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A Triangular Mixed-Valent Cu^{II}Cu^{I}Cu^{I} Cluster Supported by the Tripod Ligand 2-Quinolyl-2,2′-dipyrrolylmethane**

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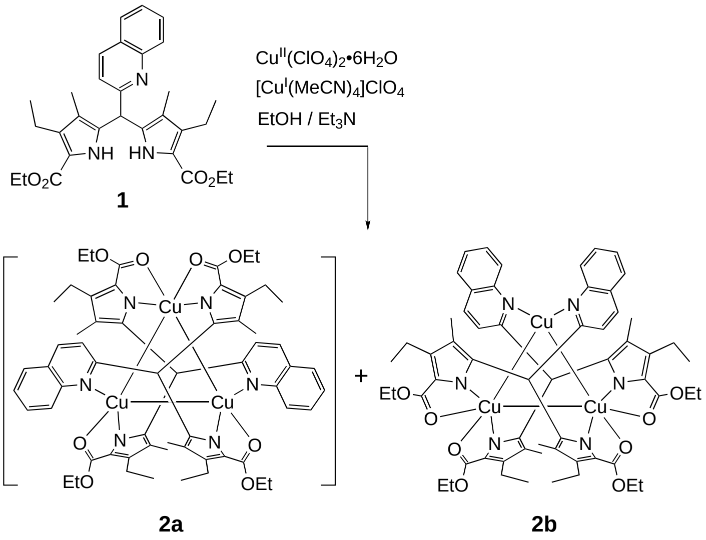
Setsuo Muraoka, Hong-wei Huang, and
Takeshi Sakurai

Trinuclear copper complexes are attracting increasing attention as models for the metal sites of multicopper oxidases.[1, 2] While triangular Cu_3 complexes with C_{3v} symmetry are well known,[3] those with lower symmetry are important because the metallosites of multicopper oxidases consist of two type-3 Cu sites and one type-2 Cu site.[1] We report here that triangular Cu_3 cluster complexes with a Cu^{II}Cu^{I}Cu^{I} mixed-valent state are obtained by using the mixed tripod ligand 2-quinolyl-2,2′-dipyrrolylmethane. The X-ray structure and spectroscopic properties of the Cu_3 complex indicate that two Cu ions interact strongly with one another.

We have shown that 2-pyridyl-2,2′-[3,3′-dimethyl-4,4′-diethyl-5,5′-bis(ethoxycarbonyl)]dipyrrolylmethane occupies three coordination sites of the basal plane of a square pyramidal Cu^{II} center through a pyridine N atom, a pyrrole N atom, and the conjugated carbonyl O atom.[4] This tridentate coordination mode would cause steric hindrance to the fourth coordination site of the Cu^{II} basal plane in the case of 2-quinolyl-2,2′-[3,3′-dimethyl-4,4′-diethyl-5,5′-bis(ethoxycarbonyl)]dipyrrolylmethane (**1**). Hence, the three arms of the tripod ligand **1** would not converge to a single metal center. When a mixture of the ligand **1** (0.194 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.194 mmol), Et_3N (0.73 mmol), and EtOH (6 mL) was stirred at room temperature for 1 h under argon, the dark green Cu complex **2a** and the light green Cu complex **2b** were obtained in 7% and 17% yield, respectively (Scheme 1). On the basis of FAB-MS ($m/z = 1189$) and analytical data, **2a** and **2b** are isomeric and composed of two doubly deprotonated ligands and three Cu atoms. Therefore, the total charge of the Cu_3 cluster seems to be +4. Indeed, the reaction of **1**, $Cu^{II}(ClO_4)_2 \cdot 6H_2O$, and $[Cu^{I}(MeCN)_4]ClO_4$ in the molar ratio of 1.0/0.5/1.0 gave improved yields of **2a** and **2b**.[5]



Scheme 1. Formation of Cu_3 cluster complexes.

Single-crystal X-ray analysis of **2b** showed a triangular Cu_3 cluster with Cu–Cu distances of 2.596(2), 2.597(2), and 2.574(3) Å that is sandwiched between two tripod ligands (Figure 1). The Cu(1) and Cu(2) sites are ligated by two anionic pyrrole nitrogen atoms and two weakly coordinating carbonyl oxygen atoms. The Cu(3) site is ligated only by two

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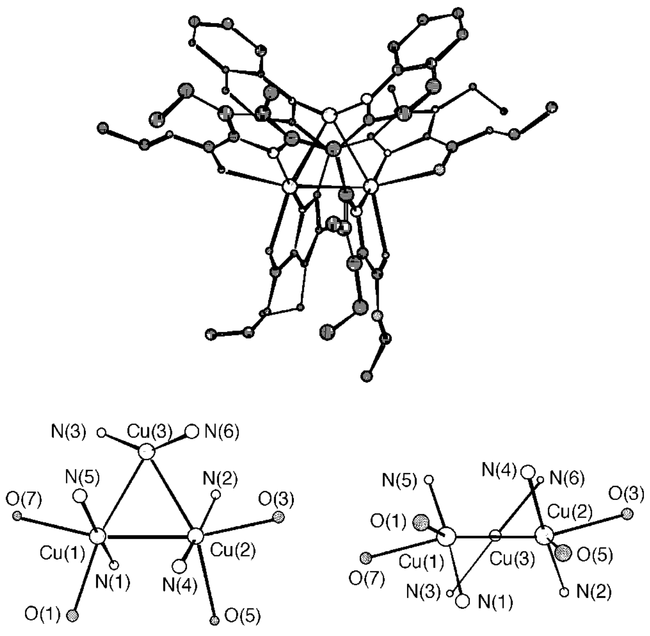

Figure 1. X-ray structure of **2b** (top) and top (bottom, left) and side views (bottom, right) of the Cu_3 core. Selected distances [Å] and angles [°]: Cu(1)–Cu(2) 2.597(2), Cu(1)–Cu(3) 2.574(3), Cu(2)–Cu(3) 2.596(2), Cu(1)–O(1) 2.223(8), Cu(1)–O(7) 2.289(8), Cu(2)–O(3) 2.331(8), Cu(2)–O(5) 2.328(8), Cu(1)–N(1) 1.888(8), Cu(1)–N(5) 1.897(9), Cu(2)–N(2) 1.907(8), Cu(2)–N(4) 1.888(8), Cu(3)–N(3) 1.987(9), Cu(3)–N(6) 1.988(9); N(1)-Cu(1)-N(5) 168.5(4), N(2)-Cu(2)-N(4) 169.2(4), N(3)-Cu(3)-N(6) 150.1(4), N(1)-Cu(1)-O(1) 81.0(3), N(2)-Cu(2)-O(3) 79.4(3), N(5)-Cu(1)-O(7) 80.4(3), N(4)-Cu(2)-O(5) 79.7(3), O(1)-Cu(1)-O(7) 88.0(3), O(3)-Cu(2)-O(5) 92.9(3), N(1)Cu(1)N(5)/Cu(1)Cu(2)-Cu(3) 85.5, N(2)Cu(2)N(4)/Cu(1)Cu(2)Cu(3) 84.5, N(3)Cu(3)N(6)/Cu(1)-Cu(2)Cu(3) 51.5.

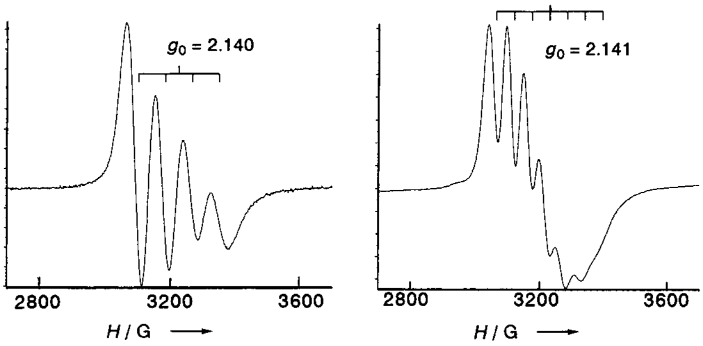

Figure 2. ESR spectra of **2a** (left) and **2b** (right) in toluene/CH_2Cl_2 (10/1) solution at room temperature. Microwave frequencies were 9.631 GHz for **2a** and 9.632 GHz for **2b**.

quinoline nitrogen atoms, N(3) and N(6). The Cu–$N_{quinoline}$ distances (1.987(9) and 1.988(9) Å) are about 0.1 Å longer than the Cu–$N_{pyrrole}$ distances. The Cu(1) and Cu(2) sites are pseudooctahedral if the Cu–Cu bonds are taken into account. The Cu(3) site has a distorted tetrahedral geometry. The N(3)-Cu(3)-N(6) and Cu(1)-Cu(3)-Cu(2) angles are 150.1(4) and 60.30(6)°, respectively, and the dihedral angle between these two planes is 51.5°. The mixed tripod ligand **1** is well preorganized for mixed-valent cluster complexes in which metal sites with strong ligand fields coexist with sites having weak ligand fields.

The seven-line ESR spectrum observed for **2b** at room temperature ($g_0 = 2.141$, $A_{0(Cu)} = 52.5$ G; Figure 2, right) shows that an $S = ½$ spin is shared by two Cu ions. The spectrum at 77 K, however, is indicative of a spin-localized d_{z^2}-based Cu^{II} site. Therefore, the delocalization of the $S = ½$ spin at room temperature is due to rapid ligand reorganization on the ESR time scale caused by intramolecular electron transfer.[6] (Further discussion of the ESR spectra will be given at a later date.) An intervalence transfer band was observed for **2b** at 1194 nm ($\varepsilon = 1700\ dm^3 mol^{-1} cm^{-1}$; half-height width 2500 cm^{-1}) in CH_2Cl_2 solution.

The X-ray structure of a triangular $[Cu_3]^{3+}$ complex **3** with two hexadentate tris[3-(2-pyridyl)pyrazol-1-yl]hydroborate tripod ligands was recently reported, and its one-electron oxidation product, the $[Cu_3]^{4+}$ complex **4**, shows a seven-line ESR spectrum below 120 K.[1c] Although the Cu–Cu distances (2.915, 3.500, 3.614 Å) of **3** are different from those of **2b**, there should be a close resemblance between **2b** and **4** in their structures and electronic properties. An electron-delocalized $Cu^{1.5+}Cu^{1.5+}$ pair is of major interest from the theoretical and bioinorganic viewpoints.[6, 7] The Cu–Cu distances of **2b** are similar to those of fully delocalized mixed-valent complexes.

Complex **2a** shows a four-line ESR signal at $g_0 = 2.140$ with $A_{0(Cu)} = 86.9$ G at room temperature (Figure 2, left). Hence, there should be a spin-localized Cu^{II} site in the $[Cu_3]^{4+}$ cluster of **2a**. A one-third turn of one tripod ligand of **2b** with respect to the other generates a single dianionic hexacoordinate site suitable for complexation with a Cu^{II} ion and two mono-anionic pentacoordinate sites suitable for Cu^{I} ions, as illustrated for **2a** in Scheme 1.[8]

Experimental Section

2a and **2b**: Triethylamine (0.1 mL, 7.2×10^{-4} mol) was added to a solution of **1** (97.1 mg; 1.94×10^{-4} mol), $Cu(ClO_4)_2 \cdot 6H_2O$ (36.0 mg; 9.72×10^{-5} mol), and $[Cu(MeCN)_4]ClO_4$ (63.4 mg; 1.94×10^{-4} mol) in ethanol (6 mL) under argon. After stirring the mixture at room temperature for 1.5 h, the solvent was removed. The first dark green band and the second bright green band obtained by chromatography (SiO_2/CH_2Cl_2) were recrystallized from CH_2Cl_2/pentane (or CH_2Cl_2/Et_2O) to give **2a** and **2b** in 25 and 14% yield, respectively.

2a: FAB-MS (dithranol): *m/z* 1189; magnetic moment (Guoy method at room temperature) $\mu = 1.96\,\mu_B$; ESR (in a frozen glass of toluene/CH_2Cl_2 (10/1) at 77 K): $g_1 = 2.004$, $A_{1(Cu)} = 100.8$ G (quartet), $g_2 = 2.160$, $g_3 = 2.278$, $A_{3(Cu)} = 84.4$ G (quartet); elemental analysis calcd for $C_{60}H_{66}N_6O_8Cu_3$: C 60.35, H 5.57, N 7.04; found: C 60.08, H 5.82, N 7.19.

2b: FAB-MS (dithranol): *m/z* 1189; magnetic moment (6–300 K; SQUID magnetometer) $\mu = 1.75\,\mu_B$; ESR (in a frozen glass of toluene/CH_2Cl_2 (10/1) at 77 K): $g_1 = 1.970$, $A_{1(Cu)} = 114$ G (quartet), $g_2 = 2.146$, $g_3 = 2.211$, $A_{3(Cu)} = 91$ G (quartet); UV/Vis/NIR (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)$ 384 (3.77), 664 (2.81), 1194 nm (3.24); elemental analysis calcd for $C_{60}H_{66}N_6O_8Cu_3$: C 60.35, H 5.57, N 7.04; found: C 60.57, H 5.70, N 6.90.

X-ray crystal structure analysis of **2b** $\cdot CH_2Cl_2$ (recrystallized from CH_2Cl_2/Et_2O): $C_{60}H_{66}N_6O_8Cu_3 \cdot CH_2Cl_2$, $M_r = 1274.79$, monoclinic, space group $P2_1/a$, $a = 12.679(3)$, $b = 23.590(2)$, $c = 20.164(3)$ Å, $\beta = 99.03(1)°$, $V = 5956(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.421\ g\,cm^{-3}$, $\mu(Cu_{K\alpha}) = 25.44\ cm^{-1}$, $T = 296$ K, $R(F) = 0.062$, $R_w(F) = 0.044$, GOF = 1.59. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132711. 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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[5] Yields: **2a** (25 %) and **2b** (14 %) under argon for 1 h; **2a** (7 %) and **2b** (29 %) under air for 46 h.

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[8] Cu_3 complexes analogous to **2a** and **2b** were obtained from 2-quinolyl-2,2′-[5,5′-bis(ethoxycarbonyl)]dipyrrolylmethane, and their X-ray structural analyses verified the structure of **2a**. Details will be reported elsewhere.

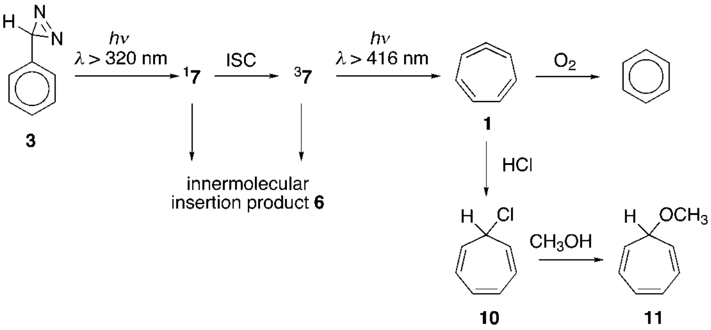
1,2,4,6-Cycloheptatetraene: Room-Temperature Stabilization inside a Hemicarcerand[**]

Ralf Warmuth* and Melissa A. Marvel

Dedicated to Professor Donald J. Cram
on the occasion of his 80th birthday

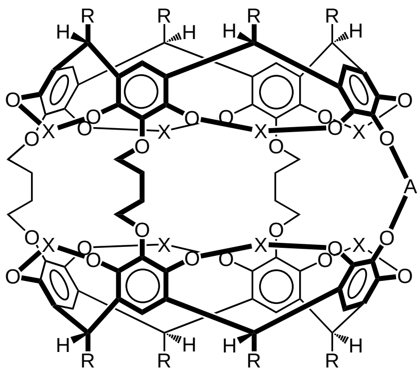
The phenylcarbene rearrangement is one of the most important and fascinating carbene rearrangements. Despite intense experimental and theoretical studies neither is the exact mechanism known nor have the energetics of the thermal interconversion between the involved intermediates been studied.[1, 2] Chapman and co-workers photochemically generated 1,2,4,6-cycloheptatetraene **1** at 15 K in argon and provided spectroscopic evidence for this highly strained allene.[3] Rapid dimerization at higher temperatures prevented a detailed study of the equilibration between **1** and cycloheptatrienylidene (**2**), which plays an important role in the solution-phase chemistry of both species.[4]

Incarceration in the inner phases of Cram's hemicarcerands is a novel, elegant, and extremely powerful way to stabilize reactive intermediates by preventing their dimerization.[5] This method has previously been used to stabilize cyclobutadiene and *o*-benzyne (1,2-didehydrobenzene) [6, 7] Here, we report the room-temperature stabilization of **1**, which we generated from phenyldiazirine (**3**) by a photochemical phenylcarbene rearrangement inside hemicarcerand **4** (Scheme 1).[8]



Scheme 1. Inner phase generation and chemistry of **1**. ISC = intersystem crossing.

We incarcerated **3** by reacting diol-host **5** with 1,4-butanediol dimethanesulfonate and Cs_2CO_3 in the presence of excess **3** in hexamethylphosphoramide.[9, 10] This reaction provided the hemicarceplex **4·3** in 80 % yield (Figure 1 a).[11] Photolysis ($\lambda > 320$ nm) of a degassed solution of **4·3** in $C_6D_5CD_3/CDCl_3$ (9:1) at 77 K gave the innermolecular phenylcarbene insertion product **6**. In the hope that a small isotope effect would slow down this competing reaction, we prepared [D$_{16}$]**4·3** in



4: X = CH_2; A = $(CH_2)_4$
[D$_{16}$]**4**: X = CD_2; A = $(CH_2)_4$
5: X = CH_2; A = H H
[D$_{16}$]**5**: X = CD_2; A = H H

R = $(CH_2)_4CH_3$

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