2420 *Inorg. Chem.* **2001,** *40,* 2420−2423

Notes

Tetrakis[(μ-hydroxo)(μ-sulfathiazolato)copper(II)] Tetrakis(dimethyl sulfoxide): A New Square-Planar Tetranuclear Copper(II) Complex Containing Four Hydroxo and Four NCN-Sulfathiazolato Bridges. Electrochemical Synthesis, Crystal Structure, and Magnetic Properties

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Received November 8, 2000

Introduction

The design of high- or low-nuclearity transition-metal clusters with novel magnetic properties is a major goal of current research. Tetranuclear copper(II) clusters are of present interest in bioinorganic modeling, multielectron transfer, catalysis, and magnetostructural research. There are many examples of Cu_4 arrays, which exhibit a large diversity of structural types,[1,2] although the most common arrangement of tetranuclear Cu(II) compounds is tetrahedral.[3] However, very few compounds with planar cyclic Cu_4 cores have been fully characterized.[4] Among the Cu_4 arrays, structurally and magnetically characterized planar cyclic structures with no diagonal bridging groups are rather scarce.[5−8] Recently, the first example of a tetranuclear copper(II) complex with a square-planar ring of copper(II) atoms has been reported.[9] The complex described here is, to our knowledge, the first example of a square-planar tetranuclear copper(II) complex where the magnetic ions are bridged by four OH^- groups and by four NCN′ moieties. This complex seems to be derived from the previously reported dimer [Cu_2(μ-sulfathiazolato)$_4$].[10]

Experimental Section

Material and Physical Methods. The variable-temperature magnetic susceptibility measurements were carried out on a microcrystalline sample (4 mg) using a Quantum Design MPMS2 SQUID susceptometer equipped with a 55 kG magnet and operating at 10 kG in the range of 1.8−400 K. The susceptometer was calibrated with $(NH_4)_2Mn(SO_4)_2\cdot 12H_2O$. Corrections for the diamagnetism were estimated from Pascal constants. The infrared spectra (ν 400−4000 cm^{-1}) were obtained on a Mattson Satellite FTIR spectrophotometer. Elemental analyses were carried out on a Carlo Erba AAS instrument. EPR spectra of ground crystals were determined at X-band with a Bruker ER200D instrument.

All chemicals were used as purchased without further purification. Copper (Baker a.r.) was used as 1 × 1 cm plates.

Electrochemical Synthesis of the Compound. The electrochemical procedure was similar to that described by Odhaln and Tuck.[11] The cell was a 100 cm^3 beaker fitted with a rubber bung, through which the electrochemical leads entered the cell. The copper anode was suspended from a platinum wire, and another platinum wire formed the cathode. A small amount of tetrabutylammonium perchlorate was added as current carrier. Direct current was obtained from a purpose-built dc power supply.

Electrolysis of a dmso solution containing sulfathiazole (0.25 g, 1 mmol) and tetrabutylammonium perchlorate (24 mg) at 20 mA and 12 V for 1 h 20 min dissolved 49.5 mg of copper ($E_f = 0.78$). At the end of the experiment a dark brownish green solution of the title compound was obtained. After 2−4 days single crystals suitable for X-ray diffraction were obtained. Yield: 42%. Anal. Calcd for $C_{44}H_{60}Cu_4N_{12}O_{16}S_{12}$ (1651.92): C, 31.99; H, 3.66; N, 10.17; Cu, 15.38. Found: C, 32.09; H, 3.45; N, 10.07; Cu, 15.25. Selected IR bands (KBr; cm^{-1}): 3550, 1618 (O−H); 3480, 3390 (N−H); 1469 (thiazole ring); 1320−1284, 1130, 570−550 (SO_2); 948 (S−N).

X-ray Structure Determination. The title compound was a pale red crystal, of size 0.20 × 0.13 × 0.06 mm. Mo Kα radiation was used with a graphite crystal monochromator on a Nonius CAD-4 single-crystal diffractometer ($\lambda = 0.710\ 73$ Å). The unit-cell dimensions were determined from the angular settings of 25 reflections with $10 < \theta < 15°$. The intensity data of 6817 reflections, in the *hkl* range −19, 0, 0 to 19, 11, 20 and θ limits $0 < \theta < 26°$ were measured using the $\omega - 2\theta$ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. The intensity decay was 73.04%, indicating a very unstable crystal. For all reflections collected, a profile analysis was performed.[12,13] Some double-measured reflections were averaged; $R_{int} = I - \langle I \rangle / I = 0.1053$, resulting in 5664 “unique” reflections, of which only 1838 with $I > 2\sigma(I)$ were observed. Lorentz and polarization corrections were applied, and the data were reduced to F_o^2 values. The structure was solved by Patterson methods.[14] Isotropic least-squares refinement on F^2 was made.[15] An empirical absorption correction was applied.[16] The relative maximum and minimum transmission factors were respectively 1.0 and 0.80. During the final stages of the refinement on F^2 the positional parameters and the anisotropic thermal parameters

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(1) Hathaway B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gill, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 5, Chapter 53.

(2) Murray, K. S. *Adv. Inorg. Chem.* **1995**, *43*, 261.

(3) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 259.

(4) Wang, S.; Trepanier, S. J.; Zheng, J. C.; Wagner, M. J. *Inorg. Chem.* **1992**, *31*, 2118.

(5) Kolks, G.; Lippard, S. J.; Waszczack, J. V.; Lilienthal, H. R. *J. Am. Chem. Soc.*, **1982**, *104*, 717.

(6) McKee, V. M.; Tandon, S. S. *J. Chem. Soc., Dalton Trans.* **1992**, 221.

(7) Chaudhuri, P.; Karpenstein, I.; Winter, M.; Lengen, M; Butzlaff, C.; Bill, E.; Trautwein, A. X.; Flörke, U.; Haupt, H. P. *Inorg. Chem.* **1993**, *32*, 888.

(8) Mimura, M.; Matsuo, T.; Nakashima, T.; Matsumoto, N. *Inorg. Chem.* **1998**, *37*, 3553.

(9) Colacio, E.; Lopez-Magaña, C.; Mckee, V.; Romerosa, A. *J. Chem. Soc., Dalton Trans.* **1999**, 2923.

(10) Casanova, J.; Alzuet, G.; LaTorre, J.; Borrás, J. *Inorg. Chem*. **1997**, *36*, 2052.

(11) Odlhan, C.; Tuck, D. G. *J. Chem. Educ.* **1982**, *59*, 420.

(12) Lehman, M. S.; Larsen, F. K. *Acta Crystallogr.* **1974**, *A30*, 580.

(13) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.

(14) Beurskens, P. T.; Admiraall, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *DIRDIF User’s Guide*; Technical Report; Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands.

(15) Sheldrick, G. M. SHELXL93. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, P., Simon, K., Eds.; IUCr/Oxford University Press: Oxford, U.K., 1993.

(16) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

10.1021/ic001239j CCC: $20.00

Table 1. Crystal Data and Structure Refinement for $[Cu_4(L)_4(OH)_4]\cdot 4dmso$

empirical formula	$C_{44}H_{60}Cu_4N_{12}O_{16}S_{12}$
fw	1651.92
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	16.129(6)
b (Å)	9.135(5)
c (Å)	21.538(16)
β (deg)	91.36(4)
V, Å^3	3172(3)
Z	8
ρ_{calcd}, mg/m^3	1.725
μ, cm^{-1}	17.90
T, K	293(2)
R1[a]	0.0615
wR2[a]	0.1445

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0955P)^2 + 2.3100P]$, $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$.

of the non-H atoms were refined. All non-hydrogen atoms were anisotropically refined, except the atoms of the two disordered dmso molecules. These have been refined in two different positions. Occupation factors are respectively as follows: dmso 1 = C(20), C(21), S(20), O(20), position a 0.708(13), position b 0.292(13); dmso 2 = C(30), C(31), S(30), O(30), position a 0.550(16), position b 0.450(16). All hydrogen atoms were geometrically placed and isotropically refined. The final conventional agreement factors were R1 = 0.0615 and wR2 = 0.1445 for the 1838 observed reflections and 388 variables. The final difference Fourier map showed no peaks higher than 0.829 e Å^{-3} nor deeper than −0.911 e Å^{-3}.

Atomic scattering factors were taken from ref 17. Geometrical calculations were carried out with PARST.[18] All calculations were carried out at the University of Oviedo on the Scientific Computer Centre and X-ray group DEC/AXP computers. Crystal data are collected in Table 1.

Results and Discussion

The electrochemical oxidation of the sacrificial metal anode, copper, in a dmso solution proved to be a convenient route to obtain a dark brownish green solution that gives rise after 2 or 4 days single crystals of the title compound. The chemical efficiency of 0.78 indicates a complex process in the electrochemical method probably due to the formation of the Cu(I) (E_f = 1) and Cu(II) (E_f = 0.5) ions, in accord with the mechanism

$$\text{cathode: } HL + e^- \rightarrow {}^1/_2H_2 + L^-$$

$$\text{anode: } Cu \rightarrow Cu^+ + e^- \qquad E_f = 1$$

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad E_f = 0.5$$

Later the Cu$^+$ is oxidized by the O$_2$ according to the reaction scheme

$$Cu^+ + {}^1/_2O_2 + H_2O \rightarrow Cu^{2+} + 2OH^-$$

Finally

$$4Cu^{2+} + 4L^- + 4OH^- \rightarrow [Cu_4(L)_4(OH)_4]$$

Crystal Structure. The complex consists of discrete $[Cu_4(L)_4(OH)_4]$ molecules linked by intermolecular hydrogen bonds between the hydroxo, the O$_{sulfonamido}$, and the N$_{amino}$ atoms from the sulfathiazolate ligands and the four disordered dmso molecules (hydrogen bond distances ranging from 2.708 to 3.088 Å). The molecular geometry and the atom-labeling scheme are shown in Figure 1. Selected bond lengths and angles are listed in Table 2.

The four Cu(II) ions in the centrosymmetric unit are arranged at the vertexes of a square-planar parallelogram with edge and diagonal Cu···Cu distances of 2.887−2.901 and 4.09 Å, respectively. The four OH$^-$ bridging ligands show also a square-planar arrangement, the two planes Cu$_4$ and (OH$^-$)$_4$ being perpendicular between them. Each Cu(II) is linked to one Cu(II) through the NCN′ groups from two sulfathiazolate ligands and to another Cu(II) through two OH$^-$ bridges. The angles Cu(2)−Cu(1)−Cu(2a) and Cu(1)−Cu(2)−Cu(1a) are 91.86(7) and 88.14(7)°, respectively, confirming that the four Cu(II) ions are in the same square plane. The angles Cu(1)−O(1a)−Cu(2a) and Cu(1)−O(2a)−Cu(2a) are 97.3(4) and 98.3(4)°, respectively. To our knowledge, this is the first tetranuclear $Cu_4(OH)_4(NCN')_4$ entity with this geometry (see Chart 1).

The Cu(1) is linked to the oxygen atoms of the hydroxo anions at distances of 1.920(7) and 1.901(9) Å and to the N(1) and N(4) atoms at distances of 1.953(12) and 2.031(9) Å. The Cu(2) presents bond distances to O(1), O(2), N(2), and N(3) of 1.923(9), 1.912(8), 2.003(11), and 1.937(9) Å, respectively. The Cu−OH bond distances are similar to those reported for other Cu(II) complexes with OH$^-$ bridges.[19] The Cu−N distances are similar to those found in the Cu$_2$(μ-sulfathiazolato)$_4$ complex.[10] Each Cu(II) ion has a highly distorted square-planar arrangement.

The monoanion of the sulfathiazole acts as a bridging ligand through the sulfonamidate and thiazole N atoms in a form similar to that reported by us in the binuclear Cu$_2$(μ-sulfathiazolato)$_4$ complex.

Spectroscopic Properties. The IR spectrum of the title compound shows the same pattern as that of Cu$_2$(μ-sulfathiazolato)$_4$. Furthermore, it exhibits a medium-intensity band at 3550 cm^{-1} due to the stretching vibration of the bridging O−H.[19]

Magnetic Properties. The temperature dependence of the molar magnetic susceptibility, χ_M, for the title compound in the temperature range 4.5−300 K is shown in Figure 2. At room temperature, χ_M is 4.72 × 10^{-3} cm^3 mol^{-1}, a value which is somewhat smaller than that expected for four magnetically uncoupled copper(II) ions ($\chi_M = 5.01 \times 10^{-3}$ cm^3 mol^{-1}, g = 2). Upon cooling, χ_M increases, reaching a maximum at around 54 K, $\chi_M = 11.32 \times 10^{-3}$ cm^3 mol^{-1}. Then χ_M decreases rapidly as the temperature is decreased. This behavior is characteristic of dominant antiferromagnetic coupling between the adjacent copper ions. The low-temperature tail corresponds to paramagnetic impurities.

According to the crystal structure data, the compound is a tetranuclear entity, which requires three coupling constants. However, we have not considered the "diagonal" coupling constant involving the spin carriers 1 and 3 and 2 and 4 (Chart 2) because it is expected to be considerably smaller than J_1 and J_2. Furthermore, the "diagonal" coupling constant has not been taken into account in order to avoid overparametrization. Hence, only two coupling constants are considered, as is shown in Chart 2.

For this system the appropriate Hamiltonian is[20]

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(17) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974 (present distributor Kluwer Academic Publishers, Dordrecht, The Netherlands); Vol. IV.

(18) (a) Nardelli, M. *Comput. Chem*. **1983**, *7*, 95. (b) Nardelli, M. *Acta Crystallogr.* **1983**, *C39*, 1141.

(19) Christou, G.; Perlepes, S. P.; Libby, E.; Foltong, K; Huffman, J. C.; Webb, R. J.; Hendrickson, D. N. *Inorg. Chem.* **1990**, *29*, 3657.

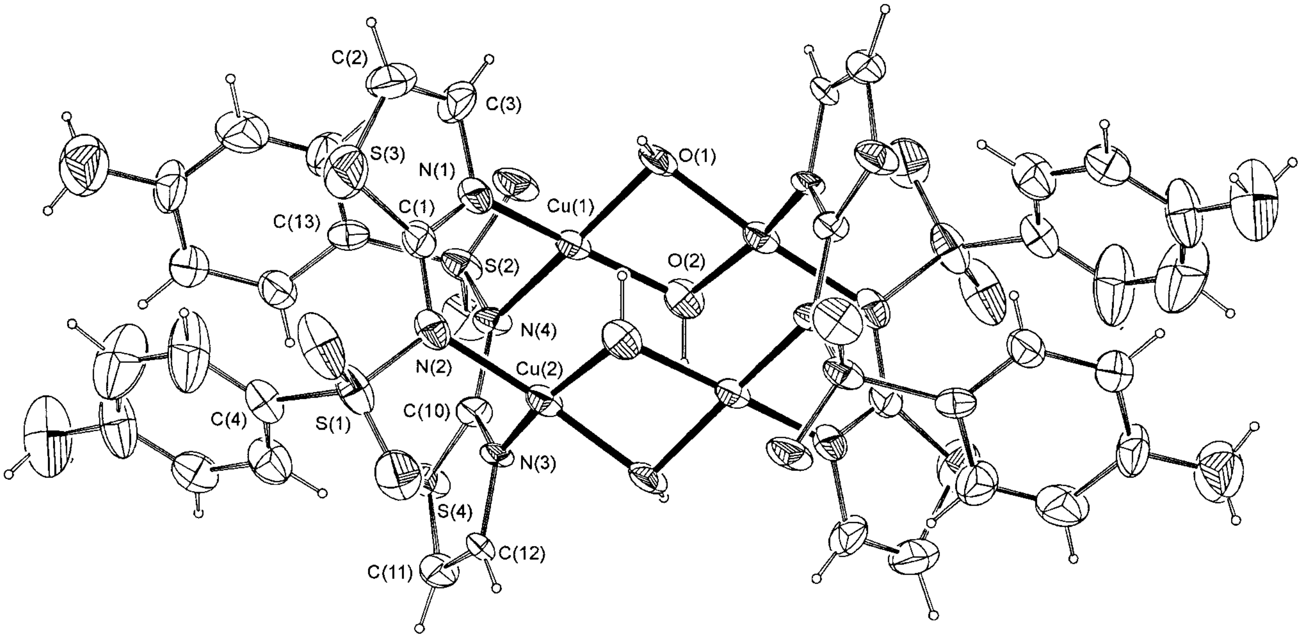


Figure 1. Molecular structure of $[Cu_4L_4(OH)_4]\cdot 4dmso$ showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_4(L)_4(OH)_4]\cdot 4dmso$[a]

Cu(1)−O(2)	1.901(9)	Cu(2)−O(2)	1.912(8)
Cu(1)−O(1)	1.920(7)	Cu(2)−O(1)	1.923(9)
Cu(1)−N(1)#1	1.953(12)	Cu(2)−N(3)	1.937(9)
Cu(1)−N(4)	2.031(9)	Cu(2)−N(2)	2.003(11)
Cu(1)−Cu(2)	2.887(3)	Cu(2)−Cu(1)#1	2.901(2)
Cu(1)−Cu(2)#1	2.901(2)		
O(2)−Cu(1)−O(1)	79.1(4)	O(2)−Cu(2)−O(1)	78.8(3)
O(2)−Cu(1)−N(1)#1	162.4(4)	O(2)−Cu(2)−N(3)	161.9(4)
O(1)−Cu(1)−N(1)#1	92.2(4)	O(1)−Cu(2)−N(3)	92.2(4)
O(2)−Cu(1)−N(4)	96.8(4)	O(2)−Cu(2)−N(2)	97.7(4)
O(1)−Cu(1)−N(4)	166.5(4)	O(1)−Cu(2)−N(2)	169.2(4)
N(1)#−Cu(1)−N(4)	94.9(4)	N(3)−Cu(2)−N(2)	93.8(4)
O(2)−Cu(1)−Cu(2)	40.9(2)	O(2)−Cu(2)−Cu(1)	40.6(3)
O(1)−Cu(1)−Cu(2)	41.3(3)	O(1)−Cu(2)−Cu(1)	41.3(2)
N(1)#−Cu(1)−Cu(2)	125.1(3)	N(3)−Cu(2)−Cu(1)	124.9(3)
N(4)−Cu(1)−Cu(2)	137.4(3)	N(2)−Cu(2)−Cu(1)	137.8(3)
O(2)−Cu(1)−Cu(2)#1	86.6(3)	O(2)−Cu(2)−Cu(1)#1	83.8(3)
O(1)−Cu(1)−Cu(2)#1	114.5(2)	O(1)−Cu(2)−Cu(1)#1	111.4(2)
N(1)#1−Cu(1)−Cu(2)#1	83.1(3)	N(3)−Cu(2)−Cu(1)#1	84.9(3)
N(4)−Cu(1)−Cu(2)#1	77.8(2)	N(2)−Cu(2)−Cu(1)#1	78.1(3)
Cu(2)−Cu(1)−Cu(2)#1	91.86(7)	Cu(1)−Cu(2)−Cu(1)#1	88.14(7)

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

Chart 1. Tetranuclear Entity of $[Cu_4L_4(OH)_4]\cdot 4dmso$

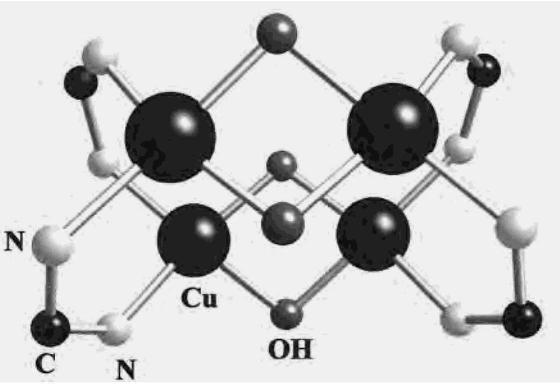
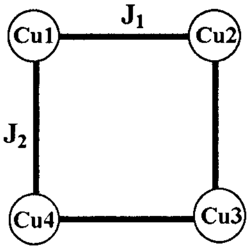


Chart 2. Coupling Constants in Cu_4



$$H = -2[J_1(S_1S_2 + S_3S_4) + J_2(S_1S_4 + S_2S_3)] + g\beta HS$$

The corresponding expression for χ_T is[5]

$$\chi_r = \frac{N\beta^2 g^2}{kT}\left\{\frac{10\exp(A/kT) + 2B}{5\exp(A/kT) + 3B + \exp[(F - A)/kT] + \exp[-(F + A)/kT]}\right\}$$

where $A = J_1 + J_2$, $B = \exp(J_1 - J_2)/kT + \exp(J_2 - J_1)/kT + \exp(-J_1 \text{-} J_2)/kT$, and $F = 2(J_1^2 + J_2^2 - J_1J_2)^{1/2}$. The complete expression for the magnetic susceptibility χ_M includes two additional terms accounting for the monomeric impurities ($\chi_{imp} = N\beta^2g^2/4kT$) and the temperature-independent paramagnetism ($\chi_{TIP} = N\alpha$): $\chi_M = \chi_T(1 - \rho) + \rho\chi_{imp} + \chi_{TIP}$.

The parameters J_1, J_2, g, ρ, and $N\alpha$ were determined by a least-squares fit minimizing $R = \sum[(\chi_M)_{obsd} - (\chi_M)_{calcd}]^2/\sum[(\chi_M)_{obsd}]^2$. The values obtained were $J_1 = -22.5$ cm^{-1}, $J_2 = -29$ cm^{-1}, $g = 2.03$, $\rho = 0.074$, $N\alpha = 221.6 \times 10^{-6}$, and $R = 5.2 \times 10^{-4}$. The resulting least-squares curve is shown by the solid line in Figure 2.

To assign either of these coupling constants to a particular NCN′ or OH^- bridge is not obvious, because they are very similar in magnitude. Concerning the Cu−OH−Cu moiety, there are studies in which the dependence of J on the geometry of the complex is detailed. Hatfield and Hogdson found a linear correlation between the experimentally determined exchange coupling constant ($2J$) and the Cu−OH−Cu bond angle (θ).[21] An antiferromagnetic character is found for complexes with θ

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(20) Jothan, R. W.; Kettle, S. F. A. *Inorg. Chim. Acta* **1970**, *4*, 145.

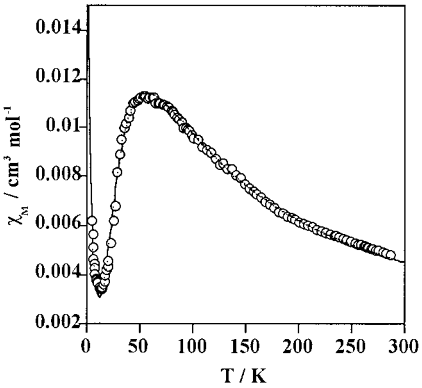

Figure 2. Temperature dependence of χ_M for $[Cu_4L_4(OH)_4]\cdot 4dmso$. The solid and broken lines represent the fitted functions as described in the text.

> 98°, while ferromagnetism appears for smaller values of θ. Ruiz et al.[22] have recently analyzed the dependence of the exchange coupling for the hydroxo-bridged complexes on the molecular geometry using density functional calculations, and they found the same correlation with the Cu−OH−Cu angle. Another structural feature that has a crucial role in the determination of the exchange coupling constant is the out-of-phase displacement, τ, of the hydrogen atom of the hydroxo group. If this atom is retained on the molecular plane, the magnetic behavior is predicted to remain antiferromagnetic for the whole range of the Cu−OH−Cu bond angles. However, both θ and τ are correlated in such a way that small θ values are usually combined with large τ values, resulting in a ferromagnetic character for these complexes.[23] The title compound displays asymmetric $[Cu_2(OH)_2]$ units, with Cu−OH−Cu angles of 97.3(4) and 98.3(4)°. The average $\theta = 97.8°$ value is very close to the critical angle of 98°. However, it has been impossible to determine the τ value because the hydrogen atoms of the OH bridging groups were not directly observed from the structure analysis. Despite this fact, the relatively small $2J$ values, estimated for the title compound as ranging from −40 to −60 cm^{-1}, are consistent with the structural features of the $[Cu_2(OH)_2]$ moiety.

There are some different binuclear Cu(II) complexes that present NCN′ bridges between the two copper atoms. In particular, those derived from the adenino ligand have been well-characterized.[24] In addition, we have reported the structure and the magnetic properties of $[Cu_2(\mu\text{-sulfathiazolato})_4]$, where the two copper atoms are linked by four NCN′ bridges in a fashion similar to that in the title compound.[10] The value of the exchange coupling constant $2J = -61$ cm^{-1} for the binuclear compound $[Cu_2(\mu\text{-sulfathiazolato})_4]$ is considerably smaller than that observed for the adenino-bridged copper pairs $[Cu_2(\mu\text{-adenino})_4]$ ($2J = -180$ to -300 cm^{-1}). Hence, if we take into account the fact that the title compound has two NCN′ bridges per each copper pair, a value around half of $2J = -61$ cm^{-1} should be expected. According to this, the value of $2J_1 = -45$ cm^{-1} could be reasonably attributed to the NCN′ bridge, while $2J_2 = -58$ cm^{-1} might be assigned to the OH$^-$ bridge.

The polycrystalline powder EPR spectrum at room temperature is silent, due to the antiferromagnetic nature of the compound.

Acknowledgment. G.A. and J.B. thank the CYCIT (project PM97-0105-C02-01) for financial support. J.A.R. thanks the DGICYT (Project PB97-1397) and the TMR European Community (Contract ERBFMRXCT-980181) for financial support.

Supporting Information Available: For the title compound, tables giving detailed crystallographic data, atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and least-squares planes and a figure showing the solvent dmso molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.

(22) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1297.

(23) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *Inorg. Chem.* **1997**, *36*, 3683.

(24) Sonnenfroh, D.; Kreilick, R. W. *Inorg. Chem.* **1980**, *19*, 1259.