DOI: 10.1002/ange.200603127

Diamagnetic–Paramagnetic Conversion of Tris(2-pyridylthio)methylcopper(III) through a Structural Change from Trigonal Bipyramidal to Octahedral[**]

Ryoko Santo, Riichi Miyamoto, Rika Tanaka, Takanori Nishioka, Kazunobu Sato, Kazuo Toyota, Makoto Obata, Shigenobu Yano, Isamu Kinoshita,[*] Akio Ichimura,[*] and Takeji Takui[*]

The coordination chemistry of copper(III) is of great importance for the understanding of dioxygen cleavage in enzymatic systems[1] and allyl cross-coupling reactions.[2] However,

---

[*] R. Santo, R. Miyamoto, Dr. R. Tanaka, Dr. T. Nishioka,
Prof. Dr. K. Sato, Dr. K. Toyota, Prof. Dr. I. Kinoshita,
Prof. Dr. A. Ichimura, Prof. Dr. T. Takui
Departments of Chemistry and Material Science
Graduate School of Science
Osaka City University
3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, 558-8585 (Japan)
Fax: (+81) 6-6605-2553
E-mail: isamu@sci.osaka-cu.ac.jp
ichimura@sci.osaka-cu.ac.jp
takui@sci.osaka-cu.ac.jp

Dr. M. Obata, Prof. Dr. S. Yano
Division of Material Science
Graduate School of Human Culture
Nara Women's University
Kitauoyanishimachi, Nara, 630-8506 (Japan)

[**] This work was supported financially by a Sasagawa Scientific Research Grant from the Japan Science Society and Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (no. 18350033 and area no. 769, no. 15087209). The X-ray absorption spectral study was performed with the approval of the Photon Factory Program Advisory Committee (proposal no. 2004G290).

Supporting Information for this article is available on the WWW under http://www.angewandte.org or from the author.

there are still only a few examples of structurally characterized Cu^{III} complexes,[3] most of which have a square-planar structure. The Cu^{III} state is stabilized by strong coordinating ligands, and its complexes have been isolated as carboxylates,[4] thiolates,[5] deprotonated amides,[6] carbamates,[7] and N-confused porphyrins.[8] The Cu–C(sp^2) bonds in the N-confused porphyrins are stabilized by the π-delocalization effect in the porphyrin ring aided by protonation–deprotonation of the peripheral nitrogen atoms.[8] Nonplanar Cu^{III} complexes are rare, and only a few structures have been reported,[3] namely square-pyramidal [Cu(PhCO$_2$)$_2$(pyridine)$_2$Cl][9] and an octahedral moiety in a Co^{III}Cu^{III}Co^{III} heterometallic cluster bridged by 1,4,7-tris(4-*tert*-butyl-2-sulfidobenzyl)-1,4,7-triazacyclononane.[10]

Herein, we report the synthesis and electronic properties of a Cu^{III} complex with a trigonal-bipyramidal (tbp) structure. This is the first report of a tbp Cu^{III} complex that has been structurally and spectroscopically well defined. We also report the diamagnetic–paramagnetic conversion of the Cu^{III} complex which accompanies a change from a trigonal-bipyramidal to an octahedral structure.

We have reported the complexes [Cu^{II}(tptm)X] (tptm = tris(2-pyridylthio)methanide; X = F, Cl, Br, I), which have a novel Cu^{II}–C(sp^3) bond and a tbp structure.[11] These complexes show a highly reversible one-electron oxidation process at around +0.1 V versus the redox potential of ferrocenium/ferrocene, $E^{\circ\prime}$(Fc$^+$/Fc), in CH$_2$Cl$_2$.[11a] These electrochemical results suggested that the one-electron-oxidized complexes retain their tbp structures in the Cu^{III} state, as predicted by density functional theory (DFT) calculations.[11a] The oxidation of [Cu^{II}(tptm)Cl] (**1**) with one equivalent of [Ce^{IV}(NH$_4$)$_2$(NO$_3$)$_6$] in the presence of KPF$_6$ produces the stable complex [Cu^{III}(tptm)Cl]PF$_6$ (**2**-PF$_6$), which was crystallized from CH$_2$Cl$_2$/cyclohexane. The crystal structure of this complex is shown in Figure 1. The asymmetric unit of **2**-PF$_6$ contains an independent complex cation. There are four independent complex molecules in the asymmetric unit of the crystal of **1**. These have a similar structure, with only small deviations of the bond parameters due to the crystal packing (See Supporting Information for selected bond lengths and angles).[12] Both complexes **1** and **2** have a tbp geometry with relatively little distortion. The Cu–Cl bond lengths in **2** are 0.05–0.06 Å shorter than those in **1**. The Cu–N bond lengths also shrink, from 2.074(7)–2.142(7) Å in **1** to 2.028(3)–2.074(3) Å in **2**, upon oxidation. Although the Cu–C bond lengths in **1** and **2** are identical within the experimental error (2.005(9)–2.020(7) Å and 2.038(4) Å respectively), complex **2** has shorter Cu–Cl and Cu–N bonds than those in **1** owing to the smaller ionic radius of the copper ion in **2**. These results suggest that complex **2** contains a copper(III) ion rather than an oxidized ligand moiety. The experimental bond lengths around the Cu atom could be reproduced by DFT calculations.[13]

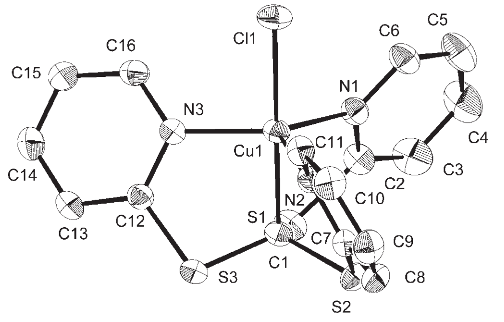

Figure 1. ORTEP drawing of **2** (thermal ellipsoids set at 50% probability). Selected bond lengths and angles are given in the Supporting Information.

The electronic spectrum of **1** in CH$_2$Cl$_2$ has two absorption maxima at 385 and 529 nm ($\varepsilon = 1.98\times10^3$ and 1.46×10^3 M^{-1}cm^{-1}), while the spectrum of **2** has three maxima at 351, 463, and 550 nm ($\varepsilon = 2.52\times10^3$, 4.37×10^3, and 5.24×10^3 M^{-1}cm^{-1}; Figure 2). The molar absorption coefficients of **2** are larger than those of **1** in this region because of the presence of the vacant d$_{z^2}$ orbital of the Cu^{III} atom, which accepts charge from the ligands. This result also suggests that complex **2** contains Cu^{III} (see Supporting Information).[14]

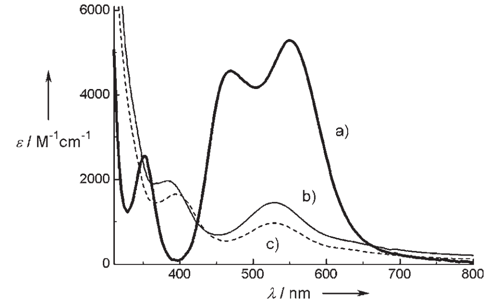

Figure 2. UV/Vis spectra of **2**-PF$_6$ (a), **1** (b), and **3** (c) recorded at room temperature in CH$_2$Cl$_2$. Spectrum (c) is obtained from a solution of **2** treated with an excess of chloride ions.

Metal K-edge X-ray absorption near-edge spectra were measured for the copper in **1** and **2**-PF$_6$. As shown in Figure 3, the energy in **2** is 8994.6 eV, which is 1.3 eV higher than that in **1**. This result supports the proposed metal-centered one-electron oxidation of **1** to **2**. Such an energy difference between the Cu^{II} and Cu^{III} states and the spectral shape resemble those of the octahedral Cu^{II} and Cu^{III} complexes reported by Krebs et al.[15]

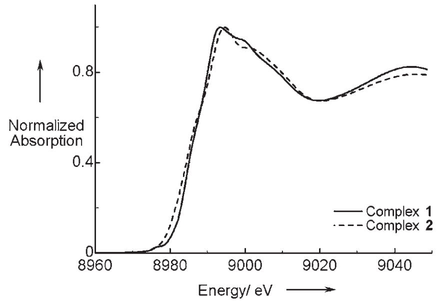

Figure 3. Metal K-edge X-ray absorption spectra of **1** and **2**-PF$_6$.

The ^{1}H NMR spectrum of **2** (Figure 4) shows well-resolved signals for the protons of the pyridine rings and

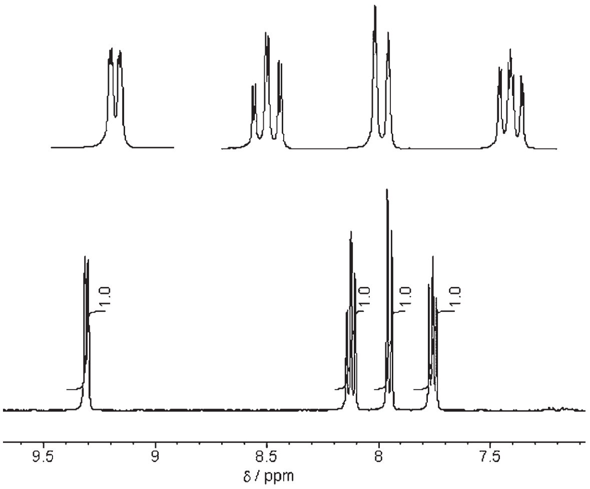

Figure 4. ^{1}H NMR spectra of **2** in CD_2Cl_2 and expansions of the signals. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.76$ (3H, $^3J = 7.6$, 5.6, $^4J \approx 0.9$ Hz; H5), 7.95 (3H, $^3J = 8.1$, $^4J = 0.9$ Hz; H3), 8.12 (3H, $^3J = 7.6$, 8.1, $^4J \approx 1.0$ Hz; H4), 9.31 ppm (3H, $^3J = 5.6$, $^4J \approx 0.9$ Hz; H6) H3–H6 are on C3–C6 (Figure 1), respectively.

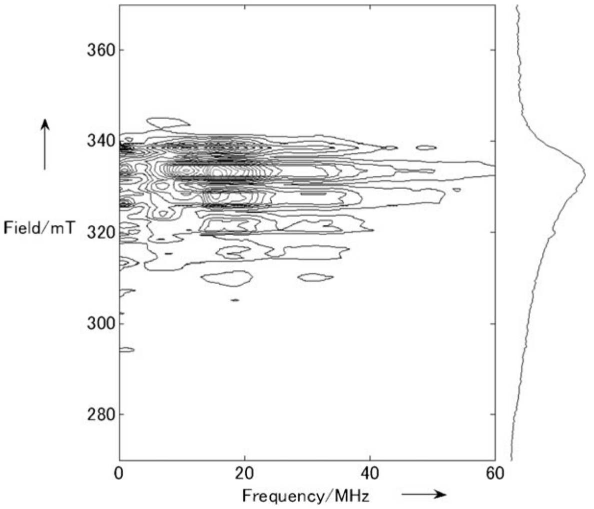

Figure 5. 2D-ESTN contour plot of **3** (that is, of a solution of **2** in CH_2Cl_2 containing one equivalent of chloride ions) recorded at 4 K. On the right is an electron-spin-echo-detected ESR spectrum.

signals for the pyridine carbon atoms are seen in the ^{13}C NMR spectra. The ^{1}H NMR spectrum, which shows an almost complete set of $^3J_{H,H}$ to $^4J_{H,H}$ couplings, demonstrates the diamagnetism of complex **2**. In the ^{13}C NMR spectrum, the signal of the carbon atom connected to copper is missing owing to the large quadrupole moment of the copper ion. The addition of chloride ions to the probe causes a significant broadening of the signals and a change in the chemical shifts. Thus, in the presence of one equivalent of chloride ions all the signals of the protons of the pyridine rings disappear. Such a remarkable change indicates that the addition of a chloride ion to complex **2** produces the paramagnetic Cu^{III} complex [Cu(tptm)Cl$_2$] (**3**) with an octahedral geometry.[16] The absorption spectrum of **2** also changes upon addition of chloride ions: with increasing concentration of chloride ion the absorbance between 450 and 800 nm decreases in intensity. Figure 2c shows the spectrum of **3** which is obtained from a solution of **2** treated with an excess of chloride ions.[17]

To identify the paramagnetic Cu^{III} species we measured the pulse-ESR-based two-dimensional electron spin transient nutation (2D-ESTN) spectrum[18] of a rigid-glass sample containing both **2** and one equivalent of chloride ions at 4 K.[18c–e] 2D-ESTN spectroscopy gives unequivocal information on the electron-spin multiplicity of paramagnetic entities, even in non-oriented media.[18] The contour plot (Figure 5) shows two nutation peaks (10.8 and 15.5 MHz) corresponding, respectively, to spin-doublet ($S = 1/2$) and spin-triplet ($S = 1$) entities in the ground state with the spin-triplet dominating in the glass sample. The ratio of the two peak-frequencies ($15.5/10.8 = 1.45$) agrees with the theoretical one ($2^{1/2}$ to the first order of the perturbation theory for the ESR-allowed transition $Ms = 0$ to $Ms = \pm 1$). Thus, we can unequivocally conclude that **2** reacts with a chloride ion to produce a ground-state triplet complex with a small g-anisotropy, which suggests a highly symmetric molecular structure, such as a pseudo-octahedron. The DFT calculations predict the possible occurrence of an octahedral Cu^{III} complex in the triplet ground-state with a tptm ligand,[19] as described below. The 2D-ESTN spectrum also shows that the fine-structure parameters of the triplet-state complex **3** are small, thus indicating a minimal departure from complete octahedral symmetry at the copper site of **3**.

The ^{1}H ENDOR spectrum of the ESR sample of **2** with one equivalent of chloride ions showed signals arising from the protons of the ligands, that is, the three pyridine rings (See Figure S1 and Tables S3 and S4 in the Supporting Information). The spin-density distribution estimated from the ENDOR measurements is consistent with that predicted by the DFT calculations with the assumed octahedral structure for **3** in the triplet ground-state ($S = 1$; Supporting Information Tables S3 and S4).[16,20] The g-values calculated for the triplet-state octahedral structure are 2.0413, 2.0513, and 2.0598, which are close to that observed (2.0899) for to the strong central peak (see the electron-spin-echo detected ESR spectrum in Figure 5).[21] All the ESR/ENDOR-based data and the DFT calculations safely exclude the possible occurrence of a square-pyramidal structure for **3** in the triplet ground-state. The minority spin-doublet species corresponding to the nutation peak at 10.8 MHz is due to the products of the disproportionation reaction, namely complex **1** and the further oxidized product.

In conclusion, the unique coordination between Cu and C produces a stable copper complex in the $+3$ oxidation state with a tbp structure. The structural and spectroscopic data for **2** unambiguously indicate that complex **2** is a diamagnetic copper(III) complex with a tbp structure. Complex **2** reacts with an additional chloride ion to produce a paramagnetic octahedral complex **3** with a triplet ground-state. Complete analysis of the products of further electrode oxidation of the Cu^{III} complex in the presence of chloride ions and investigation of the properties of the paramagnetic Cu^{III} species by cw-ENDOR spectroscopy are underway.

Experimental Section

Complex **1** was synthesized as reported previously.[11b] Green-black crystals of **1** were grown from a CH_2Cl_2 solution layered with hexane. It crystallizes in the monoclinic system, space group $P2_1/n$, with $a=15.2610(4)$, $b=8.7545(2)$, $c=54.6327(12)$ Å, $\beta=91.7111(9)°$, and $Z=16$ ($R_1=0.0774$, $wR_2=0.1556$).

2-$PF_6\cdot CH_2Cl_2$: Complex **1** (20.1 mg) and cerium(IV) ammonium nitrate (29.5 mg) were mixed in the presence of KPF_6 (9.9 mg) in acetonitrile. The solvent was evaporated, the crystals obtained were redissolved in CH_2Cl_2, and the solution purified by filtration. Reddish-black crystals of **2**-PF_6 were obtained from a CH_2Cl_2 solution layered with cyclohexane. The absorption spectrum of **2**-PF_6 agrees with that of the product obtained from electrochemical oxidation of **1**. Elemental analysis (%) calcd for $C_{17}H_{14}Cl_3CuF_6N_3PS_3$: C 30.41, H 2.10, N 6.26; found: C 30.65, H 2.04, N 6.35. ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta=124, 126, 142, 154, 162$ ppm. **2**-$PF_6\cdot CH_2Cl_2$ crystallized in the monoclinic system, space group $P2_1/c$, with $a=10.910(2)$, $b=19.638(4)$, $c=11.910(2)$ Å, $\beta=94.677(5)°$, and $Z=4$ ($R_1=0.0624$, $wR_2=0.1040$).

Received: August 2, 2006

Keywords: copper · density functional calculations · electrochemistry · N ligands · oxidation

---

[1] a) J. A. Halfen, S. Mahapatra, E. C. Wilkinson, S. Kaderli, V. G. Young, Jr., L. Que, Jr., A. D. Zuberbühler, W. B. Tolman, *Science* **1996**, *271*, 1397–1400; b) H. Hayashi, S. Fujinami, S. Nagatomo, S. Ogo, *J. Am. Chem. Soc.* **2000**, *122*, 2124–2125; c) K. Yoshizawa, N. Kihara, T. Kamachi, Y. Shiota, *Inorg. Chem.* **2006**, *45*, 3034–3041.

[2] A. S. E. Karlstöm, J. Bäckvall, *Chem. Eur. J.* **2001**, *7*, 1981–1989.

[3] a) M. Melnik, M. Kabesova, *J. Coord. Chem.* **2000**, *50*, 323–338; b) T. V. Popova, N. V. Aksenova, *Russ. J. Coord. Chem.* **2003**, *29*, 743–765.

[4] L. L. Diaddario, W. R. Robinson, D. W. Margerum, *Inorg. Chem.* **1983**, *22*, 1021–1025.

[5] J. Hanss, H.-J. Krüger, *Angew. Chem.* **1996**, *108*, 2989–2991; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2827–2830.

[6] a) J. S. Rybka, J. L. Kurtz, T. A. Neubecker, D. W. Margerum, *Inorg. Chem.* **1980**, *19*, 2791–2796; b) F. C. Anson, T. J. Collins, T. G. Richmond, B. D. Santarsiero, J. E. Toth, B. G. R. T. Treco, *J. Am. Chem. Soc.* **1987**, *109*, 2974–2979; c) R. Ruiz, C. Surville-Barland, A. Aukauloo, E. Anzolabehere-Mallart, Y. Journaux, J. Cano, M. C. Muñoz, *J. Chem. Soc. Dalton Trans.* **1997**, 745–751; d) J. Hanss, A. Beckmann, H. J. Krüger, *Eur. J. Inorg. Chem.* **1999**, 163–172.

[7] M. A. Willert-Porada, D. J. Burton, N. C. Baenziger, *J. Chem. Soc. Chem. Commun.* **1989**, 1633–1634.

[8] a) H. Maeda, Y. Ishikawa, T. Matsuda, A. Osuka, H. Furuta, *J. Am. Chem. Soc.* **2003**, *125*, 11822–11823; b) H. Maeda, A. Osuka, H. Furuta, *J. Am. Chem. Soc.* **2003**, *125*, 15690–15691.

[9] G. Speier, V. Fülöp, *J. Chem. Soc. Chem. Commun.* **1990**, 905–906.

[10] C. Krebs, T. Glaser, E. Bill, T. Weyhermüller, W. Meyer-Klaucke, K. Wieghardt, *Angew. Chem.* **1999**, *111*, 370–372; *Angew. Chem. Int. Ed.* **1999**, *38*, 359–361.

[11] a) I. Kinoshita, L. J. Wright, S. Kubo, K. Kimura, A. Sakata, T. Yano, R. Miyamoto, T. Nishioka, K. Isobe, *Dalton Trans.* **2003**, 1993–2003; b) R. Miyamoto, R. Santo, T. Matsushita, T. Nishioka, A. Ichimura, Y. Teki, I. Kinoshita, *Dalton Trans.* **2005**, 3179–3186; c) R. Miyamoto, R. T. Hamazawa, M. Hirotsu, T. Nishioka, I. Kinoshita, L. J. Wright, *Chem. Commun.* **2005**, 4047–4049.

[12] The axial bond angles Cl−Cu−C_{ax} are close to 180° for both oxidation states (i.e. in **1** and **2**). The N−Cu−N angles for **1** are in the range 106.2(2)–131.5(2)° and these values vary more widely than those found in **2**, which are in the range 114.88(13)–124.32(13)°. The copper atom in **2** is located 0.2187(17) Å out of the trigonal plane formed by the three nitrogen atoms of pyridine units in the direction of the chloride ligand.

[13] The electronic configurations for complexes **1** and **2** were calculated by DFT methods (B3LYP) with the 6-31g(d) basis set using the Gaussian 03 program package. Gaussian03 (Revision B.05): M. J. Frisch et al., see Supporting Information. See also reference [11b].

[14] The calculation reproduces the tbp structure and the electronic transition of **2** (TD method).

[15] Krebs et al. have also reported the Cu K-edge spectrum of a paramagnetic octahedral Cu^{III} complex. The energy of the Cu^{III} complex is higher than that of the Cu^{II} complex by 0.7 eV. See reference [10].

[16] The calculation of the expected octahedral structure for **3** was optimized and the paramagnetic data was also obtained. The DFT calculation of the octahedral Cu^{III} complex was performed at the B3LYP level of theory using the Gaussian 03 program package.[13] Selected calculated bond lengths and angles for **3** are also listed in the Supporting Information, Table S3. An unrestricted DFT calculation of **3** ($S=1$) with the TZ2P basis set was carried out to estimate magnetic parameters, such as the hyperfine interaction terms. A VWN density functional was used as the local density approximation with Becke and Perdew functionals as generalized gradient approximations. See Table S4 in the Supporting Information for the hyperfine terms.

[17] Spectral data of **3** were obtained in CH_2Cl_2 solutions of **2** containing an excess of chloride ions (29 mM tetrabutylammonium chloride). The electronic spectrum of **3** has two absorption maxima at 396 and 527 nm ($\varepsilon_{max}=1.6\times10^3$ and 9.7×10^2 $M^{-1}cm^{-1}$, respectively).

[18] a) J. Isoya, H. Kanda, J. R. Norris, J. Tang, M. K. Bowman, *Phys. Rev. B* **1990**, *41*, 3905–3913; b) A. V. Astashkin, A. Schweiger, *Chem. Phys. Lett.* **1990**, *174*, 595–602; c) K. Sato, D. Shiomi, T. Takui, K. Itoh, T. Kaneko, E. Tsuchida, H. Nishide, *J. Spectrosc. Soc. Jpn.* **1994**, *43*, 280–291; d) K. Sato, M. Yano, M. Furuichi, D. Shiomi, T. Takui, K. Abe, K. Itoh, A. Higuchi, K. Katsuma, Y. Shirota, *J. Am. Chem. Soc.* **1997**, *119*, 6607–6613; e) H. Tomioka, M. Hattori, K. Hirai, K. Sato, D. Shiomi, T. Takui, K. Itoh, *J. Am. Chem. Soc.* **1998**, *120*, 1106–1107.

[19] A bromide-bridged dinuclear Ni^{II} dimer complex with a tptm ligand has an octahedral geometry, as determined crystallographically (K. Kitano, R. Tanaka, N. Kuwamura, R. Santo, R. Miyamoto, T. Nishioka, A. Ichimura, I. Kinoshita, unpublished data).

[20] a) G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. F. Guerra, E. J. Baerends, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931–967; b) C. F. Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391–403; c) ADF2006.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands.

[21] S. Patchkovskii, T. Ziegler, *J. Phys. Chem. A* **2001**, *105*, 5490–5497.