An Infinite Zigzag Chain and the First Linear Chain of Four Copper Atoms; Still No Copper−Copper Bonding

**Rodolphe Clérac,[†] F. Albert Cotton,*[,‡] Lee M. Daniels,[‡] Jiande Gu,[‡]
Carlos A. Murillo,*[,‡,§] and Hong-Cai Zhou[‡]**

The Laboratory for Molecular Structure and Bonding, Department of Chemistry, P.O. Box 30012,
Texas A&M University, College Station, Texas 77842-3012, and Escuela de Química,
Universidad de Costa Rica, Ciudad Universitaria, Costa Rica

Received February 24, 2000

We have prepared and characterized ionic compounds containing linear or zigzag chains of copper ions. For $[Cu_3(DPhIP)_2](CuCl_2)$ (**1**), in addition to the well-known $[ClCuCl]^-$ anion, there is a cation with a linear chain of three Cu atoms bridged by two DPhIP anionic ligands (DPhIP represents the anion of 2,6-diphenyliminopiperidine). Each cation has weak interactions with two adjacent $CuCl_2^-$ anions, and each anion interacts with two neighboring $[Cu_3(DPhIP)_2]^+$ cations forming an infinite zigzag chain of Cu^I atoms. Also reported here is the linear tetracopper chain cation in $[Cu_4(DPhIP)_4][CuCl_2]_2$ (**2**). The $[Cu_4(DPhIP)_4]^{2+}$ cation has approximate D_{2d} symmetry. There are three Cu···Cu distances of 2.518(2), 2.479(2), and 2.525(2) Å. The terminal Cu atoms are 2-coordinate Cu^I while the two inner Cu atoms are 4-coordinate Cu^{II}. In spite of the diamagnetic nature of this compound, molecular orbital calculations (by various DFT techniques) indicate that no direct Cu−Cu bonds are present; instead the bridging ligand effects a strong coupling of the spins.

Introduction

Interest in linear metallic chains has been growing steadily over the past few years because of their potential as molecular wires.[1] Trinuclear,[2] tetranuclear,[3] and longer metallic chains[4] have been made by us and others. Although linear tricopper complexes have been reported,[5] a linear tetranuclear copper chain has never been synthesized. A recurring and very important issue in inorganic chemistry[6] and recently in bioinorganic chemistry[7] is the existence of a Cu−Cu bond. In the copper acetate case,[8] the two copper atoms are only weakly coupled, giving rise to a thermally populated excited state. For the dicopper tetra-amidinates[9] and -triazinates[10] essentially diamagnetic compounds with short Cu···Cu separations of ca. 2.45 Å have been found. Here we wish to report the synthesis and structural characterization of $[Cu_3(DPhIP)_2](CuCl_2)$ (where DPhIP represents the anion of 2,6-diphenyliminopiperidine), in which the cation is a linear tricopper chain, a tri-Cu(I) core embraced by only two DPhIP ligands. When the weak interactions with the $CuCl_2^-$ anions in the lattice are considered, there is an infinite zigzag chain of copper atoms. Also reported are the synthesis and structure of a tetracopper linear chain, $[Cu_4(DPhIP)_4]^{2+}$, its magnetic properties, and an analysis using DFT calculations.

Experimental Section

General Procedures. All syntheses and sample manipulations were carried out under an atmosphere of nitrogen with standard Schlenk and glovebox techniques. The compound H(DPhIP) (2,6-diphenyliminopiperidine) was synthesized according to a literature method.[11] Methyllithium (1.0 M solution in THF/cumene) was purchased from Aldrich Chemical Co. Anhydrous $CuCl_2$ and CuCl were purchased from Strem Chemicals. NMR spectra were recorded on a Varian VXR-300 spectrometer. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were

---

[†] Department of Chemistry, Texas A&M University.

[‡] The Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University.

[§] University of Costa Rica.

(1) Cotton, F. A. *Inorg. Chem.* **1998**, *37*, 5710.

(2) (a) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I. *Inorg. Chem. Commun.* **1998**, *1*, 1. (b) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I. *J. Am. Chem. Soc.* **1997**, *119*, 10223. (c) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV.; Murillo, C. A. *J. Am. Chem. Soc.* **1997**, *119*, 10377. (d) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV. *Chem. Commun.* **1997**, 421. (e) Wu, L.-P.; Field, P.; Morrissey, T.; Murphy, C.; Nagle, P.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1990**, 3835. (f) Clérac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Murillo, C. A.; Zhou, H.-C. *Inorg. Chem.* **2000**, *39*, 3414.

(3) (a) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wang, X. *Chem. Commun.* **1998**, 39. (b) Mashima, K.; Fukumoto, A.; Nakano, H.; Kaneda, Y.; Tani, K.; Nakamura, A. *J. Am. Chem. Soc.* **1998**, *120*, 12151. (c) Cotton, F. A.; Murillo, C. A.; Roy, L. E.; Zhou, H.-C. *Inorg. Chem.* **2000**, *39*, 1743.

(4) (a) Cotton, F. A.; Daniels, L. M.; Lu, T.; Murillo, C. A.; Wang, X. *J. Chem. Soc., Dalton Trans.* **1999**, 517. (b) Wang, C. C.; Lo, W. C.; Chou, C. C.; Lee, G. H.; Chen, J. M.; Peng, S. M. *Inorg. Chem.* **1998**, *37*, 4059.

(5) (a) Pyrka, G. J.; El-Mekki, M.; Pinkerton, A. A. *J. Chem. Soc., Chem. Commun.* **1991**, 84. (b) Aduldecha, S.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1991**, 993. (c) Beck, J.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 409.

(6) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, England, 1993.

(7) Bertagnolli, H.; Kaim, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 771.

(8) Carlin, R. L.; van Duyneveldt, A. J. *Magnetic Properties of Transition Metal Compounds*, *Inorganic Chemistry Concepts 2*; Springer-Verlag: New York, 1977.

(9) See for example: (a) Kilner, M.; Pietrzykowski, A. *Polyhedron* **1983**, *2*, 1379. (b) Halfpenny, J. *Acta Crystallogr.* **1995**, *C51*, 2542.

(10) Corbett, M.; Hoskins, B. F.; Mcleod, N. J.; O'Day, P. O. *Aust. J. Chem.* **1975**, *28*, 2377. (b) Rudolf, M. F.; Jasiewicz, B.; Jeźowska-Trzebiatowska, B. *Bull. Acad. Pol. Sci.***1974**, *22*, 351. (c) Harris, C. M.; Hoskins, B. F.; Martin, R. L. *J. Chem. Soc.* **1959**, 3728.

(11) (a) Elvidge, J. A.; Linstead, R. P.; Salaman, A. M. *J. Chem. Soc.* **1959**, 208. (b) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I.; Zhou, H.-C. *J. Am. Chem. Soc.* **1999**, *121*, 6856.

10.1021/ic000208l CCC: $19.00

Table 1. Crystal Data and Structure Refinement

	1·$0.5H_2O$	**1**·THF	**2**·$3CH_2Cl_2$·H_2O
empirical formula	$C_{34}H_{33}N_6O_{0.5}Cl_2Cu_4$	$C_{38}H_{40}N_6OCl_2Cu_4$	$C_{71}H_{72}N_{12}OCl_{10}Cu_6$
fw	858.72	921.82	1845.14
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	16.259(4)	13.875(3)	16.907(2)
b, Å	6.147(2)	8.642(2)	16.427(3)
c, Å	16.544(8)	31.850(4)	27.349(7)
α, deg	90	90	90
β, deg	93.55(3)	95.06(2)	98.525(7)
γ, deg	90	90	90
V, Å^3	1650(1)	3804(1)	7512(3)
Z	2	4	4
data collection instrument	Nonius CAD4	Nonius FAST	Nonius FAST
T, K	158(2)	213(2)	213(2)
radiation λ, Å	0.710 73	0.710 73	0.710 73
ρ(calcd), g cm^{-3}	1.728	1.609	1.630
μ(Mo Kα), cm^{-1}	27.41	23.85	20.76
R1^{a,c}/R1^{a,d}	0.068/0.094	0.050/0.064	0.098/0.117
wR2^{b,c}/wR2^{b,d}	0.181/0.206	0.110/0.122	0.246/0.271

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^2$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. [c] Denotes value of the residual considering only the reflections with $I > 2\sigma(I)$. [b] Denotes value of the residual considering all the reflections.

performed by Canadian Microanalytical Services Ltd. on samples that had been pumped under vacuum to remove interstitial solvent.

Preparation of [Cu_3(DPhIP)$_2$]($CuCl_2$), 1. To a Li(DPhIP) solution in THF, prepared by addition of MeLi in THF/cumene (2.0 mL, 2.0 mmol) to a solution of H(DPhIP) (0.53 g, 2.0 mmol), was added CuCl (0.40 g, 4.0 mmol), and the mixture was refluxed for half an hour. The yellow brown suspension was pumped to dryness under vacuum, and the brown solid was extracted with CH_2Cl_2 (20 mL). The LiCl residue was discarded, and the yellow solution was layered with hexanes. Compound **1**, as a yellow crystalline solid, was obtained in quantitative yield. Crystals of **1**·$0.5H_2O$ suitable for crystallographic study were obtained by layering a dilute solution of **1** in wet CH_3CN with diethyl ether; yellow plate-shaped crystals of **1**·THF were crystallized from THF/hexanes. NMR (δ in $CDCl_3$, ppm): 7.292 (4H), 6.992 (6H), 2.248 (4H), 1.708 (2H). IR (KBr pellet, cm^{-1}): 1593 (w), 1578 (w), 1561 (w), 1517 (vs, br), 1459 (w), 1449 (w), 1420 (w), 1402 (s), 1363 (w), 1343 (w), 1261 (w), 1220 (m), 1193 (m), 1098 (w), 1069 (w), 1028 (w), 914 (w), 858 (w), 807 (m), 763 (m), 723 (m), 696 (m), 670 (w), 637 (w), 606 (w), 509 (w). Anal. Found: C, 47.64; H, 3.89; N, 9.51. Calcd for $C_{34}H_{32}N_6Cl_2Cu_4$: C, 48.06; H, 3.80; N, 9.89.

Preparation of [Cu_4(DPhIP)$_4$]($CuCl_2$)$_2$·$3CH_2Cl_2$·H_2O, 2·$3CH_2Cl_2$·H_2O. The compound H(DPhIP) (0.53 g, 2.5 mmol) was dissolved in THF (10 mL), cooled to −78 °C, and deprotonated by methyllithium (1.0 M, 2.5 mL). After warming to room temperature, the resulting Li(DPhIP) solution was cooled to −78 °C again. At this point, a premixed sample of $CuCl_2$ (0.13 g, 1.0 mmol) and CuCl (0.20 g, 2.0 mmol) was added; the mixture turned red brown immediately. The reaction mixture was then stirred at −78 °C for 4 h until the color of the suspension changed to dark green. While the suspension was still cold, a dark green solid was collected by filtration and then washed extensively with benzene (4 H 15 mL) and cold CH_2Cl_2 (15 mL). The remaining dark green powder was dissolved in hot CH_2Cl_2 (22 mL) and layered with hexanes. Dark block-shaped crystals of **2**·$3CH_2Cl_2$·H_2O grew within a week. Yield: 0.098 g (11%). IR (KBr pellet, cm^{-1}): 1577 (w), 1560 (w), 1515 (vs, br), 1459 (w), 1448 (w), 1399 (s), 1363 (w), 1263 (w), 1215 (m), 1196 (m), 1072 (w), 1026 (w), 913 (w), 860 (w), 804 (m), 763 (m), 726 (m), 697 (m), 672 (w), 603 (w), 510 (w), 474 (w), 408 (w). Anal. Found: C, 51.57; H, 4.23; N, 10.41. Calc for $C_{68}H_{64}N_2Cl_4Cu_6$: C, 51.94; H, 4.10; N, 10.69.

Magnetic Measurements. The magnetic susceptibility data were obtained on a Quantum Design SQUID magnetometer MPMS-5 (housed in the Department of Physics and Astronomy at Michigan State University). A finely ground polycrystalline sample of 28.1 mg of compound **2** was measured between 2 and 300 K at 1000 G. The data were corrected for the sample holder and for a diamagnetic contribution (-7.8×10^{-4} emu mol^{-1} calculated from Pascal constants).[12]

X-ray Crystallography. Data collection for **1**·THF and **2**·$3CH_2Cl_2$·H_2O were carried out on a Nonius FAST area detector diffractometer with each crystal mounted on the tip of a quartz fiber under a stream of nitrogen at 213 K. Cell parameters were obtained by least-squares refinement of 250 reflections ranging in 2θ from 18° to 42°. Laue groups were confirmed by axial images. Data were collected using 0.2° intervals in φ for the range of $0° \le \varphi \le 220°$ and 0.2° intervals in ω for two different regions in the range $0° \le \omega \le 72°$; in this way, nearly a full sphere of data was collected. The highly redundant data were corrected for Lorentz and polarization effects, and for absorption.

Data collection for compound **1**·$0.5H_2O$ was performed on a Nonius CAD4 diffractometer at −115 °C, and an empirical absorption correction based on ψ-scans was applied.

For each structure, the positions of the Cu, Cl, and N atoms were found from a direct-methods *E*-map; the carbon atoms were located in alternating difference-Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in idealized positions, and displacement parameters were set at 1.2 times that of the attached atom.

In **1**·$0.5H_2O$, compound **1** has a major (∼94%) and a minor (∼6%) orientation in both anionic and cationic parts; they were modeled as ion pairs, so that the structurally related cationic and anionic parts have the same occupancy. The structure of **1**·THF displays no discernible disorder. Although crystals of **2**·$3CH_2Cl_2$·H_2O form readily and diffract well, all of the samples examined suffered from some rotational twinning. A full data set was successfully collected, and the structure was quickly solved. The positions of the linear chain of four copper atoms and the coordination sphere around each one are clearly established. However, the ligands exhibit significant disorder, and both of the independent [$CuCl_2$]$^-$ ions appear to have two distinct orientations. Furthermore, three interstitial sites apparently contain highly disordered CH_2Cl_2 molecules. The basic molecular structure is clear and the metal−metal separations are accurate, but since the overall structure is not entirely satisfactory it will not be discussed in detail.

Crystallographic data for **1**·$0.5H_2O$, **1**·THF, and **2**·$3CH_2Cl_2$·H_2O are given in Table 1; selected interatomic separations and angles for **1**·$0.5H_2O$, **1**·THF, and **2**·$3CH_2Cl_2$·H_2O are found in Table 2, Table 3 and Table 4, respectively.

Theoretical Calculations. We have performed calculations on the model compounds $Cu_2(HNNNH)_4$ and $[Cu_4(HNCHNCHNH)_4]^{2+}$. The local energy minimum structures have been fully optimized by the analytic gradient techniques using the density functional theory with Becke's three parameter (B3)[13] exchange functional along with the Lee−Yang−Parr (LYP) nonlocal correlation functional (B3LYP).[14,15] The standard valence triple-ζ basis set augmented with six d-type and three p-type polarization functions, 6-311G(d,p),[16] was used in conjunc-

---

[12] Boudreaux, E. A., Mulay, L. N., Eds. *Theory and Applications of Molecular Paramagnetism*; John Wiley & Sons: New York, 1976.

[13] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for **1** in **1**·0.5H$_2$O

Cu(1)···Cu(2)	2.441(2)
Cu(1)−N(2)	1.907(6)
Cu(2)−N(1)#1[a]	1.940(6)
Cu(2)−N(3)	1.912(6)
Cu(2)···Cu(3)	2.893(2)
Cu(2)−Cl(1)#2	2.557(3)
Cu(3)−Cl(1)	2.129(2)
N(2)#1−Cu(1)−N(2)	180.0
N(3)−Cu(2)−N(1)#1	156.4(3)
Cu(2)#1···Cu(1)···Cu(2)	180.0
Cl(1)#2−Cu(1)−Cl(1)	180.0

[a] Symmetry transformation used to generate equivalent atoms: #1 $-x, -y + 1, -z + 1$; #2 $-x, -y + 2, -z + 1$.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for **1** in **1**·THF

Cu(1)···Cu(2)	2.4017(9)	Cu(1)···Cu(2)···Cu(3)	154.79(4)
Cu(2)···Cu(3)	2.4174(9)	Cl(2)−Cu(4)−Cl(1)	166.76(7)
Cu(2)···Cu(4)	2.835(1)	N(4)−Cu(1)−N(1)	158.1(2)
Cu(1)−Cl(1)	2.576(2)	N(2)−Cu(2)−N(5)	179.1(2)
Cu(1)−N(1)	1.927(4)	N(6)−Cu(3)−N(3)	151.7(2)
Cu(1)−N(4)	1.927(4)	Cu(4)−Cl(1)−Cu(1)	89.07(5)
Cu(2)−N(2)	1.901(4)	Cu(4)−Cl(2)−Cu(3)	88.55(6)
Cu(2)−N(11)	1.909(4)		
Cu(3)−Cl(2)	2.528(2)		
Cu(3)−N(3)	1.923(4)		
Cu(3)−N(6)	1.922(4)		
Cu(4)−Cl(1)	2.143(2)		
Cu(4)−Cl(2)	2.136(2)		

Table 4. Selected Interatomic Distances (Å) and Bond Angles (deg) for **2**·3CH$_2$Cl$_2$·H$_2$O

Cu(1)···Cu(2)	2.479(2)	Cu(1)−Cu(2)−Cu(3)	178.90(6)
Cu(1)−N(1)	2.059(8)	Cu(2)−Cu(1)−Cu(4)	177.59(6)
Cu(1)−N(5)	1.974(7)	N(5)−Cu(1)−N(11)	169.0(3)
Cu(1)−N(7)	2.052(8)	N(2)−Cu(2)−N(8)	168.5(3)
Cu(1)−N(11)	1.988(7)	N(4)−Cu(2)−N(10)	158.6(3)
Cu(2)−N(2)	1.982(7)	N(3)−Cu(3)−N(9)	177.3(4)
Cu(2)−N(4)	2.045(8)	N(6)−Cu(4)−N(12)	177.5(3)
Cu(2)−N(8)	1.986(7)		
Cu(2)−N(10)	2.072(8)		
Cu(3)−Cu(2)	2.518(2)		
Cu(3)−N(3)	1.844(9)		
Cu(3)−N(9)	1.865(8)		
Cu(4)−Cu(1)	2.525(2)		
Cu(4)−N(6)	1.852(8)		
Cu(4)−N(12)	1.871(7)		

tion with the DFT method. The Gaussian 94 program package[17] was used.

Results and Discussion

Synthetic Considerations. Initially both compounds **1** and **2** were prepared in low yields from a reaction between CuCl$_2$ and Li(DPhIP) in THF at reflux temperature under a nitrogen atmosphere. Presumably some CuCl$_2$ was reduced by Li(DPhIP) since Cu(I) is present in the two compounds. A similar reaction occurred when CuCl$_2$ was reacted with Li(hpp)[18] resulting in Cu$_2$(hpp)$_2$. In order to minimize the redox reaction and to get a higher yield of **2**, the following reaction was carried out at −78 °C:

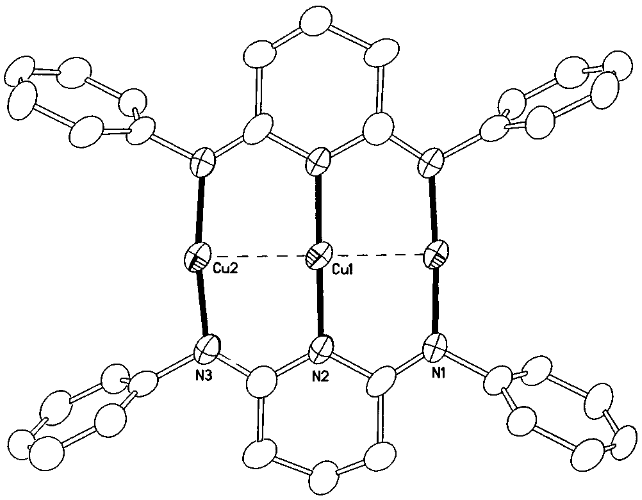


Figure 1. The structure of the [Cu$_3$(DPhIP)$_2$]$^+$ cation in **1**·0.5H$_2$O. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

$$2\mathrm{CuCl_2} + 4\mathrm{CuCl} + 4\mathrm{Li(DPhIP)} \rightarrow [\mathrm{Cu_4(DPhIP)_4}](\mathrm{CuCl_2})_2\ (\mathbf{2}) + 4\mathrm{LiCl} \quad (1)$$

However, compound **1** is produced in a competing reaction:

$$4\mathrm{CuCl} + 2\mathrm{Li(DPhIP)} \rightarrow [\mathrm{Cu_3(DPhIP)_2}](\mathrm{CuCl_2})\ (\mathbf{1}) + 2\mathrm{LiCl} \quad (2)$$

An experiment was tried in which CuCl$_2$ was allowed to react with a Li(DPhIP) solution in THF before the addition of CuCl, but the yield of **2** was still low. Presumably, this is due to the redox reaction between CuCl$_2$ and Li(DPhIP) mentioned above. A reaction having an acceptable yield of **2** was carried out at −78 °C using premixed CuCl$_2$ and CuCl (molar ratio 2:4). Compounds **1** and **2** have similar solubilities in solvents such as CH$_2$Cl$_2$, CH$_3$CN, and acetone but different solubilities in benzene; compound **1** is slightly soluble whereas **2** is not. The separation of **1** and **2** was achieved by extensively washing the mixture with benzene. Compound **1** can also be prepared in quantitative yield by a reaction of CuCl and Li(DPhIP) in a molar ratio of 2:1.

Crystallographic Considerations. Compound **1**·0.5H$_2$O crystallized from both CH$_2$Cl$_2$/hexanes and CH$_3$CN/ether as yellow blocks. The structure was solved in space group $P2_1/n$ with the central copper atom of the [Cu$_3$(DPhIP)$_2$]$^+$ unit (Figure 1) on an inversion center. The arrangement of a [Cu$_3$(DPhIP)$_2$]$^+$ unit and two adjacent [CuCl$_2$]$^-$ anions is shown in Figure 2. In Figure 1, the three Cu(I) atoms are aligned. The central copper atom, Cu(1), is linearly coordinated by N(2) and N(2a) with an N(2a)−Cu(1)−N(2) angle of 180.0°; the Cu(1)−N(2) distance is 1.907(6) Å. The two terminal copper atoms Cu(2) and Cu(2a) are related by the inversion center. As shown in Figure 2, the Cu(2) atom is 3-coordinate with bonds to two N atoms from two DPhIP ligands and a Cl atom from the nearest [CuCl$_2$]$^-$ unit. The Cu(2)−Cl(1)#2 distance is 2.557(3) Å, and the N(1)#1−Cu(2)−N(3) angle is 156.4(3)°. The other Cl atom,

---

(14) Lee, C.; Yang W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(16) Hehre, W. J.; Radom, L.; Schleyer, P. R.; Pople, J. A *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94,* revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(18) Cotton, F. A.; Murillo, C. A.; Timmons, D. J. Unpublished results.

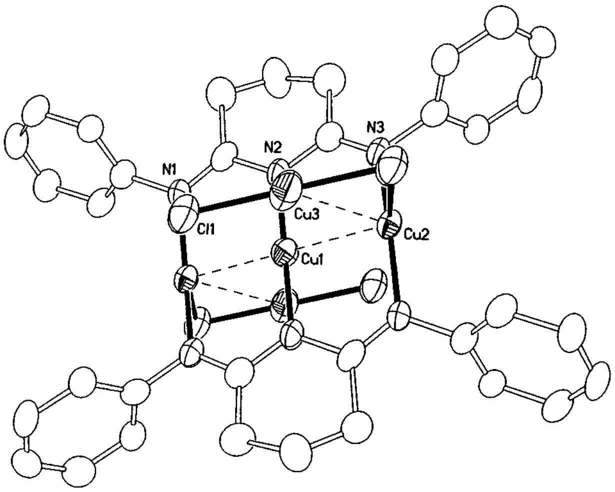


Figure 2. A drawing showing the interaction of a $[Cu_3(DPhIP)_2]^+$ cation with two adjacent $[ClCuCl]^-$ anions. Displacement ellipsoids are given at the 50% probability level; hydrogen atoms are omitted for clarity.

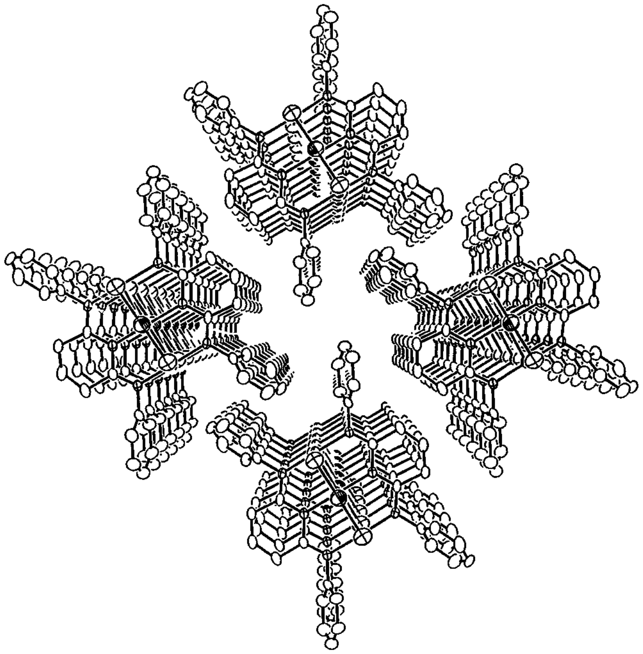


Figure 3. A schematic representation of infinite chains formed by the interaction between $[Cu_3(DPhIP)_2]^+$ cations and $[ClCuCl]^-$ anions.

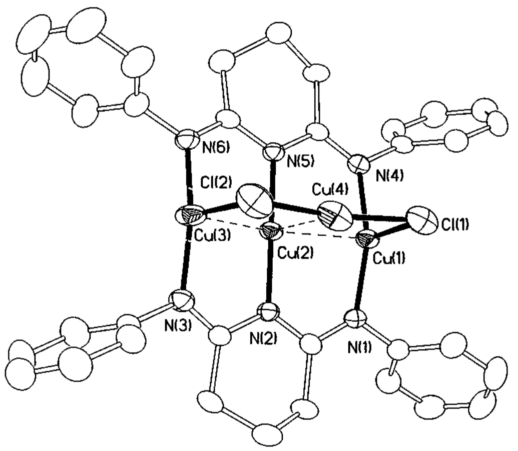


Figure 4. The $[Cu_3(DPhIP)_2][ClCuCl]$ molecule. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

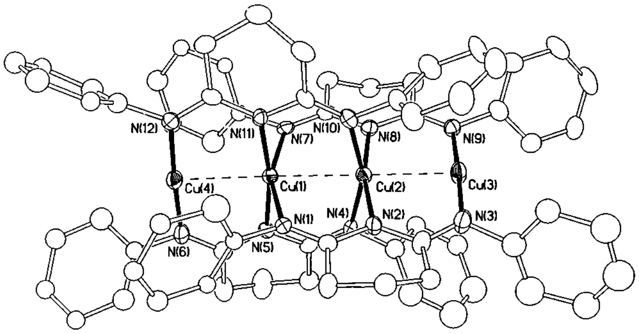


Figure 5. The structure of the $[Cu_4(DPhIP)_4]^{2+}$ cation in **2**·$3CH_2Cl_2$·H_2O. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity.

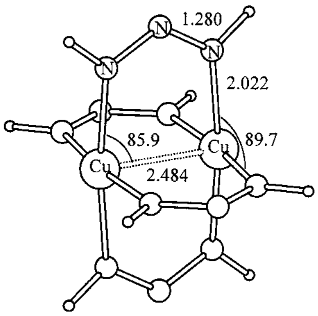


Figure 6. The fully optimized structure of $Cu_2(HNNNH)_4$ and important geometric parameters. Bond lengths are in angstroms and angles in degrees.

namely Cl(1a), interacts with another $[Cu_3(DPhIP)_2]^+$ cation to form infinite chains (Figure 3).

Compound **1**·THF was crystallized from THF/hexanes as yellow needle-shaped crystals; no crystallographic symmetry is imposed. Unlike the infinite chain structure in compound **1**·$0.5H_2O$, a $[Cu_3(DPhIP)_2]^+$ ion is closely associated with a $[CuCl_2]^-$ ion, but the ion pairs have no substantial interactions with each other (Figure 4). For the two 3-coordinate copper atoms, the Cu−Cl distances are 2.576(2) and 2.528(2) Å. The N−Cu−N angles are 158.1(2)° and 151.7(2)°. The conformations of the $[Cu_3(DPhIP)_2]^+$ cation in **1**·$0.5H_2O$ and **1**·THF are different. In a $[Cu_3(DPhIP)_2]^+$ unit in **1**·$0.5H_2O$, the two end Cu atoms deviate from the plane defined by the N atoms to two opposite directions in order to coordinate with Cl atoms from two different $[CuCl_2]^-$ anions, and the three Cu atoms are aligned. In the $[Cu_3(DPhIP)_2]^+$ unit in **1**·THF, the two N−Cu−N angles of the two end Cu atoms bend to the same direction in order to coordinate the two Cl atoms from the same $[CuCl_2]^-$ unit. Thus the $[CuCl_2]^-$ unit is bent, having a Cl−Cu−Cl angle of 166.76(7)°, and the Cu(1)−Cu(2)−Cu(3) angle deviates from 180° to 154.79(4)°.

Compound **2**·$3CH_2Cl_2$·H_2O crystallized in the space group $P2_1/n$; all atoms are in general positions. The molecular structure is shown in Figure 5. The four copper atoms are aligned along an S_4 axis of an idealized D_{2d} ligand arrangement. The two inner copper atoms are divalent and have square planar coordination environments; the two end copper atoms are monovalent with a typical linear ligand arrangement. The Cu···Cu distance between the divalent copper atoms is 2.479(2) Å, and those between a monovalent and a divalent copper atom are 2.525(2) and 2.518(2) Å.

Magnetic Properties. Except for an increase of the magnetism below ca. 30 K, which can be attributed to about 2.6% of an impurity with a spin of $^1/_2$, compound **2** has a temperature-

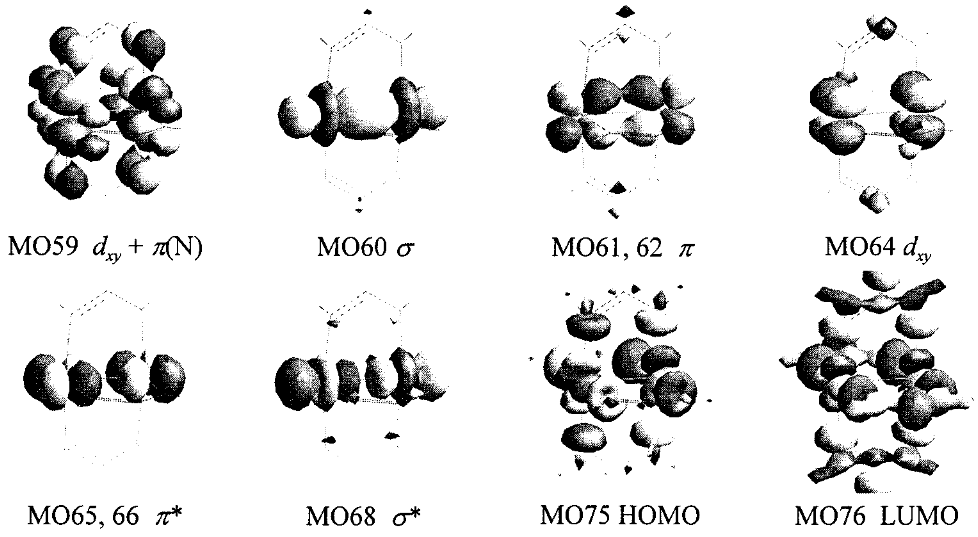


Figure 7. The frontier orbitals and the Cu atoms' related molecular orbitals for $Cu_2(HNNNH)_4$.

independent susceptibility of 8.3 × 10^{-3} emu mol^{-1} up to 300 K. This shows that **2** exhibits a singlet ground state without a thermally accessible triplet state in the temperature range of the study. This result clearly indicates that there is strong coupling between the two Cu^{II} atoms. The question that the experimental result itself cannot answer is whether this coupling is direct, that is, by Cu−Cu bond formation, or indirect, that is, an antiferromagnetic superexchange coupling through the atoms of the bridging ligand.

Theoretical Conclusions. In $Cu_2(O_2CCH_3)_4$, the two Cu atoms are weakly coupled. The ground state is a singlet, and the first excited state is a thermally populated triplet state. Thus, the effective magnetic moment is very temperature-dependent. For tetra-amidinates and tetra-triazinates, the Cu to Cu distances are much shorter (2.44−2.46 Å) and compounds are diamagnetic at room temperature. For **2** the distance between the two divalent Cu atoms (2.479(2) Å) is much shorter than that in $Cu_2(O_2CCH_3)_4(H_2O)_2$ (2.616 Å),[19] but similar to those in the amidinates and triazinates. Here there are no unpaired electrons, and the question of the existence or absence of a Cu−Cu bond here naturally arises.

To deal with this question, we have performed calculations on model compounds $Cu_2(HNNNH)_4$ and $[Cu_4(HNCHNCHNH)_4]^{2+}$ (see the Experimental Section for details). The fully optimized structure of $Cu_2(HNNNH)_4$ is depicted in Figure 6 along with the important geometric parameters. The Cu···Cu distance has been predicted to be 2.484 Å, which is only 0.005 Å longer than the experimental value. Other calculated geometric parameters also reproduce well the crystal data. The analysis of the molecular orbitals reveals that the frontier orbitals of $Cu_2(HNNNH)_4$ are mainly formed by the $d_{x^2-y^2}$ orbitals of the Cu atoms and the lone pairs of the N atoms (Figure 7). In the HOMO (MO75) two $d_{x^2-y^2}$ orbitals which are antibonded with the lone pairs of the N atoms take the opposite phase while in the LUMO (MO76) these two are in the same phase. The σ-type bonding and antibonding orbitals (σ and σ^*) formed by the d_{z^2} atomic orbital of the Cu atoms are found to have the molecular orbital numbers MO60 and MO68 which are 126 and 87 kcal/mol lower than the HOMO in energy, respectively. The degenerate π bonding and π^* antibonding orbitals rank MO66, 65 and MO62, 61, respectively. No δ-type bonding has been observed between the two Cu atoms. The two sets of d_{xy} atomic orbitals of the metal atoms split into MO64 and MO59 due to their interaction with the ligands; both metal−metal bonding and antibonding orbitals are occupied in this case. The orbital analysis definitely confirms that no metal−metal bond exists between these two divalent Cu atoms at the distance of 2.479(2) Å. Since the LUMO is the antibonding orbital between the $d_{x^2-y^2}$ of the metal and the lone pair from the ligands, these two Cu atoms should be held together through the bonds between the $d_{x^2-y^2}$ of the Cu atom and the ligand orbitals formed by the lone pairs of the N atoms.

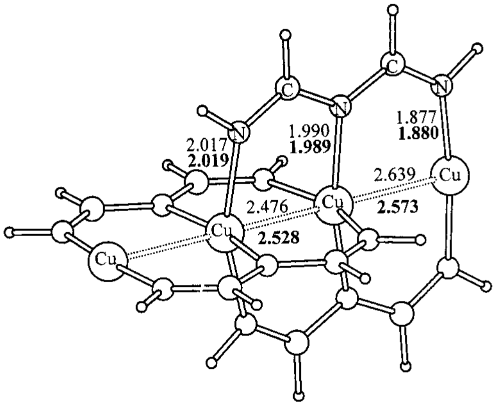
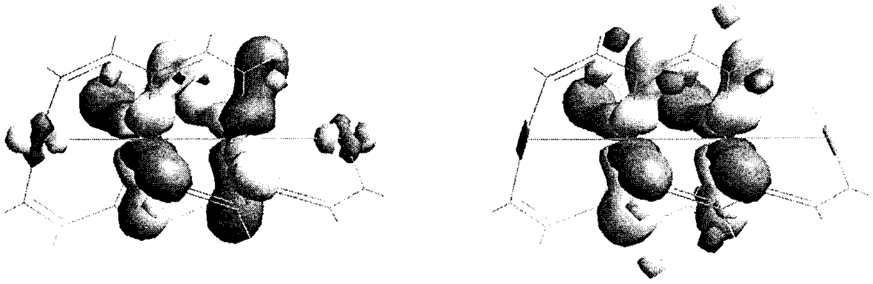


Figure 8. The optimized structure of the model compound $[Cu_4(HNCHNCHNH)_4]^{2+}$. Distances (Å) for triplet state are in boldface and singlet state in lightface type.

The optimized structural parameters of the singlet and the triplet states of the model $[Cu_4(HNCHNCHNH)_4]^{2+}$ species depicted in Figure 8 clearly demonstrate that this model mimics $[Cu_4(DPhIP)_4]^{2+}$ very well. Specifically, for the singlet state the theoretical distance between the two central Cu atoms of 2.476 Å is only 0.003 Å shorter than the experimental value of 2.479(2) Å, while the central to terminal distance of 2.639 Å is about 0.1 Å longer than the corresponding experimental value. These two Cu···Cu distances are predicted to be 2.528 and 2.573 Å in the lowest triplet state at the DFT level. In this model the HOMO and LUMO consist of the $d_{x^2-y^2}$ of the central Cu atoms and the lone pair of N atoms of the ligands (Figure 9). The σ-type metal−metal antibonding orbital which is occupied has been found to be 15 kcal/mol lower in energy than the HOMO. Notice that both HOMO and LUMO are metal−ligand bonding $d_{x^2-y^2}$ orbitals and there is no direct bond between the two central metal atoms; the Cu atoms are clearly linked only through the ligands. Since no bond directly links the central Cu atoms, the $d_{x^2-y^2}$ orbitals of the inner metal atoms have no interaction with



MO131: HOMO MO132: LUMO

Figure 9. The frontier orbitals of the model $[Cu_4(HNCHNCHNH)_4]^{2+}$ species.

each other. Accordingly, the HOMO and LUMO are expected to be nearly degenerate.

There is, however, one problem with the results of the calculations. Theoretical predictions for the total energy show that the triplet state is about 22 kcal/mol more stable than the singlet state. This obviously conflicts with the results of the magnetic measurement. Why should this be? Notice that the occupation of the frontier orbitals is dominated by electrons from the ligands, and thus correct prediction for the electronic spin states of this compound depends on the reliability of our model of the ligand. One cannot expect that the oversimplified ligand in the model $[Cu_4(HNCHNCHNH)_4]^{2+}$ should necessarily predict the spin of the ground state correctly. However, the geometric parameters predicted for both singlet and triplet states are very close and both of the states give about the same description of the Cu⋯Cu and the Cu−N interactions, as well as good geometric prediction for the Cu⋯Cu and the Cu−N distances. We believe that this simplified model is good enough for describing the metal−metal and metal−ligand interactions in the real compound, even though it fails to predict the ordering of the highly ligand-dependent populations of the HOMO and LUMO.

In conclusion, it is our belief that the diamagnetism exhibited by tetragonal lantern complexes of copper(II) with nitrogen-containing ligands is not indicative of metal−metal bonding and that this diamagnetism can be explained by electron delocalization through the ligands. This would be consistent with earlier calculations on $[Pd_2(\text{formamidinate})_4]^{+}$ cations which showed no Pd−Pd bond formation.[20]

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work.

Supporting Information Available: Two computer drawings of the structure of compound **1**. An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000208L