Synthesis and Characterization of a New Binuclear Copper(II) Complex with an Oxygen Bridge and a B−N Bonded Ligand

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Introduction

Binuclear copper(II) complexes have been investigated frequently, not only because of the interest in new inorganic materials showing molecular ferro- or antiferromagnetic interactions,[2−4] but also because of their relevance for bioinorganic model systems in copper proteins.[5,6] Bridging systems based on the imidazolate ligands are most interesting, because of their similarity to the chemical environment of copper proteins.

The structure and magnetic properties of copper(II) complexes of a Schiff base ligand containing an imidazole moiety have been intensively studied by Matsumoto and co-workers.[7−9] The same authors have very recently reported a mononuclear copper(II) complex with B−N bond formation by the reaction of *N*-(3-methoxysalicylidene)-*N′*-(imidazol-4-ylmethylene)-1,3-propanediamino) copper(II) perchlorate and sodium tetraphenylborate ($NaBPh_4$).[10] However, no binuclear copper(II) complex with B−N formation and a self-assembly reaction has been reported. It has been known that copper(II) complexes are treated with the reducing agent of $NaBPh_4$ usually to reduce the Cu(II) to Cu(I) or to give anionic complex salts.[11] Although the B−N bond formation reaction has been known for organic compounds,[12] to our knowledge metal complex preparation with accompanying B−N bond formation is rare.

Table 1. Crystallographic Data for $[Cu(LBPh_3)]_2$

chem formula	$C_{64}H_{58}N_8O_2B_2Cu_2$
fw	1119.91
temp, K	298
space group	$P2_1/c$
a, Å	8.6432(19)
b, Å	17.151(4)
c, Å	18.596(4)
β, deg	100.997(18)
V, Å^3	2706.0(10)
D_c, g cm^{-3}	1.374
Z	2
λ, Å	0.7107
μ, cm^{-1}	16.628
R^a	0.042
$R_w{}^b$	0.041

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

During the course of our study on the chemical reaction of the ligand in the binuclear copper(II) complexes, we found that direct reaction of $Cu(ClO_4)_2$ with a Schiff base containing imidazole and $NaBPh_4$ leads to ferromagnetic self-assembly O-bridging and B−N bonded binuclear copper(II) complexes, such as $[Cu(LBPh_3)]_2$ (where $LBPh_3$ = *N*-(salicylidene)-*N′*-(1-BPh_3-2-ylmethylene)-1,3-propanediamino). We report herein the synthesis, characterization, crystal structure, and magnetic measurements for this new B−N bonded binuclear copper(II) complex $[Cu(LBPh_3)]_2$.

Experimental Section

Synthesis of Complex. $[Cu(LBph_3)]_2$. This compound was obtained as dark-green crystals, suitable for X-ray analysis, by adding a mixture of 1,3-diaminopropane (2.5 mmol) and salicylaldehyde (2.5 mmol) to 25 mL of chloroform and stirring the mixture for 3 days. After this was added a solution of 2-imidazolecarboxaldehyde (2.5 mmol) in 20 mL of methanol. The mixture was warmed in a water bath at 60 °C for 1 h and then cooled to room temperature. To the solution was added a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in 15 mL of methanol followed by one drop of trimethylamine. To the resulting solution was added a solution of $NaBPh_4$ (2 mmol) in 20 mL of methanol, and this mixture was stirred for 3 days.

Prism-shaped dark-green crystals formed, which were filtered off and washed with methanol (yield 70%). Anal. Calcd for $[Cu(C_{32}H_{29}BN_4O]_2$: C, 68.64; H, 5.22; N, 10.00. Found: C, 68.79; H, 5.01; N, 9.95.

Physical Methods. Infrared spectra were recorded on a Bio-Rad FTS-40FTIR spectrophotometer as KBr pellets in the 4000−400 cm^{-1} region. X-band ESR spectra at 300 K for the complex were recorded on a Bruker ECS-106 spectrometer. Temperature dependences of magnetic susceptibilities of the polycrystalline sample were measured between 4 and 300 K at a field of 1 T using a Quantum Design Model MPMS computer-controlled SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants.[13]

X-ray Structure Determination. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation. The unit cell parameters were determined by 25 independent reflections in the range of $17 \leq 2\theta \leq 25°$. The structure was solved by the heavy-atom method and subsequent difference Fourier maps, followed by full-matrix least-squares refinement with the NRCVAX computer program.[14] All hydrogen atoms were located in a Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically. The detailed data collection, crystallographic data, and data reduction information are listed in Table 1, and the atom coordinates are listed in Table 2.

Results and Discussion

Synthesis and Chracterizations. The reaction of $Cu^{II}(ClO_4)_2$ with 2-imidazolecarboxaldehyde, 1,3-diaminopropane, salicyl-

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Table 2. Selected Final Atomic Positional Parameters and *B*(eq) Values (Å^2) for [Cu(LBPh$_3$)]$_2$[a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Cu	0.02256(6)	0.08284(3)	0.04126(3)	2.851(21)
O	−0.931(3)	−0.00834(15)	0.05953(13)	3.13(13)
N(1)	0.2072(4)	0.05519(18)	0.11443(17)	3.11(15)
N(2)	0.1126(4)	0.18598(19)	0.1143(17)	3.17(15)
N(3)	−0.2769(4)	0.22681(18)	−0.08816(17)	2.85(15)
N(4)	−0.1669(5)	0.12743(18)	−0.01976(17)	2.68(14)
C(15)	−0.4057(5)	0.35324(23)	−0.06177(22)	3.07(19)
C(21)	−0.4364(5)	0.30082(24)	−0.20304(21)	3.13(20)
C(27)	−0.1694(5)	0.35868(24)	−0.13810(22)	3.23(19)
B	−0.3230(6)	0.3134(3)	−0.1232(3)	3.20(22)

[a] Numbers in parentheses are errors in the last significant digit. [b] *B*(eq) is the mean of the principal axes of the thermal ellipsoid.

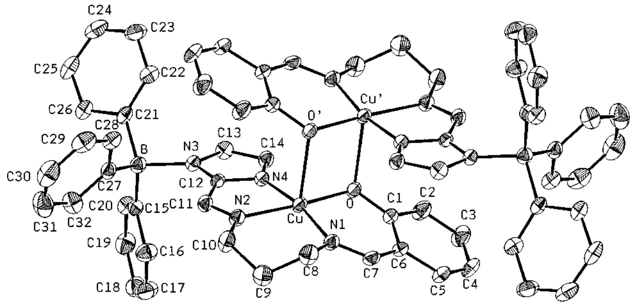

Figure 1. ORTEP stereoview of [Cu(LBPh$_3$)]$_2$ (30% probability thermal ellipsoids).

aldehyde, and NaBPh$_4$ yielded the complex [Cu(LBPh$_3$)]$_2$ (LBPh$_3$ = *N*-(salicylidene)-*N'*-(imidazol-2-ylmethylene)-1,3-propanediamine). The X-ray structural analysis reveals that this binuclear Cu(II)-complex has shown the presence of a B−N bond which is formed by reaction of BPh$_4^-$ with a nitrogen atom of the imidazolate moiety of the ligand.

The IR spectrum of the compound showed strong to medium bands assigned to ν(C=N) at 1628 cm^{-1} and ν(B−N) at 790 cm^{-1}. The assignment for the ν(BN) stretching mode is based partly on the comparison with data from the IR spectroscopic and theoretical studies of the R$_3$B−NR$_3'$ (where R or R′ are hydrogen, alkyl, or aryl groups) systems,[15−17] such as H$_3$B−NMe$_3$,[16] and Cl$_3$B−NH$_3$.[17]

Description of the Structure of [Cu(LBPh$_3$)]$_2$. An ORTEP view of the molecular structure of the compound [Cu(LBPh$_3$]$_2$ with the atom numbering scheme is shown in Figure 1. Selected bond distances and angles are given in Table 3.

The structure consists of an oxygen-bridged dimer where the geometry about each copper center is distorted square-pyramidal with an out-of-plane Cu−O distance of 2.440(3) Å. Basal coordination sites are occupied by three nitrogen atoms and one oxygen atom of the chelated ligand LBPh$_3$. The link between adjacent metal ions is formed by a self-assembly bridging oxygen atom at a basal site.

The chelated copper(II)−oxygen length of Cu−O not only is shorter at 1.921(3) Å than the bridging length of 2.440(3) Å but also is shorter than the averaged bond length 1.980 Å of Cu−N. The Cu−Cu′ separation and the Cu−O−Cu′ bridge angle are 3.085(4) Å and 94.35(10)°, respectively. The most obvious manifestation of the structure is the formation of a boron−nitrogen bond. The distance B−N(3) is 1.640(6) Å, which is significantly larger than that of 1.609 Å reported for the mononuclear complex of [Cu(L′BPh$_3$)]DMF (L′ = *N*-(3-methoxysalicylidene)-*N'*-(1-imidazol-4-ylmethylene)-1,3-propanediamine).[10]

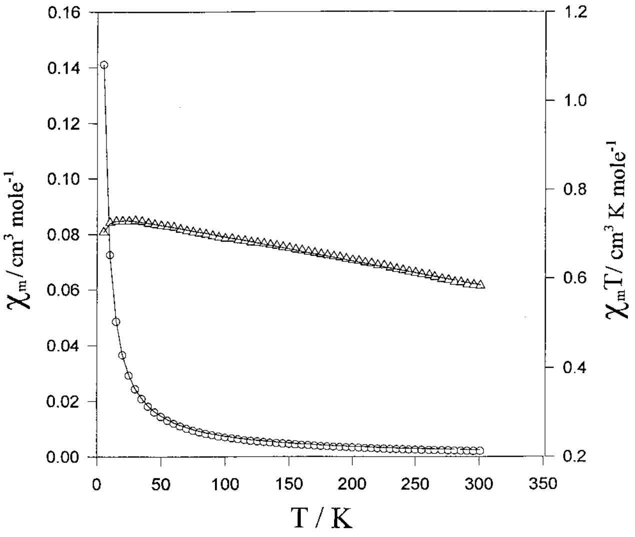

Figure 2. Thermal varition of the molar magnetic susceptibility for [Cu(LBPh$_3$)]$_2$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for [Cu(LBPh$_3$)]$_2$

	Bond Distances		
Cu−O	1.921(3)	Cu−O′	2.440(3)
Cu−N(1)	1.948(3)	Cu−N(2)	2.030(3)
Cu−N(4)	1.961(3)	B−N(3)	1.640(6)
B−C(15)	1.611(6)	B−C(21)	1.630(6)
B−C(27)	1.607(6)		
	Bond Angles		
Cu−O−Cu′	94.35(10)	O−Cu−O′	85.65(10)
O′−Cu−N(1)	96.76(12)	O′−Cu−N(2)	96.18(11)
O′−Cu−N(4)	93.63(11)	O−Cu−N(4)	90.83(12)
O−Cu−N(1)	93.60(12)	N(2)−Cu−N(1)	94.60(13)
N(3)−B−C(21)	107.5(3)	N(3)−B−C(15)	102.1(3)
N(3)−B−C(27)	111.1(3)		

EPR and Magnetic Properties. The EPR spectrum (9.81 GHz) of a powdered sample of [Cu(LBPh$_3$)]$_2$ at 300 K is, as expected, a typical triplet-state spectrum[18,19] for an exchange-coupled binuclear copper(II) ions. The resonace absorption spectrum with anisotropy and without hyperfine interaction around 3300 and 1650 G (weak absorption) arises from $\Delta M_s = \pm 1$, (given $g_1 = 1.88$, $g_2 = 2.09$, $g_3 = 2.28$) and $\Delta M_s = \pm 2$ (given $g = 4.28$) transitions in an $S = 1$ spin system arising from intramolecular dipole−dipole coupling between two copper(II) ion. The zero-field splitting parameter D is less than 0.04 cm^{-1}.[4]

The results of magnetic susceptibility measurements for [Cu(LBPh$_3$)]$_2$ are given as a function of temperature in Figure 2. The magnetic susceptibility increases from a value of $\chi T = 0.58$ cm^3 mol^{-1} K ($\mu_{\text{eff}} = 2.16\ \mu_B$) at 300 K steadily with decreasing temperature until it reaches a maximum at 30 K, with $\chi T = 0.73$ cm^3 mol^{-1} K ($\mu_{\text{eff}} = 2.42\ \mu_B$) showing a ferromagnetic behavior. Below 30 K, the χT value decreases slowly to 0.70 at 5 K, indicating the existence of weak intermolecular interaction. We have attempted to reproduce theoretically the experimental susceptibility in this complex by use of the expression

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of the Bleaney−Bowers equation (1)[20] for intramolecular

$$\chi_M = Ng^2\beta^2/k(T - \Theta)[1 + {}^1/_3 \exp(-2J/kT)] - 1 + N\alpha \quad (1)$$

exchange-coupled pairs of copper(II). In this expression $2J$ is the triplet−singlet splitting or exchange parameter. The parameters giving the best fit are g_i (averaged g_1, g_2, and g_3 obtained from EPR data) = 2.09, $\Theta = 0.2$ K, $2J = 1.60$ cm^{-1}, and $N\alpha = 85 \times 10^{-6}$ cm^3 mol^{-1}. The quantity minimized in the least-squares fitting process was $R = \sum[\chi_M(\text{obsd}) - \chi_M(\text{calcd})]^2 = 3.82 \times 10^{-6}$, and each point was given equal weight. The smaller positive value obtained for the exchange coupling constant J indicates a weak ferromagnetic exchange interaction of two copper ions with a small energy gap between the triplet ground state and the singlet state in this compound.

Finally, at this stage although the B−N bond formation−reaction mechanism is not clear for the present binuclear copper(II) complex, it seems likely that the triphenylborate radical anion reacts with the imidazolate moiety of the ligand instead of reducing the copper(II) ions.

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Supporting Information Available: Tables S1−S4 giving detailed crystallographic and experimental data, complete bond distances and angles, atom positions (with H atoms), and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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