)	1.40(3)
Cl(2)–O(24)	1.42(7)	C(14)–C(15)	1.39(2)
N(1)–C(2)	1.45(3)	C(15)–C(16)	1.32(2)
N(1)–C(3)	1.51(3)	C(21)–C(22)	1.43(3)
N(2)–C(4)	1.47(2)	C(21)–C(26)	1.36(2)
N(2)–C(5)	1.47(2)	C(22)–C(23)	1.37(2)
N(11)–C(11)	1.40(2)	C(23)–C(24)	1.37(2)
N(11)–C(17)	1.35(2)	C(24)–C(25)	1.43(3)
N(12)–C(16)	1.39(2)	C(25)–C(26)	1.41(2)
N(12)–C(17)	1.35(3)	C(5)–C(6)	1.60(2)
		C(3)–C(4)	1.49(3)
Cu–O(11)	4.82(3)	Cu–O(21)	7.00(1)
Cu–O(12)	2.61(2)	Cu–O(22)	6.73(2)
Cu–O(13)	4.29(1)	Cu–O(23)	7.80(1)
Cu–O(14)	2.85(1)	Cu–O(24)	8.75(3)

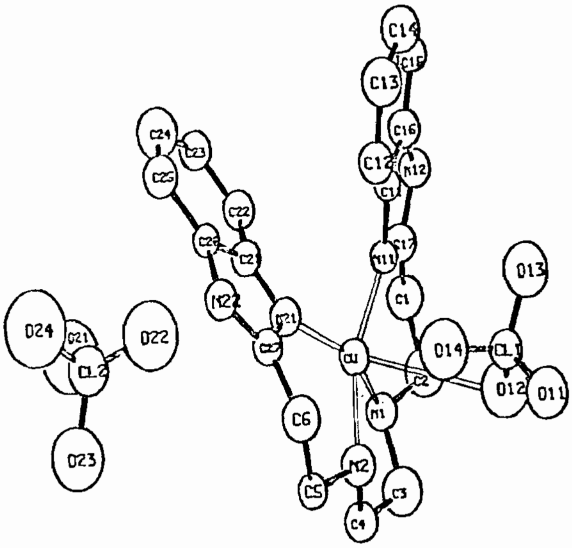

Fig. 1. ORTEP drawing of (Cu(BEEDA)(ClO$_4$))ClO$_4$.

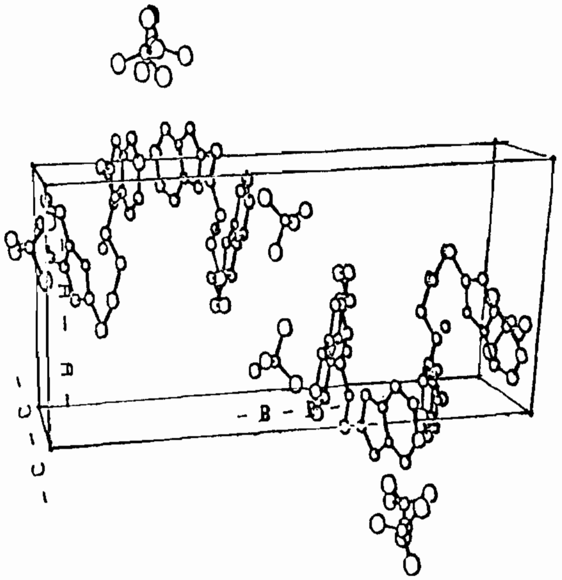

Fig. 2. Drawing of the unit cell contents of (Cu(BEEDA)(ClO$_4$))ClO$_4$.

TABLE 3. Bond angles (deg)

N(1)–Cu–N(2)	86.2(7)	N(11)–C(11)–C(16)	110.0(1)
N(1)–Cu–N(11)	94.9(9)	C(12)–C(11)–C(16)	118.0(1)
N(1)–Cu–N(21)	147.0(3)	C(11)–C(12)–C(13)	119.0(2)
N(2)–Cu–N(11)	156.0(3)	C(12)–C(13)–C(14)	118.0(2)
N(2)–Cu–N(21)	95.0(1)	C(13)–C(14)–C(15)	122.0(2)
N(11)–Cu–N(21)	96.7(8)	C(14)–C(15)–C(16)	116.0(2)
Cu–N(1)–C(2)	116.0(2)	N(12)–C(16)–C(11)	104.0(1)
Cu–N(1)–C(3)	106.0(1)	N(12)–C(16)–C(15)	130.0(2)
C(2)–N(1)–C(3)	113.0(2)	C(11)–C(16)–C(15)	126.0(1)
Cu–N(2)–C(4)	107.0(1)	N(11)–C(17)–N(12)	109.0(1)
Cu–N(2)–C(5)	122.0(1)	N(11)–C(17)–C(1)	126.0(2)
C(4)–N(2)–C(5)	111.0(2)	N(12)–C(17)–C(1)	125.0(2)
Cu–N(11)–C(11)	130.0(1)	N(21)–C(21)–C(22)	128.0(1)
Cu–N(11)–C(17)	124.0(1)	N(21)–C(21)–C(26)	117.0(2)
Cu(11)–N(11)–C(17)	106.0(2)	C(22)–C(21)–C(26)	115.0(1)
C(16)–N(12)–C(17)	110.0(2)	C(21)–C(22)–C(23)	121.0(1)
Cu–N(21)–C(21)	135.0(2)	C(22)–C(23)–C(24)	122.0(2)
Cu–N(21)–C(27)	123.0(1)	C(23)–C(24)–C(25)	121.0(2)
C(21)–N(21)–C(27)	101.0(1)	C(24)–C(25)–C(26)	114.0(2)
C(26)–N(22)–C(27)	106.6(9)	N(22)–C(26)–C(21)	104.0(1)
N(1)–C(2)–C(1)	114.0(2)	N(22)–C(26)–C(25)	129.0(1)
N(1)–C(3)–C(4)	109.0(1)	C(21)–C(26)–C(25)	127.0(2)
N(2)–C(4)–C(3)	109.0(2)	N(21)–C(27)–N(22)	111.0(1)
N(2)–C(5)–C(6)	109.0(2)	N(21)–C(27)–C(6)	122.0(1)
C(5)–C(6)–C(27)	113.0(1)	N(22)–C(27)–C(6)	127.0(1)
N(11)–C(11)–C(12)	131.0(2)	C(2)–C(1)–C(17)	113.0(2)

1.93(3) Å, respectively. The bond lengths of Cu–N$_1$ and Cu–N$_2$ (amine N) are in good agreement with analogous interatomic distances in other published compounds, such as in (Cu$_2$(dien)$_2$Br$_2$)(ClO$_4$)$_2$ (dien = diethylenetriamine); the Cu–N bonds are 2.003, 2.005 and 2.029 Å [9]. In the complex (Cu$_2$(dien)$_2$Cl$_2$)(ClO$_4$)$_2$, the Cu–N bond lengths are 2.015 and 2.042 Å [10]. Bond lengths of Cu–N$_{11}$ and Cu–N$_{21}$ (imidazole N) are very similar to those Cu–N bond lengths (1.91–1.99 Å) in the following complexes: (Cu(BBDH)Cl)$^+$, (Cu(BBDH)(H$_2$O))$^{2+}$, (Cu(BBDHp)(H$_2$O))$^{2+}$, (Cu(BBIDH)Br)$^+$, and (Cu^I(BBDHp))$^+$, described by Reedijk *et al.* [11–15]. The Cu–O distance, 2.61(2) Å, is very similar to the Cu–O bond length, 2.60 Å, in (Cuen$_2$)(ClO$_4$)$_2$ [16]. In the complex (Cu(BEEDA)(ClO$_4$))ClO$_4$, a small but significant distortion occurs in the perchlorate ion (Cl–O = 1.38(2), 1.44(2), 1.40(2), 1.37(2) Å); we suggest that the perchlorate ion is weakly or semi-coordinated to the copper ion [16].

Redox, ESR and electronic spectral properties of this complex are under investigation.

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