Steric Control of the Electronic Ground State in Six-Coordinate Copper(II) Complexes**

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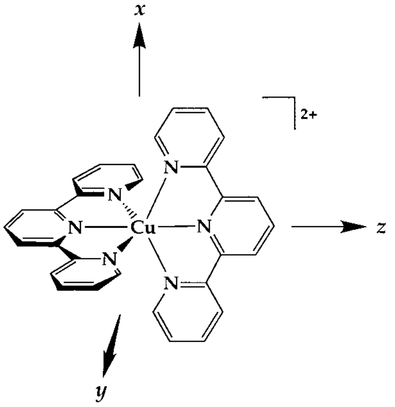
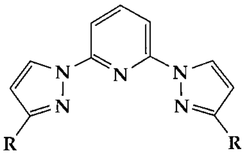
Although the six-coordinate Cu^{II} ion is a paradigm for the Jahn–Teller effect in d-block chemistry, the number of Cu^{II} complexes that exhibit an axially compressed octahedral or rhombic geometry, as characterized by a $\{d_{z^2}\}^1$ electronic ground state, is extremely small.[1, 2] The salts $[Cu(terpy)_2]X_2$ (terpy = 2,2′:6′,2″-terpyridyl; $X = NO_3^-$,[3] PF_6^-,[4] Br^-[5]) were long believed to exhibit this property in the solid state,[1] since this complex has a compressed rhombic geometry along the molecular z axis according to room-temperature crystallography (Scheme 1), whereas its room-temperature powder EPR spectra exhibit an "inverse" $g_\perp > g_\parallel > g_e$ pattern.[5] However, detailed EPR studies have shown that these observations in fact reflect a dynamically disordered axis of elongation about the molecular x and y vectors. Thus, at low temperatures in the solid the Jahn–Teller axis of $[Cu(terpy)_2]X_2$ becomes static in the molecular xy plane (an example of "Jahn–Teller cooperativity"[2]), and the low-temperature EPR spectra of this complex exhibit the more usual $g_\parallel > g_\perp > g_e$ pattern consistent with a $\{d_{x^2-y^2}\}^1$ ground state.[5, 6]



Scheme 1. Molecular axes of $[Cu(terpy)_2]^{2+}$.

The Jahn–Teller distortion of $[Cu(terpy)_2]^{2+}$ depends on the ability of the Cu–N distances along the molecular x and y axes to vary between 2.0 and 2.3 Å.[5] We reasoned that addition of bulky substituents in the position α to the "outer" N atoms in terpy or related tris-imine ligands might prevent close approach of these donors to the metal ion, and thus enforce an axial compression at the Cu^{II} center along the molecular z axis. Rather than 6,6″-disubstituted terpy derivatives, we chose 3,3″-disubstituted 2,6-di(pyrazol-1-yl)pyridines (L^R; Scheme 2) because of their straightforward synthesis.[7] While $[M(L^R)_2]^{2+}$ (M = Ru, R = H) has been prepared,[8] no other complexes of this stoichiometry with other metal ions or L^R ligands have been reported.



Scheme 2. L^R; R = H, Mes.

Ligand L^H was prepared by the literature procedure,[7] while L^{Mes} was synthesized from 3{5}-mesitylpyrazole[9] and 2,6-dibromopyridine by the same methodology. Complexation of various Cu^{II} salts by two equivalents of L^R in $MeNO_2$ followed by crystallization from Et_2O afforded green solids of composition $[Cu(L^R)_2]X_2$ ($L^R = L^H, L^{Mes}$; $X^- = BF_4^-, ClO_4^-$). The UV/Vis spectra of both complexes are typical of six-coordinate Cu^{II},[10] showing one absorption with $\varepsilon_{max} \approx 50\,M^{-1}cm^{-1}$ and no long-wavelength shoulder. In each case the energy of this peak is identical for solutions in MeCN and $MeNO_2$, which suggests that ligand dissociation in these solvents is minimal.

Single-crystal X-ray structures of $[Cu(L^H)_2](BF_4)_2$ and $[Cu(L^{Mes})_2](ClO_4)_2 \cdot 2\,CH_3NO_2$ were determined at 223 and 180 K, respectively. Both complexes exhibit the expected compressed-rhombic stereochemistry (Figures 1 and 2). The Cu–N bond lengths can be grouped into crystallographically distinct short z [N(1)-Cu-N(4)], medium y [N(2)-Cu-N(3)], and long x [N(5)-Cu-N(6)] axes at the copper center. In

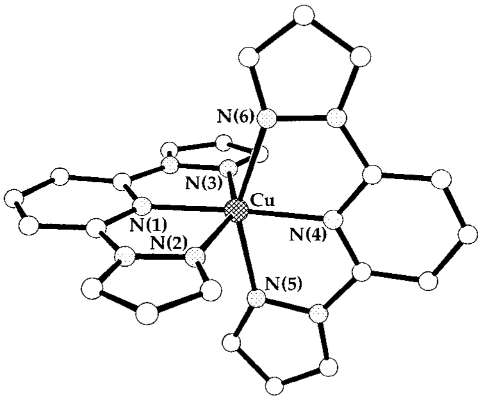


Figure 1. Perspective view of the dication of $[Cu(L^H)_2](BF_4)_2$. For clarity, all hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°]: Cu–N(1) 1.980(5), Cu–N(2) 2.153(7), Cu–N(3) 2.142(7), Cu–N(4) 2.001(6), Cu–N(5) 2.196(8), Cu–N(6) 2.213(8); N(1)-Cu-N(2) 76.8(2), N(1)-Cu-N(3) 76.7(2), N(1)-Cu-N(4) 176.8(4), N(1)-Cu-N(5) 100.0(3), N(1)-Cu-N(6) 107.3(3), N(2)-Cu-N(3) 153.5(2), N(2)-Cu-N(4) 102.7(2), N(2)-Cu-N(5) 93.6(3), N(2)-Cu-N(6) 95.3(3), N(3)-Cu-N(4) 103.7(2), N(3)-Cu-N(5) 90.2(3), N(3)-Cu-N(6) 93.3(3), N(4)-Cu-N(5) 76.8(3), N(4)-Cu-N(6) 75.9(3), N(5)-Cu-N(6) 152.6(2).

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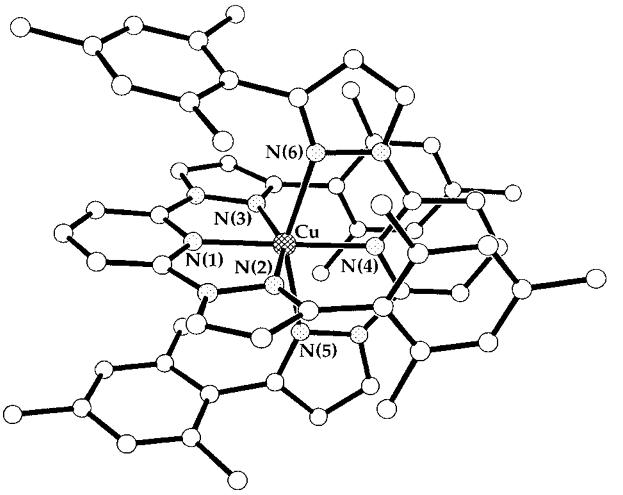

Figure 2. Perspective view of the dication of $[Cu(L^{Mes})_2](ClO_4)_2\cdot 2CH_3NO_2$. For clarity, all hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°]: Cu–N(1) 1.948(6), Cu–N(2) 2.136(6), Cu–N(3) 2.142(6), Cu–N(4) 1.972(6), Cu–N(5) 2.227(6), Cu–N(6) 2.256(6); N(1)-Cu-N(2) 78.3(2), N(1)-Cu-N(3) 78.8(2), N(1)-Cu-N(4) 179.5(2), N(1)-Cu-N(5) 103.9(2), N(1)-Cu-N(6) 102.1(2), N(2)-Cu-N(3) 157.0(2), N(2)-Cu-N(4) 102.0(2), N(2)-Cu-N(5) 92.2(2), N(2)-Cu-N(6) 92.3(2), N(3)-Cu-N(4) 100.9(2), N(3)-Cu-N(5) 95.2(2), N(3)-Cu-N(6) 90.6(2), N(4)-Cu-N(5) 76.5(2), N(4)-Cu-N(6) 77.5(2), N(5)-Cu-N(6) 154.0(2).

comparison with the structure of $[Cu(L^H)_2]^{2+}$, $[Cu(L^{Mes})_2]^{2+}$ has a slightly shorter z and longer x axis, as well as a slightly larger ligand bite angle.

All EPR spectra in this study were recorded at the Q band; simulation data are listed in Table 1. As a powder at 293 K, $[Cu(L^H)_2](BF_4)_2$ shows an axial $g_\perp > g_\parallel > g_e$ pattern, which gains rhombic character as the temperature is lowered. In MeCN at 115 K, the same compound shows a typical $\{d_{x^2-y^2}\}^1$ spectrum.[11] The EPR behavior of this complex in solid and solution phases thus closely resembles that of $[Cu(terpy)_2]^{2+}$ salts.[2, 5, 6] The powder EPR spectra of $[Cu(L^{Mes})_2]X_2$ ($X = BF_4^-$, ClO_4^-) are barely distinguishable and exhibit the rhombic symmetry expected from the three distinct molecular axes detected crystallographically (Figure 3a); these spectra show only small variations with decreasing temperature. The spectrum of this complex in solution at 115 K is axial (Figure 3b) and clearly shows the $g_\perp > g_\parallel \approx g_e$ pattern indicative of an approximate $\{d_{z^2}\}^1$ ground state. The nearly temperature independent g values of $[Cu(L^{Mes})_2]X_2$ as a powder and in frozen solution are consistent with an axially compressed electronic structure of $[Cu(L^{Mes})_2]^{2+}$. The spectra of both $[Cu(L^R)_2]^{2+}$ complexes in MeCN and $MeNO_2$ were indistinguishable.

Table 1. Selected Q-band EPR parameters of $[Cu(L^H)_2](BF_4)_2$ and $[Cu(L^{Mes})_2](ClO_4)_2$.

	T [K]	g_1	g_2	g_3	A_1[a]	A_2[a]	A_3[a]
$[Cu(L^H)_2](BF_4)_2$ (powder)	290	2.190		2.042	–	–	–
$[Cu(L^H)_2](BF_4)_2$ (powder)	115	2.223	2.162	2.042	–	–	–
$[Cu(L^H)_2](BF_4)_2$ (in solution)[b]	115	2.279	2.096	2.053	156	–	–
$[Cu(L^{Mes})_2](ClO_4)_2$ (powder)	290	2.237	2.157	2.017	104	–	94
$[Cu(L^{Mes})_2](ClO_4)_2$ (powder)	115	2.248	2.145	2.015	110	–	94
$[Cu(L^{Mes})_2](ClO_4)_2$ (in solution)[b]	115	2.200		2.007		77	97

[a] Hyperfine coupling constants to $^{63,65}Cu$ [$10^{-4}cm^{-1}$]. [b] Spectrum in MeCN/toluene (10/1).

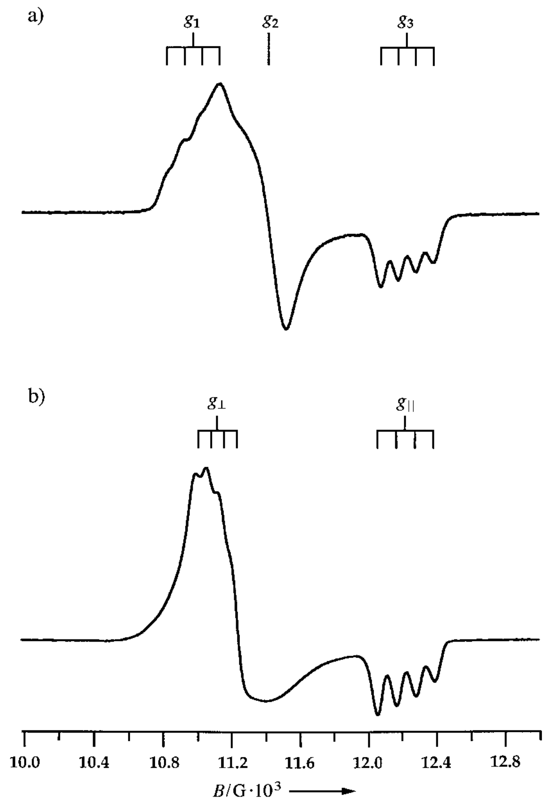

Figure 3. Q-band EPR spectra of $[Cu(L^{Mes})_2](ClO_4)_2$ as a powder at 290 K (a) and in MeCN/toluene (10/1) at 115 K (b).

To conclude, we have shown that by a simple ligand substitution an unprecedented change in electronic ground state can be enforced onto a six-coordinate Cu^{II} center, from the usual $\{d_{x^2-y^2}\}^1$ structure to a $\{d_{z^2}\}^1$ form. This effect derives from steric interactions within the molecules and is thus an intrinsic molecular property rather than simply a solid-state phenomenon. In light of this result, the similarity of the solution d–d spectra of $[Cu(L^H)_2]^{2+}$ ($\tilde{\nu}_{max} = 14.3\times 10^3\,cm^{-1}$) and $[Cu(L^{Mes})_2]^{2+}$ ($\tilde{\nu}_{max} = 14.4\times 10^3\,cm^{-1}$) is striking; this implies that, despite their different ground states, the Cu^{II} ions in these two complexes experience almost identical ligand fields. Full characterization of the electronic structures of these complexes and studies of the coordination chemistry of L^{Mes} and related ligands with other metals are in progress.

Experimental Section

L^{Mes}: To a solution of 3{5}-mesitylpyrazole[9] (11.8 g, 0.064 mol) in diglyme (80 mL) under N_2 was added KH (2.6 g, 0.064 mol), and the mixture was stirred at room temperature for 2 h. 2,6-Dibromopyridine (7.5 g, 0.032 mol) was then added, and the mixture stirred at 130 °C for 5 d. After cooling, addition of an equal volume of water afforded a cream precipitate, which was recrystallized from THF to give white needles (7.0 g). ^1H NMR (250.1 MHz, $CDCl_3$): $\delta = 8.67$ (d, $J = 2.6$ Hz, 2H), 7.87 (pseudo t, $J = 3.4$ Hz, 3H), 6.97 (s, 4H), 6.44 (d, $J = 2.6$ Hz, 2H), 2.34 (s, 12H), 2.21 (s, 6H); MS (EI): m/z: 448 $[M+H]^+$; elemental analysis calcd for $C_{29}H_{29}N_5$: C 77.8, H 6.53, N 15.6; found: C 77.3, H 6.65, N 15.4.

$[Cu(L^H)_2](BF_4)_2$: MS (FAB): m/z: 485 $[^{63}Cu(L^H)_2]^+$, 274 $[^{63}Cu(L^H)]^+$; elemental analysis calcd for $C_{22}H_{18}B_2CuF_8N_{10}$: C 40.1, H 2.75, N 21.2; found: C 39.6, H 2.74, N 20.8; UV/Vis (MeCN): $\tilde{\nu}_{max}$ $[10^3 cm^{-1}]$ (ε_{max} $[M^{-1} cm^{-1}]$) = 14.3 (58), 24.4 (105), 32.8 (27700), 36.7 (35100), 37.7(31900), 40.2 (44700).

$[Cu(L^{Mes})_2](BF_4)_2$: MS (FAB): m/z: 958 $[^{63}Cu(L^{Mes})_2]^+$, 510 $[^{63}Cu(L^{Mes})]^+$; elemental analysis calcd for $C_{58}H_{58}B_2CuF_8N_{10}$: C 61.5, H 5.16, N 12.4; found: C 61.3, H 5.17, N 12.3; UV/Vis (MeCN): $\tilde{\nu}_{max}$ $[10^3 cm^{-1}]$ (ε_{max} $[M^{-1} cm^{-1}]$) = 14.4 (46), 24.0 (sh), 29.8 (25200), 30.6 (sh), 35.5 (sh), 36.6 (31100), 45.4 (sh).

$[Cu(L^{Mes})_2](ClO_4)_2$: elemental analysis calcd for $C_{58}H_{58}Cl_2CuN_{10}O_8$: C 60.2, H 5.05, N 12.1; found: C 59.4, H 5.03, N 11.9.

Crystal data for $[Cu(L^H)_2](BF_4)_2$: $C_{22}H_{18}B_2CuF_8N_{10}$, crystal dimensions 0.50 × 0.50 × 0.30 mm, monoclinic, space group $P2_1$ (no. 4), $a = 8.4555(13)$, $b = 8.531(2)$, $c = 18.828(5)$ Å, $\beta = 96.639(13)°$; $V = 1349.0(5)$ Å^3, $\rho_{calcd} = 1.624$ g cm^{-3}; Siemens P4 diffractometer, $4 \leq 2\theta \leq 50°$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\theta/2\theta$ scans, $T = 223(2)$ K; of 3515 measured reflections, 2893 were independent and 2000 were observed with $I > 2\sigma(I)$, $-10 \leq h \leq 1$, $-1 \leq k \leq 10$, $-22 \leq l \leq 22$; $R = 0.048$, $wR = 0.129$, GOF = 0.972 for 388 parameters, Flack parameter = $-0.02(3)$, $\Delta\rho_{max} = 0.59$ e Å^{-3}. Crystal data for $[Cu(L^{Mes})_2](ClO_4)_2 \cdot 2CH_3NO_2$: $C_{60}H_{64}Cl_2CuN_{12}O_{12}$, crystal dimensions 0.30 × 0.25 × 0.25 mm, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.048(4)$, $b = 19.808(8)$, $c = 25.36(2)$ Å, $\beta = 99.92(4)°$; $V = 5963(5)$ Å^3, $\rho_{calcd} = 1.426$ g cm^{-3}; Rigaku AFC7R diffractometer, $5 \leq 2\theta \leq 50°$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $\omega/2\theta$ scans, $T = 180(2)$ K; of 12975 measured reflections, 10518 were independent and 6041 were observed with $I > 2\sigma(I)$, $0 \leq h \leq 14$, $0 \leq k \leq 23$, $-30 \leq l \leq 29$; $R = 0.083$, $wR = 0.309$, GOF = 1.040 for 784 parameters, $\Delta\rho_{max} = 1.10$ e Å^{-3}. The structures were solved by direct methods (SHELXTL Plus[12]) and developed by least-squares refinement against $|F^2|$ (SHELXL93[13]). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101277. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Enantioselective Ring Opening of Epoxides with 4-Methoxyphenol Catalyzed by Gallium Heterobimetallic Complexes: An Efficient Method for the Synthesis of Optically Active 1,2-Diol Monoethers**

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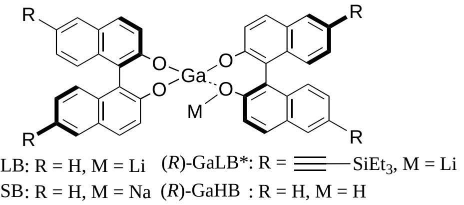
The enantioselective ring opening of achiral epoxides by nucleophilic addition is an attractive method, which is invaluable in asymmetric synthesis.[1] We reported recently an asymmetric ring opening reaction of epoxides with *t*BuSH that is catalyzed by a Ga-Li-bis(binaphthoxide) complex (GaLB) in the presence of 4-Å molecular sieves (Scheme 1).[2] The high enantioselectivity of these reactions prompted us to investigate the possible use of other nucleophiles. Oxygen nucleophiles are interesting candidates since their reaction with achiral epoxides provides an effective route to valuable chiral building blocks such as 1,2-diol derivatives.[3] Quite recently Jacobsen et al. reported the enantioselective ring opening of symmetrical epoxides with carboxylic acids, and an efficient kinetic resolution of racemic terminal epoxides with water by using a (salen)Co^{II} catalyst (salen = *N,N'*-bis(salicylidene)ethylenediamine dianion).[4] However, this type of reaction has not been realized so far with alcohols or phenols. Herein we report the development of a catalytic enantioselective ring opening of epoxides with 4-methoxyphenol by utilizing gallium heterobimetallic complexes.



Scheme 1. Proposed structures of Ga-M-bis(binaphthoxide) (GaMB) and of Ga-Li-bis((6,6′-(triethylsilyl)-ethynyl)binaphthoxide) (GaLB*).

Hydroxyarene derivatives, such as 4-chlorophenol, 2,4-dinitrophenol, and 4-methoxyphenol, were first examined as nucleophiles for the epoxide opening reaction [Eq. (1)]

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