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B−N Bond Formation by the Reaction of (*N*-(3-Methoxysalicylidene)-*N*′-(imidazol-4-ylmethylene)-1,3-propanediamino)copper(II) Perchlorate and Sodium Tetraphenylborate

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The copper(II) complex (*N*-(3-methoxysalicylidene)-*N*′-(imidazol-4-ylmethylene)-1,3-propanediamino)copper(II) perchlorate, [Cu(HL)]ClO$_4$ (**1**), reacts with sodium tetraphenylborate (NaBPh$_4$) in *N*,*N*-dimethylformamide to give an electrically neutral complex exhibiting a B−N bond, [Cu(LBPh$_3$)]·DMF (**2**). The syntheses and the crystal structures of **1**, **2**, and the *N*-methylimidazole adduct of **2**, [Cu(LBPh$_3$)(*N*-MeIm)] (**3**), are reported. Crystal data: **1**, triclinic, $P\bar{1}$, a = 11.842(5) Å, b = 12.074(7) Å, c = 7.000(2) Å, α = 92.35(4)°, β = 96.63(3)°, γ = 115.16(3)°, Z = 2; **2**, triclinic, $P\bar{1}$, a = 16.716(6) Å, b = 18.148(4) Å, c = 12.717(2) Å, α = 106.31(2)°, β = 104.67(3)°, γ = 66.20(3)°, Z = 4; **3**, monoclinic, $P2_1/n$, a = 11.945(8) Å, b = 12.025(9) Å, c = 23.638(4) Å, β = 99.14(3)°, Z = 4. The most striking feature of **2** and **3** is the formation of a B−N bond, in which the boron atom bonds to the nitrogen atom of the imidazolate moiety of the copper(II) complex and to three carbon atoms of the phenyl groups.

Introduction

We have previously reported that a series of copper(II) complexes of quadridentate Schiff base ligands involving an imidazole moiety exhibits a self-assembly process, where the copper(II) complexes have potentially both donor and acceptor abilities in the coordination mode.[1] When the complexes were conditioned in the high pH region, the imidazole proton deprotonates and then a self-assembly reaction is motivated.[1] In the processes, a monomer species with the general formula of [Cu(HL)]ClO$_4$ converts to a self-assembly polymer species exhibiting an infinite helical or zigzag chain structure [Cu(L)]$_n$, where the reverse conversion from [Cu(L)]$_n$ to [Cu(HL)]$^+$ is also available by protonation. During the course of our study, it was noticed that a compound obtained by mixing of the perchlorate salt and sodium tetraphenylborate (NaBPh$_4$) in *N*,*N*-dimethylformamide (DMF) does not show the same self-assembly process. Since it was found that the compound had a unique structure with a B−N bond, [Cu(LBPh$_3$)] (**2**), as shown in Scheme 1, we report herein the synthesis, characterization, and crystal structure of **2**, together with those of the precursor complex [Cu(HL)]ClO$_4$ (**1**) and the *N*-methylimidazole adduct of **2**, [Cu(LBPh$_3$)(*N*-MeIm)] (**3**).

Experimental Section

Materials. All chemicals and solvents used for the synthesis were reagent grade. Reagents used for the physical measurements were of spectroscopic grade. 4-Formylimidazole was prepared according to the literature method.[2]

[Cu(LBPh$_3$)]·DMF (2). Method A. The perchlorate salt of the copper(II) complex [Cu(HL)]ClO$_4$ (**1**) was prepared by a previously reported method.[1c] The perchlorate salt [Cu(HL)]ClO$_4$ and a slight molar ratio excess of NaBPh$_4$ were dissolved in a minimum amount of DMF and the solution was diffused in 2-propanol to give dark green cubic crystals of **2**. Anal. Calcd for $C_{36}H_{38}BN_5O_3Cu$: C, 65.21; H, 5.78; N, 10.56; Cu, 9.58. Found: C, 65.30; H, 5.80; N, 10.51; Cu, 9.62. Mp: 268−270 °C. Λ_M (in DMF): 1.2 S cm^2 mol^{-1}. λ_{max}(nm) (ϵ_{max}, dm^3 mol^{-1} cm^{-1}) (in DMF): 573 (100), (in CH$_2$Cl$_2$): 556 (150), (solid state): 557, 640 (sh). IR (KBr disks, cm^{-1}): ν(C═O), 1680 (s), ν(C═N), 1650 (vs), δ(C−H), 710 (vs monosubstrate benzene).

Safety Note. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and these samples should be handled with great caution.

Method B. Bis(3-(aminopropyl)-3-methoxysalicylideneaminato)nickel(II) was prepared by the method of Elder.[3] The nickel(II) complex (5 mmol) and two equivalents of dimethylglyoxime (10 mmol) were mixed in 50 cm^3 of methanol and the mixture was refluxed for 2 h. After this was cooled to room temperature, red precipitates, (bis(dimethylglyoximato)nickel(II)), were filtered out. To the resulting filtrate was added a solution of 4-formylimidazole (0.96 g, 10 mmol) in 20 cm^3 of methanol. The mixture was warmed in a water bath at 50 °C for 30 min and then cooled to room temperature. To the solution was added a solution of Cu(CH$_3$COO)$_2$·H$_2$O (1.99 g, 10 mmol) in 30 cm^3 of methanol. After this was allowed to stand for several hours, a solution of NaBPh$_4$ (3.42 g, 10 mmol) in 20 cm^3 of methanol was added that immediately precipitated yellowish-green microcrystalline materials. They were collected by suction filtration, washed with methanol and diethyl ether, and then dried in vacuo. The crude product was resolved in a minimum amount of DMF, and the solution was diffused in 2-propanol to give dark green cubic crystals after standing for several days.

[Cu(LBPh$_3$)(*N*-MeIm)] (3). To a solution of complex **2** (0.66 g, 1 mmol) in 10 cm^3 of DMF a solution of *N*-methylimidazole (0.16 g, 2 mmol) in 5 cm^3 of methanol was added. The solution was diffused in 2-propanol to give green cubic crystals after standing for several days. Anal. Calcd for $C_{37}H_{37}BN_6O_2Cu$: C, 66.12; H, 5.55; N, 12.50; Cu, 9.46. Found: C, 65.85; H, 5.63; N, 12.40; Cu, 9.42. Mp: >280 °C dec. Λ_M (in DMF): 1.5 S cm^2 mol^{-1}. λ_{max}(nm) (ϵ_{max}, dm^3 mol^{-1} cm^{-1})

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(1) (a) Matsumoto, N.; Yamashita, S.; Ohyoshi, A.; Kohata S.; Ōkawa, H. *J. Chem. Soc., Dalton Trans.* **1988**, 1943. (b) Matsumoto, N.; Nozaki, T.; Ushio, H.; Motoda, K.; Ohba, M.; Mago, G.; Ōkawa, H. *J. Chem. Soc., Dalton Trans.* **1993**, 2157. (c) Nozaki, T.; Ushio, H.; Mago, G.; Matsumoto, N.; Ōkawa, H.; Yamakawa, Y.; Anno, T.; Nakashima, T.; *J. Chem. Soc., Dalton Trans.* **1994**, 2339. (d) Matsumoto, N.; Akui, T.; Murakami, H.; Kanesaka, J.; Ohyoshi, A.; Ōkawa, H. *J. Chem. Soc., Dalton Trans.* **1988**, 1021.

(2) (a) Totter, J. R.; Darby, W. J. *Org. Synth.* **1955**, *3*, 460. (b) Papadopolulos, E. P.; Jarrar, A.; Issidorides, C. H. *J. Org. Chem.* **1966**, *31*, 615.

(3) Elder, R. C. *Aust. J. Chem.* **1978**, *31*, 35.

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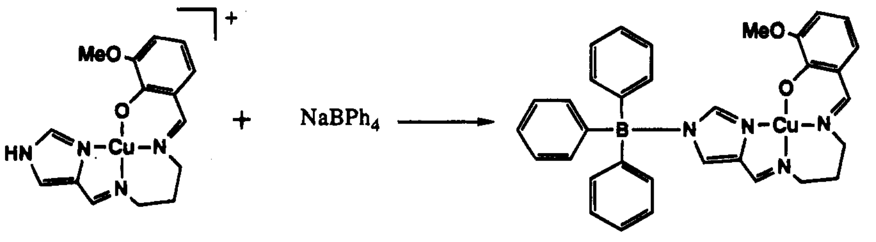
Scheme 1



(1) (2)

(in DMF): 578 (120), (solid state): 620. IR (KBr disks, cm^{-1}): ν(C=N), 1650(s), δ(C−H), 710 (vs monosubstrate benzene).

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Kyushu University. Copper analyses were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Melting points were measured on a Yanagimoto micro melting points apparatus, Model MP-4, and the data were uncorrected. Infrared spectra were measured using KBr disks with a JASCO IR-810 spectrophotometer. Electrical conductivity measurements were carried out on a Denki Kagaku Keiki AOL-10 digital conductometer in *ca.* 1×10^{-3} mol dm^{-3} solutions. Electronic spectra were measured on a Shimadzu MPS-2000 multipurpose recording spectrophotometer. X-Band ESR spectra were recorded on a JEOL JEX-FE3X ESR spectrometer at room and liquid nitrogen temperatures using DPPH (1,1′-diphenyl-2-picrylhydrazyl) as the standard marker. Magnetic susceptibilities were measured using a HOXSAN HSM-D SQUID susceptometer and a Faraday balance in the temperature range 4.2−300 K. Magnetic susceptibilities were calibrated by the use of $(NH_4)_2Mn(SO_4)_2{\cdot}6H_2O$ for the SQUID magnetometer and $[Ni(en)_3]S_2O_3$ for the Faraday balance.[4] Diamagnetic corrections were made with Pascal's constants.[5] Effective magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_A T)^{1/2}$, where χ_A is the magnetic susceptibility per copper.

X-ray Crystal Structural Determination for $[Cu(HL)]ClO_4$ (1), $[Cu(LBPh_3)]{\cdot}DMF$ (2), and $[Cu(LBPh_3)(N\text{-}MeIm)]$ (3). Single crystals suitable for X-ray analysis were obtained by the diffusion method, where the DMF solution is diffused in 2-propanol at room temperature. A crystal was mounted on a glass fiber and coated with epoxy resin. X-ray data were collected using a Rigaku Denki AFC7R four-circle diffractometer with graphite-monochromatized Mo Kα radiation and a 12 kW rotating generator at ambient temperature. The unit cell parameters were determined by 25 reflections in the range of $20° \le 2\theta \le 30°$. Three standard reflections were monitored every 150 reflections and showed good stability. Intensity data were corrected for Lorentz and polarization effects, and an emprical absorption correction based on azimuthal scans was applied. The details of data collection, crystallographic data, and data reduction are summarized in Table 1.

The structure was solved by direct method and refined by a full-matrix least-squares method. Reliability factors were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where the weighting scheme, $w = 1/\sigma^2(|F_o|)$, was used. Neutral atomic scattering factors were taken from the literature.[6] The final difference Fourier syntheses were featureless. The computation was performed using the teXsan crystallographic software package from the Molecular Structure Corp.[7]

Table 1. Crystallographic Data for $[Cu(HL)]ClO_4$ (**1**), $[Cu(LBPh_3)]{\cdot}DMF$ (**2**), and $[Cu(LBPh_3)(N\text{-}MeIm)]$ (**3**)[a]

	1	2	3
formula	$C_{15}H_{17}N_4O_6ClCu$	$C_{36}H_{38}N_5O_3BCu$	$C_{37}H_{37}N_6O_2BCu$
f.w.	448.32	663.08	672.09
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	11.842(5)	16.716(6)	11.945(8)
b, Å	12.074(7)	18.148(4)	12.025(9)
c, Å	7.000(2)	12.717(2)	23.638(4)
α, deg	92.35(4)	106.31(2)	90
β, deg	96.63(3)	104.67(3)	99.14(3)
γ, deg	115.16(3)	66.20(3)	90
V, $Å^3$	895.3(8)	3344(3)	3352(2)
Z	2	4	4
ϱ_{calcd}, g cm^{-3}	1.663	1.317	1.332
F(000)	458	1388	1404
μ, cm^{-1} (Mo Kα)	14.10	6.96	6.94
cryst size, mm^3	0.1 × 0.1 × 0.05	0.3 × 0.4 × 0.4	0.3 × 0.2 × 0.1
no. of data used	1854	7718	3246
R	0.081	0.047	0.075
R_w	0.084	0.043	0.070

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

Results and Discussion

The perchlorate salt, $[Cu(HL)]ClO_4$ (**1**) showed a characteristic IR band due to the N(imidazole)−H(proton) stretching vibration at 3200 cm^{-1}, and a molar electrical conductivity in DMF of 80 S mol^{-1} cm^{-3} is in the expected range for 1:1 electrolytes.[8] Complex **1** exhibits a convertible deprotonation and protonation behavior at the imidazole proton, $n[Cu(HL)]^+ \rightleftharpoons nH^+ + [Cu(L)]_n$, at the $pK_h = log\{[Cu(L)]/([Cu(HL)][OH^-])\}$ of 5.4 in which $[Cu(HL)]^+$ is a monomer species with square planar coordination geometry and $[Cu(L)]_n$ is a polymer species with an infinite zigzag-chain structure bridged by an imidazolate group.[1c] When complex **1** is mixed with $NaBPh_4$ in a solution of DMF and 2-propanol, complex **2** is obtained. Complex **2** showed no N−H band and the molar electrical conductivity measured in DMF was nearly zero. Further, complex **2** showed no self-assembly behavior observed in **1**, while **2** reacts with *N*-methylimidazole to give the adduct **3**. These characterizations suggest that **2** assumes a structure different from **1**.

Structural Descriptions of $[Cu(HL)]ClO_4$ (1), $[Cu(LBPh_3)]{\cdot}DMF$ (2), and $[Cu(LBPh_3)(N\text{-}MeIm)]$ (3). Selected interatomic bond distances and angles with their estimated standard deviations for **1**, **2**, and **3** are given in Table 2.

The molecular structure of **1** with the atom numbering scheme is shown in Figure 1. The complex consists of $[Cu(HL)]^+$ cation and ClO_4^- anion, in which the equatorial coordination sites around the copper(II) ion are occupied by N_3O donor atoms of a quadridentate ligand involving an imidazole moiety. The cation complex and its most neighboring complex related by a symmetry operation (−*x*, −*y*, −*z*) form a dimer structure in out-of-plane fashion with a Cu(1)−O(1)* distance of 2.50(1) Å and a Cu(1)···Cu(1)* distance of 3.280(4) Å, indicating that each copper(II) ion assumes a square pyramidal coordination geometry. This out of-plane binuclear structure has been known for dimeric (*N*, *N*′-ethylenebis(salicylideneaiminato))copper(II) (abbreviated as [Cu(salen)]) and related compounds.[9]

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(4) Gagne, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 6709 .

(5) Boudreaux, E. A.; Mulay, L. N. *Theory and Application of Molecular Paramagnetism*; Wiley, New York, 1976; p 491.

(6) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.

(7) Crystal Structure Analysis Package, Molecular Structure Corp., 1985 and 1992.

(8) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table 2. Relevant Bond Distances (Å) with Their Estimated Standard Deviations in Parentheses for [Cu(HL)]ClO_4 (**1**), [Cu($LBPh_3$)]·DMF (**2**), and [Cu($LBPh_3$)(*N*-MeIm)] (**3**)[a]

	[Cu(HL)]ClO_4 (**1**)		
Cu(1)−O(1)	1.921(9)	Cu(1)−N(2)	2.00(1)
Cu(1)−N(3)	2.05(1)	Cu(1)−N(4)	1.98(1)
Cu(1)−O(1)*	2.50(1)	Cu(1)··Cu(1)*	3.280(4)
	[Cu($LBPh_3$)]·DMF (**2**)		
molecule A		molecule B	
Cu(1)−O(1)	1.914(3)	Cu(2)−O(3)	1.892(3)
Cu(1)−N(2)	1.966(3)	Cu(2)−N(6)	1.964(3)
Cu(1)−N(3)	2.021(3)	Cu(2)−N(7)	2.017(3)
Cu(1)−N(4)	1.950(3)	Cu(2)−N(8)	1.952(3)
N(1)−B(1)	1.609(5)	N(5)−B(2)	1.611(5)
C(16)−B(1)	1.624(6)	C(49)−B(2)	1.634(6)
C(22)−B(1)	1.626(6)	C(55)−B(2)	1.634(6)
C(28)−B(1)	1.628(6)	C(61)−B(2)	1.626(6)
Cu(1)··O(1)*	2.455(3)	Cu(2)··O(3)**	3.911(3)
Cu(1)··Cu(1)*	3.150(1)	Cu(2)··Cu(2)**	3.887(2)
	[Cu($LBPh_3$)(*N*-MeIm)] (**3**)		
Cu(1)−O(1)	1.940(7)	Cu(1)−N(2)	2.054(8)
Cu(1)−N(3)	2.059(8)	Cu(1)−N(4)	2.030(8)
Cu(1)−N(5)	2.388(10)	Cu(1)−Cu(1)*	3.720(3)
N(1)−B(1)	1.59(1)	C(16)−B(1)	1.61(2)
C(22)−B(1)	1.60(2)	C(28)−B(1)	1.64(2)

[a] A single asterisk denotes the symmetry operation −*x*, −*y*, −*z*; **; two asterisks denote −*x* − 1, −*y* − 1, −*z*.

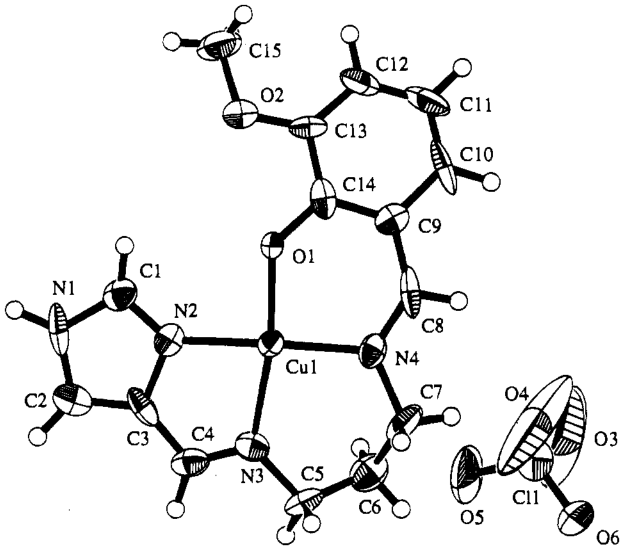

Figure 1. ORTEP drawing of [Cu(HL)]ClO_4 (**1**) showing the atom numbering scheme (the thermal ellipsoids at 50% probability level).

Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 4$, indicating that there are two unique molecules, A and B, in the unit cell. The molecular packing diagram in the unit cell is deposited as supplementary material. An ORTEP drawing of molecule A of **2** with the atom numbering schemes is shown in Figure 2. The most striking feature confirmed by the X-ray analysis is the formation of a boron−nitrogen bond. The boron atom bonds to an imidazolate nitrogen atom of the copper(II) complex and to three carbon atoms of three phenyl groups. The bond distances of B−N are 1.609(5) and 1.611(5) Å for molecules A and B, respectively, which are considerably longer than those of metal complexes with hydrotris(pyrazolyl)borate.[10] The bond distances of B−C(phenyl) observed in molecules A and B are 1.624(6)-1.634(6) Å, which are longer than those of the B−N bonds and shorter than those found for the BPh_4^- anion (average = 1.65 Å).[11] The bond angles of C(phenyl)−B−C(phenyl) are larger than those of C(phenyl)−B−N(imidazolate), where the angles are 111.4(5)−112.7(6) and 105.8(6)−107.9(6)°, respectively.

The crystal consists of two crystallographically unique A and B molecules. Molecule A and its most neighboring molecule A* related by a symmetry operation (−*x*, −*y*, −*z*) form a dimer structure of out-of-plane fashion with a Cu(1)−O(1)* distance of 2.455(3) Å and a Cu(1)··Cu(1)* distance of 3.150(1) Å. On the other hand, molecule B and the symmetry related molecule B** (−*x* − 1, −*y* − 1, −*z*) show a parallel packing with the dihedral angle between two planes defined by N_3O of 0.082° but there is no axial coordination between the two complex molecules, because the distances of Cu(2)··Cu(2)** and Cu(2)··O(3)** are 3.887(2) and 3.911(3) Å, respectively. The coordination geometries around Cu(1) of molecule A and Cu(2) of molecule B can be best described to be five-coordinated square-pyramid and four-coordinated square-planar, respectively.

An ORTEP drawing of **3** is shown in Figure 3. The *N*-methylimidazole coordinates axially to copper(II) ion with the Cu(1)−N(5) bond distance of 2.388(10) Å, giving a square pyramidal coordination environment around the copper(II) ion. The bond distances of Cu−equatorial donor atoms of **3** are longer than the corresponding distances of **2**, due to the axial coordination of *N*-methylimidazole. The parrallel packing between the two neighboring complexes is observed, as similary found for molecule B of **2**, where the Cu··Cu distance is 3.720(3) Å.

The reflectance spectrum of **2** measured on the powdered sample shows two bands at 557 nm and 640 nm (sh), where the former and the latter bands are assignable to the d−d bands of a four-coordinated square planar species and a five-coordinated square-pyramidal species, respectively.[1c] The spectral result agrees well with the result of the X-ray analysis of **2**. The reflectance spectrum of **3** shows a broad d−d band at 620 nm, indicating that the copper(II) ion assumes a five-coordinated square-pyramidal coordination geometry with the axial coordination of *N*-methylimidazole. It should be noted that the electronic spectra of **2** and **3** measured in the *ca.* 1×10^{-3} mol dm^{-3} DMF solutions show d−d band maxima at 573 and 578 nm, respectively, indicating a dissociation of a dimer structure of **2** and that of *N*-methylimidazole of **3** in the solutions.

ESR spectra of powdered samples of **2** and **3** were measured at room and liquid nitrogen temperatures. The ESR spectra showed an axial pattern due to ($S = {}^1/_2$) and several absorptions due to ($S = {}^1/_2 + {}^1/_2 = 1$). The parameters of $S = {}^1/_2$ are 3036 and 3272 G ($g_\perp = 2.09$, $g_\parallel = 2.25$) for **2** and 2972 and 3215 G ($g_\perp = 2.13$, $g_\parallel = 2.30$) for **3**. The parameters of $S = 1$ are 1670, 2564, and 3480 G for **2** and 1661, 2550, and 3377 G for

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(9) (a) Stynes, D. V.; Leznoff, D. B.; Harshani de Silva, D. G. A. *Inorg. Chem.* **1993**, *32*, 3989. (b) Verhage, M.; Hoog Water, D. A.; van Bekkum, H.; Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1982**, 101, 351. (c) Schneider, W. F.; Narula, C. K.; Noth, H.; Bursten B. E. *Inorg. Chem.* **1991**, *30*, 3919. (d) Lewis, J.; Walton, R. A. *J. Chem. Soc. A* **1966**, 1559.

(10) Kitajima, N.; Tamura, N.; Amagai, H.; Fukui, H.; Moro-oka, Y.; Mizutani, Y.; Kitagawa, T.; Mathur, R.; Heerwegh, K.; Reed, C. A.; Randall, C. R.; Que, L.; Tatsumi, K. *J. Am. Chem. Soc.* **1994**, *116*, 9071.

(11) (a) Matsumoto, N.; Ohta, S.; Yashimura, C.; Ohyoshi, A.; Kohata, S.; Ōkawa, H.; Maeda, Y. *J. Chem. Soc., Dalton Trans.* **1985**, 2575. (b) Matsumoto, N.; Akui, T.; Ohyoshi, A.; Ōkawa, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2250. (c) Akui, T.; Ohyoshi, A.; Matsumoto, N.; Ōkawa, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4155. (d) Tōmita, M.; Matsumoto, N.; Akagi, H.; Ōkawa, H.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1989**, 179. (e) Ōkawa, H.; Nishio, J.; Ohba, M.; Tadokoro, M.; Matsumoto, N.; Koikawa, M.; Kida, S.; Fenton, D. E. *Inorg. Chem.* **1993**, *32*, 2949.

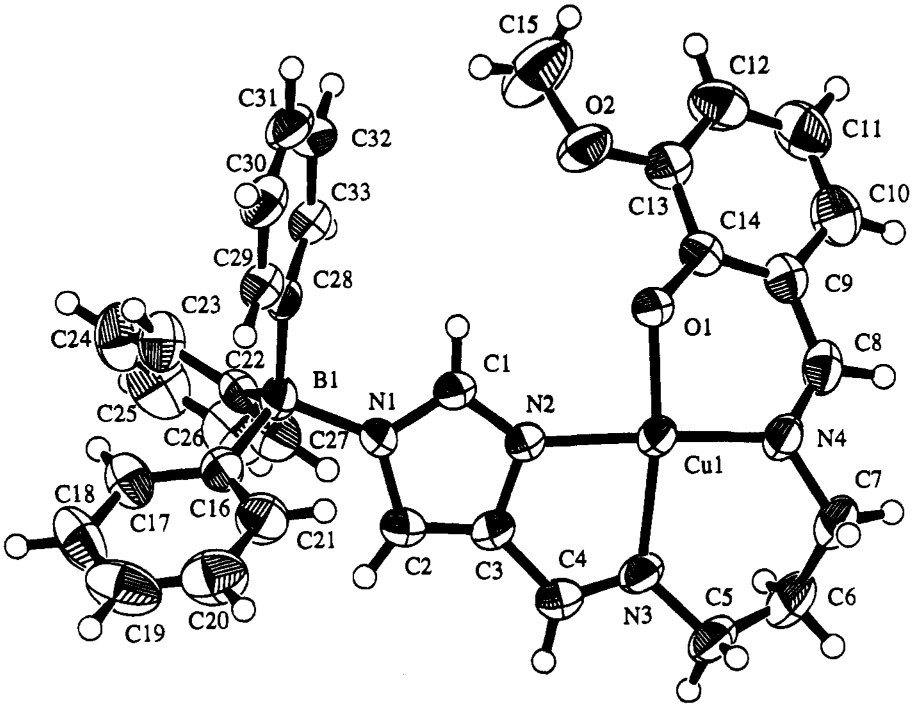

Figure 2. ORTEP drawing of molecule A of [Cu(LBPh$_3$)] (**2**) showing the atom numbering scheme (the thermal ellipsoids at 50% probability level).

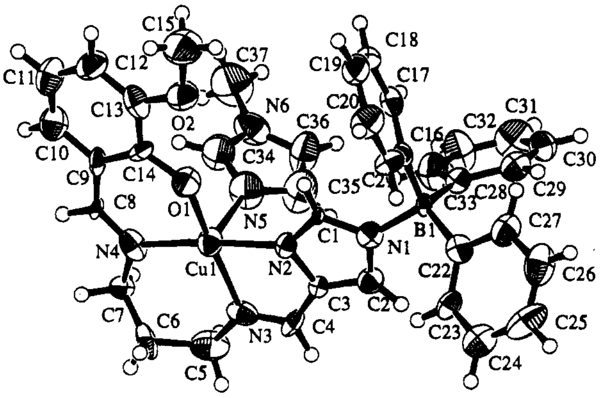

Figure 3. Molecular drawing of [Cu(LBPh$_3$)(NMeIm)] (**3**) showing the atom numbering scheme.

3, respectively, where the half-field absorption that occurs at *ca.* 1600 G is due to the $\Delta M_s = \pm 2$ transition.[12]

The temperature dependence of the magnetic susceptibilities of **1**, **2**, and **3** were measured in the temperature range 4.2–300 K and they nearly obey the Curie law, indicating that the magnetic interaction between two copper(II) ions in the out-of-plane binuclear structure is very weak for all the complexes. When the temperature is lowered, the μ_{eff} values of **1** and **3** decreases slightly and on the other hand that of **2** increases from 1.87 μ_B at 290 K to 1.96 μ_B at 4.4 K. The observed magnetic susceptibilities can be reproduced by the theoretical expression on the basis of the binuclear structures confirmed by the X-ray analyses. The magnetic susceptibilities of **1** and **3** were well reproduced by the Bleaney−Bowers equation[11] (based on the dimer structure), where the best-fit parameters of $g = 2.09$ and $J = -0.5$ cm^{-1} and $g = 2.10$ and $J = -1.1$ cm^{-1} are obtained for **1** and **3**, respectively, indicating a very weak antiferromagnetic interaction. The magnetic susceptibilities of **2** were analyzed using equation (1) with $\varrho = 0.5$ on the basis of the X-ray structure consisting of one dimer and two monomer copper(II) molecules

$$\chi_{A_v} = \frac{Ng^2\beta^2}{kT}\left[\frac{1}{3 + \exp(-2J/kT)}(1 - \varrho) + \frac{\varrho}{4}\right] + N_\alpha \quad (1)$$

The best-fit parameters, $J = +1.2$ cm^{-1} and $g = 2.15$, were obtained, indicating a weak ferromagnetic interaction within the dimer.[13]

It has been reported that a number of metal complexes react with sodium tetraphenylborate (NaBPh$_4$), in which Ph$^-$ formed in a metal-assisted decomposition of BPh$_4^-$ takes part in the reactions such as reduction of the metal ion and nucleophilic attack at the azomethine carbon of the ligand.[14] In these reactions the boron-containing fragment has not been characterized. It has been also reported that potassium dimesityldiphenylborate decomposes to give a phenyl radical and dimesitylphenylborane radical anion under light irradiation (253.7 nm) in protonic solvent.[15] Although the mechanism is not clear for the present complex, it is likely that triphenylborane radical anion reacts with [Cu(HL)]$^+$ cation to produce an electrically neutral speceis **2**. When the B−N bond formed, the electronic structures around the boron atom and the nitrogen atom of **2** satisfy the octet rule. Although B−N bond formation reaction has been known for organic compounds,[16] to our knowledge the present compound is the first metal complex produced by the reaction accompanying B−N bond formation. The B−N bond of complex **2** is rather stable to acid and base. Complex **2** has the acceptor ability to receive a donor atom such as *N*-methylimidazole at the fifth coordination site to give the

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(12) Bleany, B.; Bowers, K. D. *Proc. R. Soc. London, A* **1952**, *214*, 451.

(13) (a) Hall, D.; Waters, T. N. *J. Chem. Soc.* **1960**, 2644. (b) Calvin, M.; Barkelew, C. H. *J. Am. Chem. Soc.* **1946**, *68*, 2267. (c) Carisle, G. O.; Hatfield, W. E. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 633.

(14) (a) Fachinetti, G., Funaioli, T., Zanazzi, F. *J. Chem. Soc., Chem. Commun.* **1988**, 1100. (b) Karlin, K. D.; Cohen, B. I.; Farooq, A.; Liu, S.; Zubieta, *J. Inorg. Chim. Acta*, **1988**, 153, 9. (c) Drew, M. G. B.; Cairns, C.; McFall, S. G.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2020.

(15) Grisdale, P. J.; Babb, B. E.; Doty, J. C.; Regan, T. H.; Maier, D. P. ; Williams, J. L. R. *J. Organomet. Chem.* **1968**, *14*, 63.

(16) (a) Carpenter, J. D.; Ault, B. S. *J. Phys. Chem.* **1991**, 95, 3502. (b) Komorowski, L.; Maringgele, W.; Meller, A.; Niedenzu, K.; Serwatowski, J. *Inorg. Chem.* **1990**, 29, 3845.

adduct but has no donor ability to coordinate to other species becuase of the stable B−N bond. Due to lack of one of the two abilities, this complex does not show a self-assembly reaction.

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Supplementary Material Available: Text describing the structure determinations, complete listings of atomic parameters of non-hydrogen atoms, hydrogen atoms, anisotropic thermal parameters, bond distances and angles, and a packing diagram of **2** (45 pages). Ordering information is given on any current masthead page.

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