

First Cu^{II} Diamondoid Net with 2-Fold Interpenetrating Frameworks. The Role of Anions in the Construction of the Supramolecular Arrays

Miao Du, Xian-He Bu,* Ya-Mei Guo, and He Liu

Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

Stuart R. Batten

School of Chemistry, PO Box 23, Monash University, Clayton, Victoria 3800, Australia

Joan Ribas

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal, 647, 08028-Barcelona, Spain

Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hongkong, Hongkong, P.R. China

Received February 22, 2002

The synthesis and crystal structure of the three-dimensional coordination polymer of an angular dipyriddy ligand 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (L) and Cu(ClO₄)₂, exhibiting the *first* Cu^{II} diamondoid network with 2-fold interpenetration, {[Cu(L)₂(H₂O)₂](ClO₄)(OH)(H₂O)_{2.5}}_n (**1**), together with the Cu(OAc)₂ complex of L, [Cu(L)₂(OAc)₂(H₂O)](H₂O)₂(CH₃OH) (**2**), with an unexpected mononuclear structure, are reported. Crystal data for **1**: tetragonal, space group *I*₄/a, *a* = *b* = 13.477(3) Å, *c* = 46.167(13) Å, *Z* = 8. Crystal data for **2**: triclinic, space group *P* $\bar{1}$, *a* = 7.847(2) Å, *b* = 13.189(4) Å, *c* = 15.948(5) Å, α = 75.225(7)°, β = 79.945(6)°, γ = 77.540(5)°, *Z* = 2. The magnetic properties and anion effect are also discussed.

Introduction

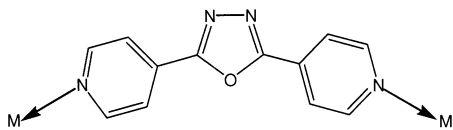
The rational design of multidimensional infinite architecture has been an interesting area of chemistry that has received ever-increasing attention because the topology of the network profoundly influences the final bulk physical and chemical properties and functions of the solid.¹ The interpenetrating polymeric networks, such as the diamondoid structure motif that can be observed for 3D structures based upon tetrahedral building blocks, is now becoming increasingly common.² Topologically related coordination polymers where tetrahedral metal cations (Cu^I and Ag^I) are linked together with spacer ligands display the tendency to form diamondoid networks with various degrees of interpenetration including 2-fold,³ 3-fold,⁴ 4-fold,⁵ 5-fold,⁶ 7-fold,⁷ 9-fold,⁸ and *even* 11-fold⁹ degeneracy, which can be regarded as infinite “poly-catenanes”.¹⁰

In our efforts^{1h,11} to investigate the control of the self-assembly of an organic/inorganic supramolecular motif, 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (L), an angular dipyriddy ligand (see Chart 1) has attracted our attention in connection with structural control of discrete or divergent coordination

- (1) For examples: (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494. (b) Yaghi, O. M.; Li, H.; David, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474–484. (c) Chui, S. S.-Y.; Lo, S. M.-F.; Chartmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148–1150. (d) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638–2684. (e) Reineke, T. M.; Eddaoudi, M.; Moler, D.; O’Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 4843–4844. (f) Zaworotko, M. J. *Chem. Commun.* **2001**, 1–9. (g) Leininger, S.; Olenyuk, B.; P. J. Stang. *Chem. Rev.* **2000**, *100*, 853–908. (h) Bu, X. H.; Chen, W.; Lu, S. L.; Zhang, R. H.; Liao, D. Z.; Shionoya, M.; Brisse, F.; Ribas, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3201–3203. (i) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O’Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021–1023. (j) Katsuki, I.; Motoda, Y.; Sunatsuki, Y.; Matsumoto, N.; Nakashima, T.; Kojima, M. *J. Am. Chem. Soc.* **2002**, *124*, 629–640. (k) Noro, S. I.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. *J. Am. Chem. Soc.* **2002**, *124*, 2568–2583.

* Corresponding author. E-mail: buxh@nankai.edu.cn. Fax: +86-22-23530850.

Chart 1



networks. This ligand has a rigid 137° angle between the central oxadiazole ring and two N-donors of the 4-pyridine rings and, therefore, could potentially provide both discrete and divergent products upon metal complexation under appropriate conditions. We describe here the synthesis and crystal structure of the *first* Cu^{II} diamondoid complex with 2-fold interpenetrating nets. The effects of different anions on product formation and magnetic properties have also been studied.

Experimental Section

Materials and General Methods. Most of the starting materials and solvents for syntheses were obtained commercially and used as received. The ligand L was synthesized according to the literature method.¹² FTIR spectra (KBr pellets) were taken on an FTIR 170SX (Nicolet) spectrometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer 240C analyzer. ESR spectra were recorded on powder samples at X-band frequency with a Bruker 300E automatic spectrometer, varying the temperature between 4 and 300 K. The variable-temperature magnetic susceptibilities were measured in the “Servei de Magnetoquímica (Uni-

versitat de Barcelona)” with a Quantum Design MPMS SQUID susceptometer operating at a magnetic field of 0.1 T between 2 and 300 K. The diamagnetic corrections were evaluated from Pascal’s constants for all the constituent atoms. XPRD data were recorded on a Rigaku RU200 diffractometer at 60 kV, 300 mA for Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), with a scan speed of 2 deg/min and a step size of 0.02° in 2θ . Thermal stability (TG-DTA) experiments were carried out on a Dupont thermal analyzer from room temperature to 800 °C under helium atmosphere at a heating rate of 10 °C/min.

Syntheses of Cu^{II} Complexes. $\{[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2](\text{ClO}_4)(\text{OH})(\text{H}_2\text{O})_{2.5}\}_n$ (**1**). Complex **1** was prepared by mixing the ligand L (115 mg, 0.5 mmol) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (92 mg, 0.25 mmol) in molar ratios of 2:1 in a methanol/water medium. After ca. 30 min of stirring, the blue solution was filtered and left to stand at room temperature. Block blue single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent. Yield: 90%. Found: C, 40.21; H, 4.18; N, 15.69. Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{ClCuN}_8\text{O}_{11.5}$: C, 40.63; H, 3.69; N, 15.80. IR (KBr, cm^{-1}): ν 3424b, 3107m, 1625s, 1569m, 1547m, 1488m, 1429s, 1101vs, 1079s, 1059vs, 624s. It should be noted that the well-shaped blue crystals of complex **1** are unstable when exposed to air (change into light-blue powders having the same composition as the crystals) and the structure was determined in a sealed capillary.

$[\text{Cu}(\text{L})_2(\text{OAc})_2(\text{H}_2\text{O})_2](\text{CH}_3\text{OH})$ (**2**). The same synthetic procedure as for **1** was used except that the $\text{Cu}(\text{ClO}_4)_2$ was replaced by $\text{Cu}(\text{OAc})_2$ ($\text{OAc}^- = \text{acetate anion}$), giving dark-blue single crystals in 65% yield. Found: C, 48.57; H, 4.29; N, 15.77. Anal. Calcd for $\text{C}_{29}\text{H}_{32}\text{CuN}_8\text{O}_{10}$: C, 48.63; H, 4.50; N, 15.65. IR (KBr, cm^{-1}): ν 3387b, 1618s, 1607s, 1588s, 1563vs, 1544s, 1486m, 1420vs, 1387s, 1334s, 1219m, 1061m, 758s.

Caution. Although no problems were encountered in this study, transition metal perchlorate complexes are potentially explosive and should be handled with proper precautions.

X-ray Data Collection and Structure Determinations. Single-crystal X-ray diffraction studies of complexes **1** ($0.35 \times 0.30 \times 0.20 \text{ mm}^3$) and **2** ($0.30 \times 0.25 \times 0.20 \text{ mm}^3$) were performed on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) with ω scan mode in the range $3.40^\circ < \theta < 25.03^\circ$ (for **1**) and $2.66^\circ < \theta < 25.03^\circ$ (for **2**). The program SAINT¹³ was used for integration of the diffraction profiles. Both structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL (semiempirical absorption corrections were applied using SADABS program).¹⁴ Cu^{II} atoms in each complex were located from the E-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 . Hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Further details for structural analysis are summarized in Table 1.

Results and Discussion

Synthesis and General Characterization. Compound **1** was obtained as blue block crystals in 90% yield by the

- (2) (a) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 4878–4883. (b) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. In *Supramolecular Architecture: Synthetic Control in Thin Films and Solids*; Bein, T., Ed.; ACS Symposium Series 499; American Chemical Society: Washington, DC, 1992; pp 256–273. (c) Blake, A. J.; Champness, N.; Hubberstey, P.; Li, W.-S.; Withersby, A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117–138. (d) Batten, S. R.; Robson, R. *Molecular Catenanes, Rotaxanes and Knots, A Journey Through the World of Molecular Topology*; Sauvage, J. P., Dietrich-Buchecker, C., Eds.; Wiley-VCH: Weinheim, 1999; pp 77–105. (e) Batten, S. R. *CrystEngComm* **2001**, *18*, 1–7.
- (3) (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546–1554. (b) Yaghi, O. M.; Li, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 207–209. (c) Lopez, S.; Kahraman, M.; Harmata, M.; Keller, S. W. *Inorg. Chem.* **1997**, *36*, 6138–6140.
- (4) (a) Blake, A. J.; Champness, N. R.; Khlobystov, A. N.; Lemenovskii, D. A.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 1339–1340. (b) Siebel, E.; Ibrahim, A. M. A.; Fischer, R. D. *Inorg. Chem.* **1999**, *38*, 2530–2532.
- (5) (a) MacGillivray, L. R.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325–1326. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755–2756. (c) Carlucci, L.; Ciani, G.; Moret, M.; Proserpio, D. M.; Rizzato, S. *Chem. Mater.* **2002**, *14*, 12–16.
- (6) (a) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 1005–1006. (b) Ino, I.; Zhong, J. C.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Kitamori, Y. *Inorg. Chem.* **2000**, *39*, 4273–4279.
- (7) Sinzer, K.; Hünig, S.; Jopp, M.; Bauer, D.; Bietsch, W.; von Schütz, J. U.; Wolf, H. C.; Kremer, R. K.; Metzenthin, T.; Bau, R.; Khan, S. I.; Lindbaum, A.; Lengauer, C. L.; Tillmanns, E. *J. Am. Chem. Soc.* **1993**, *115*, 7696–7705.
- (8) Hirsch, K. A.; Venkataraman, D.; Wilson, S. R.; Moore, J. S.; Lee, S. *J. Chem. Soc., Chem. Commun.* **1995**, 2199–2200.
- (9) Reddy, D. S.; Dewa, T.; Endo, K.; Aoyama, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 4266–4268.
- (10) Whang, D.; Kim, K. *J. Am. Chem. Soc.* **1997**, *119*, 451–452.
- (11) (a) Bu, X. H.; Chen, W.; Du, M.; Zhang, R. H. *CrystEngComm* **2001**, *30*, 1–3. (b) Bu, X. H.; Chen, W.; Du, M.; Biradha, K.; Wang, W. Z.; Zhang, R. H. *Inorg. Chem.* **2002**, *41*, 437–439. (c) Bu, X. H.; Weng, W.; Du, M.; Chen, W.; Li, J. R.; Zhang, R. H.; Zhao, L. J. *Inorg. Chem.* **2002**, *41*, 1007–1010.
- (12) Bentiss, F.; Lagrenee, M. *J. Heterocycl. Chem.* **1999**, *36*, 1029–1032.

- (13) *SAINT Software Reference Manual*; Bruker AXS: Madison, WI, 1998.
- (14) Sheldrick, G. M. *SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystal Data and Structure Refinement Parameters for $\{[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2](\text{ClO}_4)(\text{OH})(\text{H}_2\text{O})_{2.5}\}_n$ (**1**) and $[\text{Cu}(\text{L})_2(\text{OAc})_2(\text{H}_2\text{O})](\text{H}_2\text{O})_2(\text{CH}_3\text{OH})$ (**2**)

	1	2
chemical formula	$\text{C}_{24}\text{H}_{26}\text{ClCuN}_8\text{O}_{11.5}$	$\text{C}_{29}\text{H}_{32}\text{CuN}_8\text{O}_{10}$
fw	709.52	716.17
cryst syst	tetragonal	triclinic
space group	$I4_1/a$	$P\bar{1}$
T (K)	293(2)	293(2)
a (Å)	13.477(3)	7.847(2)
b (Å)	13.477(3)	13.189(4)
c (Å)	46.167(13)	15.948(5)
α (deg)	90	75.225(7)
β (deg)	90	79.945(6)
γ (deg)	90	77.540(5)
V (Å ³)	8385(3)	1545.8(8)
Z	8	2
ρ_{calcd} (g/cm ³)	1.124	1.539
μ (cm ⁻¹)	6.37	7.78
R^a	0.0579	0.0582
R_w^b	0.1132	0.1237

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

reaction of $\text{Cu}(\text{ClO}_4)_2$ and the neutral dipyriddy ligand **L**. The thermogravimetric analysis under helium of compound **1** shows that there is no loss of weight except solvents until heating to 160 °C (see Supporting Information); however, as stated previously, the crystals are not stable when exposed to air even at room temperature. X-ray powder diffraction (see Supporting Information) shows that part of the crystals has changed into an amorphous substance, although some major features could be found compared with the theoretic powder pattern (the calculated XPRD pattern was produced using the SHELXTL-XPOW program and single-crystal reflection data). When the sample of **1** was heated to 120 °C inside an oven for 4 h, the crystal structure collapsed completely, and a green amorphous substance was obtained. In the IR spectra of both complexes, the broad band centered at ca. 3400 cm⁻¹ indicates the O–H stretching of the solvent molecules, and the absorption bands resulting from the skeletal vibrations of aromatic rings appear in the 1400–1600 cm⁻¹ region. For **1**, the occurrence of split $\nu_{\text{Cl-O}}$ stretches of the ClO_4^- ions at ~1100 cm⁻¹ provides good evidence of their involvement in the formation of hydrogen bonding. The IR spectra for **2** display the characteristic bands of the acetate anions at 1618 and 1607 cm⁻¹ for $\nu_{\text{asym}(\text{C-O})}$, 1387 and 1334 cm⁻¹ for $\nu_{\text{sym}(\text{C-O})}$, and 758 cm⁻¹ for $\delta_{(\text{O-C-O})}$. The Δ values ($\nu_{\text{as}} - \nu_{\text{sym}}$) indicate that the acetate anions coordinate to the Cu^{II} center in monodentate mode, which is consistent with the crystal structure as described later.

X-ray Single-Crystal Structures. The structure of **1** contains an octahedral Cu^{II} atom, located on a crystallographic 2-fold axis that is coordinated to four trans ligands **L** and two axial water ligands. The ORTEP view of the coordination geometry around the central Cu^{II} ion is shown in Figure 1. The Cu^{II} center shows considerable Jahn–Teller distortion (see Table 2), with the axial Cu–O distance (2.470(3) Å) elongated in comparison to the two independent Cu–N equatorial distances (2.022(4) and 2.028(4) Å). The structure also contains one disordered perchlorate anion and four water molecules of solvation per Cu^{II}. The positions of the disordered water molecules were refined at half or quarter

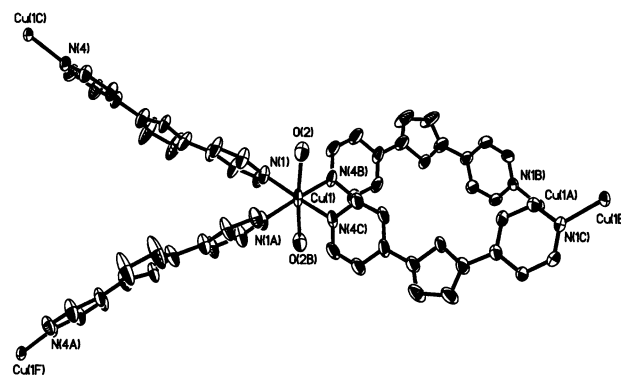


Figure 1. ORTEP structure for the coordination geometry around the Cu^{II} center in complex **1**.

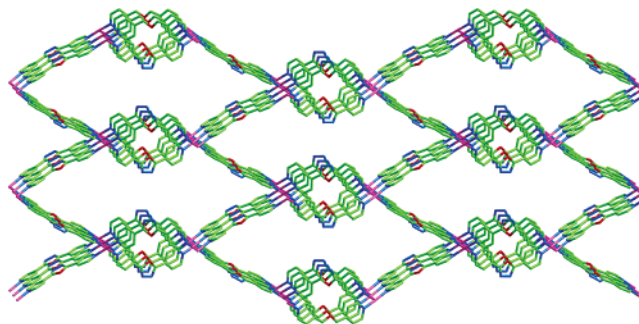


Figure 2. The diamondlike 3D network of **1** (the water ligands are omitted).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **1**

Cu(1)–N(1)	2.029(4)	Cu(1)–N(4B)	2.017(4)
Cu(1)–O(2)	2.470(3)		
N(4B)–Cu(1)–N(4C)	88.7(2)	N(4C)–Cu(1)–N(1)	175.24(18)
N(4B)–Cu(1)–N(1)	92.69(15)	N(1A)–Cu(1)–N(1)	86.3(2)
O(2)–Cu(1)–O(2B)	174.5(2)	O(2)–Cu(1)–N(1)	88.5(2)
O(2)–Cu(1)–N(1A)	95.5(2)	O(2)–Cu(1)–N(4)	89.1(2)
O(2)–Cu(1)–N(4A)	87.0(2)		

site occupancy. As for the Cu atom, given the octahedral geometry and blue color of the crystals, it is obviously in the oxidation state +2 (further confirmed by magnetic measurement as described later). Thus, one of the water molecules must be OH⁻, although a definite assignment could not be made.

The ligands **L** connect the Cu^{II} atoms into 3D diamondlike¹⁵ networks as depicted in Figure 2. The mean atomic displacement from the least-squares plane of **L** is equal to 0.0567 Å. Although the bridging ligands coordinate to the metal atoms in a square-planar arrangement, the bent geometry of these ligands allows the metal centers to act effectively as distorted tetrahedral nodes. The Cu–L–Cu angle is 125.3°, and the dihedral angle of two opposite trans ligand (**L**) planes is 102.2°. Because of the spacious nature of the network, there is, in fact, a pair of identical complementary diamondoid networks, which interpenetrate to generate the crystal structure in the normal fashion.^{15,16} As can be seen in Figure 3, the diamondlike nets are

(15) Wells, A. F. *Three-dimensional Nets and Polyhedra*; Wiley-Interscience: New York, 1977.

(16) (a) Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2002**, *124*, 376–377. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *Chem.—Eur. J.* **2002**, *8*, 1519–1526.

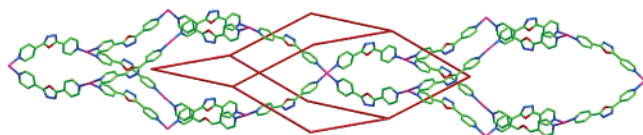


Figure 3. Interpenetrating adamantane cages from the two separate networks in **1** (the adamantane unit of one of the nets is shown schematically).

significantly distorted such that the adamantane cavities are considerably elongated in the z -direction. The Cu–Cu distance across the diamondoid cavity parallel to the z -axis (46.2 Å) is more than twice the two topologically equivalent distances perpendicular to this axis (19.1 Å). A notable feature in this structure is the lack of π – π stacking interactions that are often observed in interpenetrating diamondoid network structures (in most cases, the ligands are in fact side-on to their nearest neighbors from the other network).^{3–9} This may be due to the elongation of the cavities in the z -direction. In addition, the coordinated water molecules, perchlorate anions, and three of the four crystallographically distinct waters of solvation are involved in 2D hydrogen bonding networks parallel to the xy -plane. The coordinated water ligands and two of the solvent water molecules participate in two hydrogen bonds each, while the third solvent water participates in four hydrogen bonds. The disordered perchlorate anion makes two hydrogen-bonding interactions with solvent water molecules. An analysis of the voids¹⁷ shows ca. 20% of the space empty even if calculated with the water molecules, and after the removal of these solvents, the empty space adds up to 44%, and a set of mutually perpendicular cylindrical channels running along [100] and [010] directions are visible. Almost all the previously reported metal–organic diamondoid frameworks were constructed from tetrahedral metal and either linear or tetrahedral link species. The present structure represents a unique extended Cu^{II} coordination polymer that shows the propensity of the system to adopt a diamondlike structure, even if it contains the dramatically angular bridging ligand.

To examine the role of counterions in the formation of the interpenetrated diamondoid nets, the reaction was repeated with Cu(OAc)₂ instead of Cu(ClO₄)₂. Single-crystal X-ray analysis of **2** reveals the formation of an unexpected mononuclear complex and not the anticipated diamondoid net. Here, the Cu^{II} center is pentacoordinated (CuN₂O₃) to two L molecules and two OAc[–] anions forming the basal planes, and one aqua ligand at the apical positions as shown in Figure 4. Important bond lengths and angles are listed in Table 3. The coordination polyhedron for Cu(1) could be best described as a square-pyramid, which is reflected by the τ value (0.01 here) defined by Addison et al. ($\tau = 0$ for an ideal square pyramid, and 1 for an ideal trigonal bipyramid).¹⁸ Cu(1) atom is 0.161 Å above the mean basal plane defined by N(1)–N(5)–O(4)–O(5) toward the apical

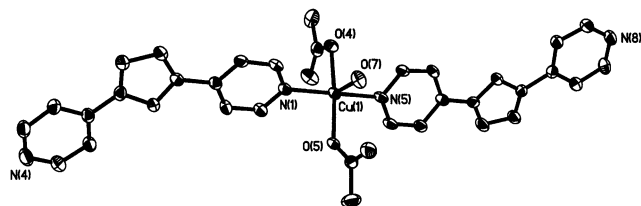


Figure 4. ORTEP structure for the neutral mononuclear complex **2** showing 50% thermal ellipsoids.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **2**

Cu(1)–O(5)	1.956(3)	Cu(1)–O(4)	1.966(3)
Cu(1)–N(1)	2.038(4)	Cu(1)–N(5)	2.052(4)
Cu(1)–O(7)	2.299(3)		
O(5)–Cu(1)–O(4)	166.94(13)	O(5)–Cu(1)–N(1)	91.50(12)
O(4)–Cu(1)–N(1)	88.64(13)	O(5)–Cu(1)–N(5)	89.42(12)
O(4)–Cu(1)–N(5)	89.18(13)	N(1)–Cu(1)–N(5)	174.26(16)
O(5)–Cu(1)–O(7)	97.20(13)	O(4)–Cu(1)–O(7)	95.85(13)
N(1)–Cu(1)–O(7)	92.19(13)	N(5)–Cu(1)–O(7)	93.32(13)

O(7) atom. It should be noted that, in this complex, the ligand L uses only one of the four nitrogen donors, acting as a *monodentate* ligand, and the dihedral angle of the two trans L planes is only 5.0°.

Magnetic Properties of Complex 1. Magnetic measurement was carried out in a magnetic field of 0.1 T in the temperature range 2–300 K, and ESR spectra were recorded in the solid state at X-band (see Supporting Information). The value of $\chi_M T$ at room temperature is 0.416 cm³ mol^{–1} K, corresponding to an isolated Cu^{II} ion without any coupling ($g = 2.1$ approximately). The $\chi_M T$ value is maintained at a constant, decreasing slightly from 25 K, achieving a value of 0.40 cm³ mol^{–1} K at 2 K. This global feature is characteristic of a paramagnet following the Curie law for an $S = 1/2$ Cu^{II} ion. Taking the structure into account, the Cu^{II} ions are linked to each other by a long organic fragment in which the possibility of overlap of magnetic orbitals through the C and N atoms of the ligand L is negligible. The shortest Cu–Cu distance is 13.4 Å; thus, the coupling is nil, and the system behaves as paramagnetic (at very low temperature, some very small intra- or intermolecular coupling is shown). The ESR spectra of **1** have been registered at different temperatures (from room temperature to 4 K), and there is no important variation with the temperature. In all temperatures, it exhibits the typical pattern for a square geometry (or elongated octahedron, due to the water molecules), with the unpaired electron mainly located in the $d_{x^2-y^2}$ orbital ($g_{\parallel} (2.16) > g_{\perp} (2.06) > 2.00$). The g_{\parallel} part is broader indicating the hyperfine coupling, which is more visible at 4 K.

Conclusion and Comments

Whereas diamondoid structures based on tetrahedral Cu^I or Ag^I were well-known before this study, such a framework based upon Cu^{II} in **1** is rare. The present study also clearly indicates the important role that the coordination ability of the counteranions can play in crystal engineering and suggests that, given the simple permutations of the anions, Cu^{II} alone might have a rich and diverse role in framework chemistry. We hope that the use of larger anions (such as

(17) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: The Netherlands, 1999.

(18) (a) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356. (b) O'Sullivan, C.; Murphy, G.; Murphy, B.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1999**, 1835–1844.

BPh₄⁻) or a bulky substituent on one of the pyridine rings will prevent interpenetration and create large, acentric voids in the structure which can be used to include (and possibly manipulate) a variety of chiral molecules.

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China (No. 29971019), the Australian Research Council, and the Spanish

government (Grant BQU2000-0791). We also thank Prof. Hong-Gen Wang for X-ray data collection.

Supporting Information Available: X-ray crystallographic data in CIF format, ESR spectra, TGA curve, XPRD diffractograms, and magnetic diagram of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC025559+