A New Mononuclear Copper(II) Complex Containing Two Imidazolyl Moieties as Precursor of Self-Assembled and Ni^{II}Cu^{II}Ni^{II} Heterobimetallic Complexes

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A novel bis-imidazolyl tetradentate Schiff base ligand (H_2L) has been prepared from the condensation of imidazole-2-carbaldehyde and 1,3-diaminopropane. The ligand reacts with copper(II) perchlorate in neutral medium to yield the mononuclear complex $[Cu(H_2L)(ClO_4)]ClO_4 \cdot H_2O$. A single-crystal X-ray diffraction study confirmed the expected structure, $C_{11}H_{16}N_6O_9Cl_2Cu$, triclinic, $P\bar{1}$, $a = 8.875(2)$ Å, $b = 10.842(2)$ Å, $c = 10.888(2)$ Å, $a = 68.09(3)°$, $b = 84.47(3)°$, $g = 70.96(3)°$, $Z = 2$, in which the copper(II) ion occupies the inner N_4 site of the nondeprotonated ligand. Under basic conditions $[Cu(H_2L)(ClO_4)]ClO_4 \cdot H_2O$ can coordinate another metal ion through the deprotonated imidazole nitrogen atoms and simultaneously to accept a donor atom at the axial coordination site. This donor atom can belong to another deprotonated $[Cu(L)]$ unit, giving rise, by a self-assembly process, to the polymer $[Cu(L)]_n$. The crystal structure of this complex, $C_{11}H_{11}N_6Cu$, orthorombic, *Pbca*, $a = 18.132(12)$ Å, $b = 14.927(6)$ Å, $c = 8.629(4)$ Å, $Z = 8$, consists of zigzag chains formed by $[Cu(L)]$ units, in which copper(II) ions are sequentially bridged by imidazolate groups, with a copper−copper distance of 5.993 Å. The variable-temperature magnetic susceptibility measurements revealed the existence of an antiferromagnetic interaction between copper(II) ions through the imidazolate bridge. The analysis of the magnetic data on the basis of the spin Hamiltonian $H = -2\sum J_{ij}\hat{S}_i \cdot \hat{S}_j$ leads to J and g values of -1.2 cm^{-1} and 2.05, respectively. In addition, the reaction of $[Cu(H_2L)](ClO_4)_2 \cdot H_2O$ with an excess of bis(hexafluorocetylacetonato)-nickel(II) ($Ni(hfac)_2$) in basic medium leads to the heterotrinuclear complex $\{Cu(L)(H_2O)[Ni(hfac)_2(H_2O)]_2\}$. The magnetic properties of this complex agree well with those expected for a Ni^{II}Cu^{II}Ni^{II} trinuclear system with irregular spin state structure and zero-field splitting of the quartet ground state. The analysis of the magnetic data leads to $J = -25.4$ cm^{-1}, $g_{Ni} = 2.07$, $g_{Cu} = 2.01$, and $D = \pm 4.0$ cm^{-1}.

Introduction

A common synthetic strategy for homo- and heteropoly-nuclear complexes is the use of metal complexes as "ligands", that is to say, metal complexes containing potential donor atoms for another metal ion or metal complex with empty coordination sites. This method is very useful for the synthesis of hetero-metallic complexes with a systematic combination of metal ions. Both homo- and heteronuclear complexes thus obtained are of interest in connection with magnetic exchange interactions, in the design of new molecular materials, such as molecular-based magnets,[1] and in the area of the bioinorganic chemistry for their potential use as models for the active site of many metallopro-teins,[2] especially when the bridging group between the metal ions is of biological relevance, such as imidazolate, carboxylate, etc. In addition, if a metal complex acts as a "ligand" and simultaneously has the ability to receive a donor atom from another metal complex molecule a self-assembly process will occur, leading to a polymer complex. The self-assembly processes are of current interest in connection with the design of supramolecular structures from small molecules and because of their relevance in biological processes.[3]

We have designed a symmetrical tetradentate Schiff base ligand containing two imidazole groups (hereafter H_2L, see Scheme 1), which is able to accommodate a copper(II) ion at the inner N_4 coordination site, leading to the mononuclear complex $[Cu(H_2L)](ClO_4)_2 \cdot H_2O$, **1**. It is noteworthy that this complex can either undergo a self-assembly process leading to the polymeric $[Cu(L)]_n$ **2** or act as a "complex ligand" toward bis(hexafluoroacetylacetonato)nickel(II), $Ni(hfac)_2$, to give the heterometallic trinuclear complex $\{Cu(L)(H_2O)[Ni(hfac)_2-(H_2O)]_2\}$, **3**. The latter complex is one of the few examples exhibiting irregular distribution of spin so far reported.[4,5] This paper deals with the structure and magnetic properties of these complexes.

(1) (a) *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; NATO ASI Series E198; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991. (b) *Magnetism: A Supramolecular Function*; Kahn, O. Ed.; NATO ASI Series C484; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996. (c) *Molecular Magnetism: From the Molecular Assemblies to the Devices*; Coronado, E., Delhaes, P., Gatteschi, D., Miller, J. S., Eds.; NATO ASI Series E321; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996. (d) *Research Frontiers in Magnetochemistry*; O'Connor, C. J., Ed.; World Scientific Publishing Co. Pte. Ltd.: Singapore, 1993. (e) Kahn, O. *Adv. Inorg. Chem.* **1995**, *43*, 179.

(2) *Metal Clusters in Proteins*. Que, L., Ed.; ASC Symposium Series 372; American Chemical Society: Washington, DC, 1988.
(3) (a) Whitesikes, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1987**, *254*, 1312. (b) Lehn, J. M. *Science* **1993**, *260*, 1763.

Scheme 1

Experimental Section

Preparation of the Ligand H₂L. 1,3-Diaminopropane (5 mmol, 0.42 mL) was directly added to a methanolic suspension of imidazole-2-carbaldehyde (10 mmol, 0.96 g). After 2 h at 50 °C, a yellow solution resulted, which was filtered to remove any amount of insoluble material. The solvent was removed by rotary evaporation leading to a yellow oil that was dissolved in the minimum amount of chloroform. Addition of diethyl ether produced the precipitation of a white powder, which was filtered off and air-dried. Yield, 85%. Anal. Calcd for $C_{11}H_{14}N_6$: C, 57.4; H, 6.1; N, 36.5. Found: C, 57.5; H, 6.1; N, 36.4. ^{1}H NMR [$(CD_3)_2SO$]: δ 12.70 ($-$NH, s, 2H), 8.19 ($-$H$-$C$=$N, s, 2H), 7.2 and 7.05 ($-$HC$=$CH$-$, s, 2H and (s, 2H), 3.63 ($-$H$_2$C$-$C$=$N, t, 4H, J_{H-H} = 6 Hz), and 1.95 ($-$C$-$CH$_2$$-C-$, q, 2H, J_{H-H} = 6 Hz).

Preparation of the Complexes. Warning! *Perchlorate salts are potentially explosive and should only be handled in small quantities.* All reagents were of analytical grade and used without further purification.

[Cu(H₂L)](ClO₄)₂·H₂O (1). An ethanolic solution of copper(II) perchlorate hexahydrate (1 mmol, 0.371 g) was slowly added to a solution of H₂L (1 mmol, 0.230 g) in ethanol (40 mL) with continuous stirring. The resulting blue solution kept at room temperature for 1 day provided well-developed blue crystals of **1**. Anal. Calcd for $C_{11}H_{16}N_6O_9CuCl_2$: C, 25.8; H, 3.1; N, 16.4. Found: C, 25.8; H, 3.1; N, 16.5.

[CuL]$_n$ (2). A methanolic$-$aqueous solution (5:1, 20 mL) of KOH (1 mmol, 0.056 mg) was added directly to 50 mL of a solution of **1** (0.5 mmol, 0.246 g) in methanol. A green powder immediately precipitated, which was filtered off, washed with methanol and diethyl ether, and air-dried; yield, 92%. Anal. Calcd for $C_{11}H_{12}N_6Cu$: C, 45.3; H, 4.1; N, 28.8. Found: C, 45.3; H, 4.1; N, 28.8. Suitable crystals for X-ray analysis were obtained by slow evaporation of the filtrate at room temperature.

On the other hand, addition of perchloric acid to a water suspension of **2** until the precipitate has dissolved gives rise to a blue solution, from which crystals of **1** are obtained.

{Cu(L)(H₂O)[Ni(hfac)₂(H₂O)]₂} (3). Bis(hexafluoroacetylacetonate)nickel(II) (1 mmol, 0.473 g) was added to a solution of **1** (0.25 mmol, 0.132 g) in 40 mL of methanol/water (5:1) mixture. Addition of triethylamine (0.5 mmol, 0.07 mL) produced the precipitation of a green powder, which was filtered off, washed with methanol and diethyl ether, and dried in air. Yield, 81%. Anal. Calcd for $C_{31}H_{22}N_6O_{11}F_{24}$CuNi$_2$: C, 28.8; H, 1.7; N, 6.5. Found: C, 28.7; H, 1.9; N, 6.4.

Physical Measurements. Elemental analyses were carried out at the Technical Services of the University of Granada on a Fisons-Carlo Erba analyzer model EA 1108. IR spectra were recorded on a Perkin-Elmer 983 G spectrometer using KBr pellets. Variable-temperature magnetic susceptibility data were collected on powdered samples of the compounds with use of a pendulum type magnetometer (MANICS DSM8) equipped with a helium continuous flow cryostat working in the 300$-$4 K range and a Drusch EAF 164E electromagnet. The magnetic field was approximately 15 000 G. Data were corrected for the diamagnetism of the ligands using Pascal's constants. X-band EPR spectra were recorded on a Bruker 200 TT spectrometer.

X-ray Data Collection and Structure Determination of the Complexes 1 and 2. A blue prismatic crystal of **1**, 0.18 × 0.25 × 0.22 mm, and a thin green crystal of complex **2**; 0.29 × 0.29 × 0.04 mm, were mounted on a Siemens P4 and a Stoe AED2 four-circle diffractometers, respectively. Data were collected using $\omega-2\theta$ scans out, in 2θ to 55° for **1** and 45° for **2** since the crystal was extremely small and diffracted weakly. The lattice parameters were optimized from least-squares refinement of 25 and 18 reflections in the range 5 < θ <15° and 7.6 < θ <13.25° for **1** and **2**, respectively. Crystallographic data are summarized in Table 1. Lorentz$-$polarization and an empirical absorption correction using the programs SHELXTL V5[6a] and DIFABS,[6b] were applied to the data for **1** and **2**. The minimum and maximum transmission factors were 0.847 and 0.956 for **1** and 0.635 and 1.000 **2**. The structures were solved by direct methods using SHELXS-86[6c] and refined using SHELXL-93.[6d] The H atoms were included in calculated positions and treated as riding atoms using

(4) (a) Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1988**, *27*, 399. (b) Ribas, J.; Diaz, C.; Costa, R.; Journaux, Y.; Mathoniere, C.; Kahn. O.; Gleizes, A. *Inorg. Chem.* **1990**, *29*, 2042.

(5) *Molecular Magnetism*; Kahn, O.; VCH Publishers, Inc.: Weinheim, 1993.

(6) (a) *SHELXTL PC*, Version 5.0; Siemens Analytical X-ray Instruments: Madison, WI, 1990. (b) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. (c) Sheldrick, G. M. SHELXS-86 A Program for Crystal Structure Determination. *Acta Crystallogr.* **1990**, *A46*, 467. (d) Sheldrick, G. M. *SHELXL-93*; Universität Göttingen: Göttingen, Germany, 1993.

Table 1. Crystallographic Data for the Complexes **1** and **2**

	1	**2**
empirical formula	$C_{11}H_{16}Cl_2CuN_6O_9$	$C_{11}H_{11}CuN_6$
fw	510.74	290.82
T, K	293(2)	293(2)
λ, Å	0.710 73	0.710 73
space group	$P\bar{1}$	Pbca
a, Å	8.875(2)	18.132(12)
b, Å	10.842(2)	14.927(6)
c, Å	10.888(2)	8.629(4)
α, deg	68.09(3)	90
β, deg	84.47(3)	90
γ, deg	70.96(3)	90
V, Å^3	918.5(3)	2336(2)
Z	2	8
ρ_{calcd}, g cm^{-3}	1.847	1.654
μ, mm^{-1}	1.542	1.786
R $(F^2)^a$	0.0470	0.0836
Rw $(F^2)^b$	0.1156	0.1244

^{a} $R = \sum||F_0| - |F_c||/\sum|F_0|$. ^{b} $Rw = [\sum w(|F_0|^2 - |F_c|^2)^2]/\sum w|F_0|^4]^{1/2}$.

SHELXL-93 default parameters. The non-hydrogen atoms were refined anisotropically. For **1**, the noncoordinated perchlorated anion and the aliphatic chain of the ligand were disordered. To avoid nonpositive-definite atoms the disordered atoms were refined, their thermal parameters having been restrained to be equal. In the final difference map the maximum and minimum residual density were 0.409/−0.454 and 0.695/−0.521 e Å^{-3} for **1** and **2**.

Results and Discussion

The H$_2$L ligand was prepared by 2:1 condensation of imidazole-2-carbaldehyde with 1,3-diaminopropane. ^{1}H NMR spectroscopy provides a good characterization. The assignments (see Experimental Section) are based on the chemical shift, intensity, and multiplicity values, and they are supported by comparison with literature data for similar compounds.

The ligand reacts with copper(II) perchlorate hexahydrate to afford the copper(II) complex **1**. The IR spectrum shows the imidazole NH stretching vibrations at 3104 and 3082 cm^{-1} and the characteristic bands due to the ClO$_4^-$ anions about 1110 cm^{-1}, thus indicating that the imidazole groups remain un-deprotonated.

The crystal structure of this compound was determined by X-ray crystallography and consists of mononuclear copper cations [Cu(H$_2$L)]$^{2+}$, two perchlorate anions, one of them semicoordinated, and one lattice water molecule. A perspective view of the mononuclear fragment together with the atom numbering scheme is shown in Figure 1, whereas selected bond distances and angles are listed in Table 2. The coordination geometry of the copper(II) ion is very close to a perfect square pyramid, $\tau = 0.015$ (according to the procedure proposed by Addison et al.,^{7} τ is 1 for the regular trigonal bipyramid and 0 for the square pyramid). In this geometry, the coordination basal plane is defined by the N$_4$ donor atoms of the nondeprotonated H$_2$L ligand, with typical Cu−N distances of about 2 Å, whereas the O(21) atom belonging to one of the perchlorate anions occupies the apical position with a longer bond distance of 2.432(3) Å. The four basal nitrogen atoms are coplanar while the copper(II) ion deviates 0.116 Å from this N$_4$ plane toward the apical position. The imidazole rings are planar and form dihedral angles with the mean coordination basal plane of 2.1 and 4.8, so that the cation [Cu(H$_2$L)]$^{2+}$ is essentially planar.

Interestingly, this complex, under basic conditions, has the ability to coordinate another metal through the deprotonated nitrogen atoms of the imidazole groups and simultaneously to

(7) Addison, A. W.; Burke, P. J.; Henrick, H. *Inorg. Chem.* **1982**, *21*, 60.

Figure 1. Perspective view of the mononuclear complex [Cu(H$_2$L)]-(ClO$_4$)$_2$·H$_2$O (**1**). Hydrogen atoms, except those of the imidazolyl nitrogen atoms, the second perchlorate anion, and the water molecule are omitted for clarity (ellipsoids represent 50% of probability).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**^{a}

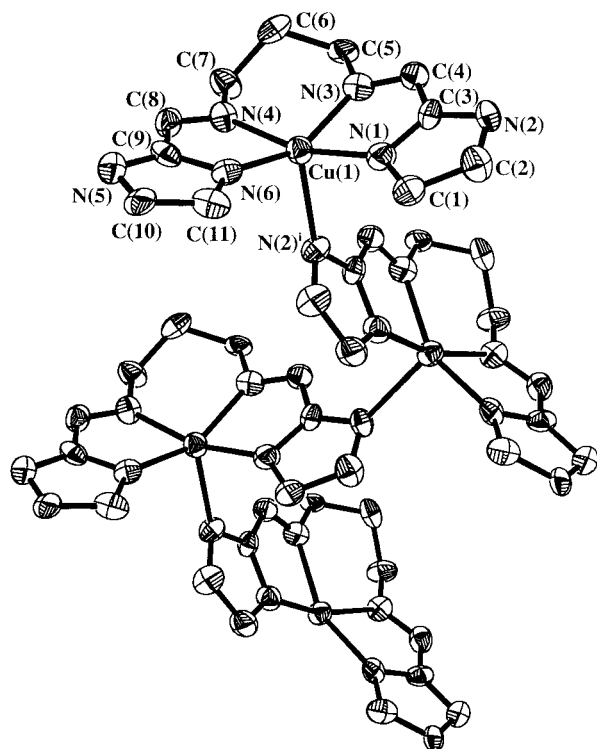|	**1**	**2**
Cu(1)−N(1)	1.992(3)	2.000(9)
Cu(1)−N(3)	2.003(3)	2.049(9)
Cu(1)−N(4)	2.018(3)	1.992(9)
Cu(1)−N(6)	1.979(3)	2.013(9)
Cu(1)−X	2.432(3)	2.214(9)
N(1)−Cu(1)−N(6)	101.6(1)	99.8(4)
N(1)−Cu(1)−N(3)	82.3(1)	81.5(4)
N(1)−Cu(1)−N(4)	171.7(1)	163.2(4)
N(1)−Cu(1)−X	93.0(1)	90.7(5)
N(3)−Cu(1)−N(4)	93.3(1)	89.6(4)
N(3)−Cu(1)−N(6)	172.6(1)	152.8(4)
N(3)−Cu(1)−X	90.5(2)	109.8(4)
N(4)−Cu(1)−N(6)	82.0(1)	81.7(4)
N(4)−Cu(1)−X	94.1(1)	105.8(4)
N(6)−Cu(1)−X	95.5(1)	97.4(4)

^{a} For **1**, X = O(1); for **2** X = N(2)^i, i = x, $^1/_2 - y$, $^1/_2 + Z$).

receive at the axial coordination site the deprotonated imida-zolate nitrogen atom of another molecule, yielding the self-assembled polymer [Cu(L)]$_n$ (**2**). This reaction is reversible, since when the polymer is treated with perchloric acid the structure is broken, leading to the protonated monomeric units. As expected, **2** is insoluble in common solvents and its IR spectrum shows no bands due to ν(N−H) and ν(Cl−O) stretching vibrations.

The structure of **2** has been established by single-crystal X-ray analysis. A perspective view of the polymer with the atom numbering scheme is shown in Figure 2. Selected bond distances and angles are listed in Table 2. As observed in **1**, the copper(II) ion occupy the N$_4$ coordination site of the ligand, also adopting a (4+1) surrounding. Nevertheless in **2**, the apical position is occupied by the N(2)^i atom of an adjacent and symmetry-related (i: x, $^1/_2 - y$, $^1/_2 + z$) fragment, with a Cu−N(2)^i distance of 2.214(9) Å. This gives rise to a polynuclear structure formed by [Cu(L)] units, in which copper(II) ions are sequentially bridged by imidazolate groups, with a copper−copper distance of 5.993 Å. Although both N(2) and N(5) imidazole atoms are deprotonated, only N(2) coordinates to the Cu(II) ion from another adjacent unit. This results in the formation of infinite zigzag chain running parallel to the crystallographic *b* axis.

Figure 2. Perspective view of the zigzag chain structure of the complex [Cu(L)]$_n$ **2**. Hydrogen atoms are omitted for clarity (ellipsoids represent 50% of probability).

The Cu(II) coordination geometry can be considered as distorted square-pyramidal ($\tau = 0.17$). The N$_4$ coordination basal plane is almost planar, with a maximum deviation of 0.10 Å for the N(4) atom. As usual, the copper(II) ion is lifted by 0.372 Å from the mean basal N$_4$ plane toward the N(2)^i axial donor. The two imidazole rings are planar and form a dihedral angle of 30.6°, thus indicating that the mononuclear fragment LCu is significantly less planar than that found in **1**. Regarding the bridging site, the imidazolate group bridges two copper(II) ions involving equatorial and axial positions and makes angles of 18.3 and 61.3 with the N$_4$ mean coordination planes of Cu and Cu^{II}, respectively. The dihedral angle between two adjacent coordination basal planes is 45.8°.

As previously noted, the mononuclear copper(II) complex **1** might be used, after deprotonation, as a ligand toward a second metal ion to produce heterobimetallic systems. Nevertheless, all attempts to obtain bimetallic chains with [Ni(hfac)$_2$] always led to a mixture of products, which contained unidentified heterobimetallic compounds and the self-assembled complex of the mononuclear precursor. This should be due to the great tendency of **1** to bring about the self-assembly reaction. By reacting **1** with an excess of [Ni(hfac)$_2$] in basic medium, however, the complex of formula {Cu(L)(H$_2$O)[Ni(hfac)$_2$-(H$_2$O)]$_2$} **3** could be obtained as a pure microcrystalline powder. The IR spectrum of **3** does not show any band corresponding to ν(N−H) vibrations, thus indicating that the imidazole groups of the copper(II) fragment are deprotonated whereas intense ν-(C−F) bands of the Ni(hfac)$_2$ fragments are observed at about 1200 cm^{-1}. From the analytical, spectroscopic, and magnetic data (see below) it is reasonable to propose for **3** the structure given in the chart. It seems that working at a high molar ratio of Ni(hfac)$_2$ to **1**, the mononuclear copper(II) precursor is prevented from the self-assembly reaction, thus allowing the isolation of the heterotrinuclear NiCuNi complex **3**.

Magnetic Properties. Magnetic susceptibility data for **2** were collected on a powdered sample in the range 80−6 K. The χT product remains constant until 20 K and equal to 0.39 cm^3 mol^{-1} K, which is the expected value for isolated copper-(II) ions with $g = 2.05$. From that temperature, χT gradually decreases to 0.3 cm^3 mol^{-1} K at 6 K, thus suggesting a weak antiferromagnetic interaction between copper(II) ions mediated by the imidazolate bridge. In keeping with the structure, the magnetic susceptibility data were analyzed on the basis of the Ising model for a one-dimensional infinite chain derived from the spin Hamiltonian $H = -2\sum J_{ij}\hat{S}_i\cdot\hat{S}_j$.[8]

$$\chi T = \frac{Ng^2\beta^2}{12k}\frac{e^{4x} + (2 + x^{-1})e^{2x} - x^{-1}e^{2x} + 5}{e^{2x} + e^{-2x} + 2}$$

The best fitting of the experimental data led to $J = -1.2$ cm^{-1} and $g = 2.05$. The small J value is not unexpected in view of the fact that the imidazolate group bridges two neighboring copper(II) ions at the equatorial and axial positions of their respective slightly distorted square-pyramidal coordination polyhedra. Because in this geometry the unpaired spin density at axial position is very poor, the antiferromagnetic exchange interaction is basically not operative. In close accordance with this, the J values observed for imidazolate-bridged polynuclear copper(II) complexes, in which the imidazolate anion adopts an equatorial−axial bridging mode, are small and fall in the range from −1.2 to −15 cm^{-1}.[9] On the other hand, as expected, relatively strong antiferromagnetic interactions (typical J values are in the range from −40 to −120 cm^{-1}) have been observed when the imidazolate anion adopts an equatorial−equatorial bridging mode between two copper(II) ions.[10]

The magnetic behavior of **3** is shown in the Figure 3 in the form a χT versus T plot. At 290 K, χT is equal to 2.37 cm^3 mol^{-1} K, which corresponds well to the sum of the contributions of the isolated ions. On lowering the temperature χT gradually decreases, reaches a minimum around 23 K with χT of 1.76 cm^3 mol^{-1} K, then increases to a maximum at 9 K, and finally slightly decreases again upon cooling to 5 K. This behavior agrees quite well with that expected for a Ni^{II}Cu^{II}Ni^{II} complex with the quartet ground-state split in zero field into two Kramer's doublets, which is responsible for the decrease of χT below 9 K. The spin Hamiltonian (1) appropriate to interpret the magnetic data is
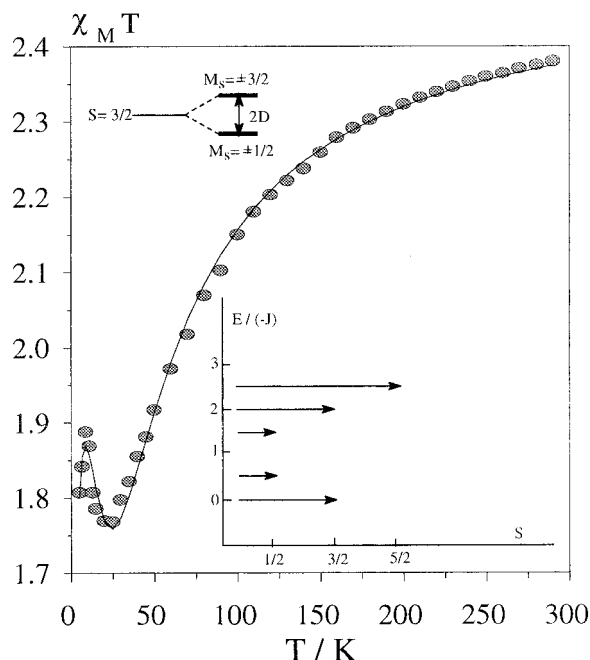
$$H = -J(\hat{S}_{Ni1}\hat{S}_{Cu} + \hat{S}_{Ni2}\hat{S}_{Cu}) + D[(\hat{S}_z^2 - \tfrac{1}{3}S)(S + 1)]\delta_{S,3/2}\delta_{S',2} + \beta[g_{Ni}(\hat{S}_{Ni1} + \hat{S}_{Ni2}) + g_{Cu}\hat{S}_{Cu}]\cdot\vec{H} \quad (1)$$

where it has been assumed that the splitting within the ground quartet state is axial, that the local g factors are isotropic, and that the spin states do not couple through the local anisotropy of the Ni(II) ion. The relative energies $E(S,S')$ of the low-lying spin states arising from the isotropic interaction can be easily calculated using the vector model with $S = S' + S_{Cu}$ and $S' = S_{Ni1} + S_{Ni2}$. They are indicated in Figure 3 together with the relations between molecular $g_{S,S'}$ and the local g_{Ni} and g_{Cu}

(8) Sinn, E. *Coord. Chem. Rev.* **1970**, *5*, 313.

(9) (a) Nozaki, T.; Oshio, H.; Mago, G.; Matsumoto, N.; Okawa, H.; Yamakawa, Y.; Anno, T.; Nakashima, T. *J. Chem. Soc. Trans.* **1994**, 2339. (b) Matsumoto, N.; Nozaki, T.; Oshio, H.; Ohba, M.; Mago, G.; Okawa, H. *J. Chem. Soc. Trans.* **1993**, 2157. (c) Matsumoto, N.; Yamashita, S.; Ohyoshi, A.; Kohata, S.; Okawa, H. *J. Chem. Soc. Trans.* **1988**, 1943.

(10) (a) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 2328 and references therein. (b) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1986**, *25*, 398.

$$\chi_{\parallel} = \left(\frac{N\beta^2}{kT}\right)\left\{g_{3/2,2}^2\left[9\exp\left(\frac{-D}{kT}\right) + \exp\left(\frac{D}{kT}\right)\right] + g_{1/2,1}^2\exp\left(\frac{J}{2kT}\right) + g_{1/2,0}^2\exp\left(\frac{3J}{2kT}\right) + 10g_{3/2,1}^2\exp\left(\frac{2J}{kT}\right) + 35g_{5/2,2}^2\exp\left(\frac{5J}{kT}\right)\right\}/$$
$$\left\{\exp\left(\frac{-D}{kT}\right) + \exp\left(\frac{D}{kT}\right) + \exp\left(\frac{J}{2kT}\right) + \exp\left(\frac{3J}{2kT}\right) + 2\exp\left(\frac{2J}{kT}\right) + 3\exp\left(\frac{5J}{kT}\right)\right\} \quad (2)$$

$$\chi_{\perp} = \left(\frac{N\beta^2}{4kT}\right)\left\{g_{3/2,2}^2\left[\frac{-3kT}{D}\exp\left(\frac{-D}{kT}\right) + \left(4 - \frac{3kT}{D}\right)\exp\left(\frac{D}{kT}\right)\right] + g_{1/2,1}^2\exp\left(\frac{J}{2kT}\right) + g_{1/2,0}^2\exp\left(\frac{3J}{2kT}\right) + 10g_{3/2,1}^2\exp\left(\frac{2J}{kT}\right) +$$
$$35g_{5/2,2}^2\exp\left(\frac{5J}{2kT}\right)\right\}/\left\{\exp\left(\frac{-D}{kT}\right) + \exp\left(\frac{D}{kT}\right) + \exp\left(\frac{J}{2kT}\right) + \exp\left(\frac{3J}{2kT}\right) + 2\exp\left(\frac{2J}{kT}\right) + \exp\left(\frac{5J}{kT}\right)\right\} \quad (3)$$

Figure 3. Temperature dependence of χT (cm^3 mol^{-1} K) per copper-(II) atom for {Cu(L)(H$_2$O)[Ni(hfac)$_2$(H$_2$O)]$_2$} (**3**) (●). Solid lines were generated from the corresponding best-fitting magnetic parameters.

Figure 4. Powder X-band EPR spectrum of **3** at 4.2 K.

Zeeman factors. The spin state structure is irregular since the energy of the states does not vary linearly with the spin. On going down in energy, *S* first decreases from $^5/_2$ to $^1/_2$ and then increases from $^1/_2$ to $^3/_2$. This leads to the minimum observed in the χT vs *T* plot. The experimental data were fitted to the theoretical expression of the magnetic susceptibility, deduced from the spin Hamiltonian (1), $\chi = (2\chi_{\perp} + \chi_{\parallel})/3$; see eqs 2 and 3. The best fit led to $J = -25.4$ cm^{-1}, $g_{Ni} = 2.07$, $g_{Cu} = 2.01$, and $D = \pm 4.0$ cm^{-1}. The *J* value agrees quite well with that obtained from the theoretical relationship between the temperature of the minimum T_{min} and J, $J = kT_{min}/0.6435 = -24.8$ cm^{-1}. It should be noted that the calculated *J* value is of the same order as those found for two CuNiCu trinuclear complexes ($J = -21.6$ and 20.3 cm^{-1}), in which the imidazolate bridging group is incorporated, as in this case, into a polydentate Schiff base ligand.[11]

The X-band powder EPR spectrum of **3** at 4.2 K is shown in Figure 4. This spectrum is very complicated with many overlapping resonances spread out in the range 38−369 mT. Since the doublet excited states are not far in energy from the quartet ground state, the spectrum should be the result of the superimposition of transitions within all these states. Owing to the complexity of the spectrum, its qualitative interpretation

is practically impossible. Nevertheless, the features at 369 mT ($g = 1.82$), 270 mT ($g = 2.5$), which can be observed only at 4.2 K, and 135 mT ($g = 5.0$) might be tentatively assigned to transitions within the Kramer's doublet $\pm^1/_2$ arising from the $S = ^3/_2$ ground state, where the zero-field splitting is larger than the microwave quantum.[4] The features at 302 mT ($g = 2.23$) and 285 mT ($g = 2.36$) might correspond to transitions within the excited doublet states. In accordance with this, the intensity of these signal increases upon warming to 20 K. An explanation cannot be given for the remaining very weak transitions at 169, 145, 76, and 38 mT. The three former might suggest $\Delta Ms = \pm 2, \pm 3$, and ± 4 transitions, but this could occur only for the $S = ^5/_2$ multiplet, which is depopulated at low temperature. When the temperature is increased from 20 K to room temperature, the intensity of these signals decreases and only the feature at 327 mT ($g \cong 2.06$) remains in the spectrum with a well-resolved hyperfine splitting into four lines in the $g_{\parallel}$ region ($A_{\parallel} \cong 17.7$ mT), as would be expected for a copper(II) ion. In view of this, this feature might be due to the presence of some copper-(II) impurity.

The isolation of the NiCuNi complex seems to indicate that imidazolate-bridged bimetallic chains might be prepared if the precursor is prevented from the self-assembly reaction. In view of this, we have designed mononuclear precursors of the type [M(HL′)$_2$](ClO$_4$)$_2$ (HL′ = tridentate Schiff base involving one or two imidazole groups). Because the coordination positions on the central metal ion are saturated, these precursors are prevented from the self-assembly reaction. Studies of the reactivity of these paramagnetic ligands toward a second metal ion or metal complex are in progress.

Supporting Information Available: Listing of complete crystallographic data, atomic coordinates, bond distances and angles and anisotropic thermal parameters (Tables S.1−S.8) is available on the Internet only. Access information is given on any current masthead page.

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(11) (a) Matsumoto, N.; Inoue, K.; Ohba, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2283. (b) Colacio, E.; Dominguez-Vera, J. M.; Ghazi, M.; Kivekas, R.; Klinga, M.; Moreno, J. M. *Inorg. Chem.* In press.