

# A Rational Design for Imidazolate-Bridged Linear Trinuclear Compounds from Mononuclear Copper(II) Complexes with 2-[(Imidazol-2-ylmethylidene)amino]ethylpyridine (HL): Syntheses, Structures, and Magnetic Properties of $[\text{Cu}(\text{L})(\text{hfac})\text{M}(\text{hfac})_2\text{Cu}(\text{hfac})(\text{L})]$ ( $\text{M} = \text{Zn}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Mn}^{\text{II}}$ )

Enrique Colacio,<sup>\*,†</sup> Mustapha Ghazi,<sup>†</sup> Raikko Kivekäs,<sup>‡</sup> Martti Klinga,<sup>‡</sup> Francesc Lloret,<sup>§</sup> and José María Moreno<sup>†</sup>

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain, Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland, and Departament de Química Inorgánica, Facultat de Ciències, Universitat de València, Dr. Moliner 50, 46100 Burjassot, Spain

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Two mononuclear copper(II) complexes with the unsymmetrical tridentate ligand 2-[(imidazol-2-ylmethylidene)amino]ethylpyridine (HL),  $[\text{Cu}(\text{HL})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Cu}(\text{HL})\text{Cl}_2]$  (**2**), have been prepared and characterized. The X-ray analysis of **2** revealed that the copper(II) ion assumes a pentacoordinated square pyramidal geometry with an  $\text{N}_3\text{Cl}_2$  donor set. When **1** and **2** are treated with an equimolecular amount of potassium hydroxide, the deprotonation of the imidazole moiety promotes a self-assembled process, by coordination of the imidazolate nitrogen atom to a  $\text{Cu}^{\text{II}}$  center of an adjacent unit, leading to the polynuclear complexes  $\{[\text{Cu}(\text{L})(\text{H}_2\text{O})](\text{ClO}_4)\}_n$  (**3**) and  $\{[\text{Cu}(\text{L})\text{Cl}]\cdot 2\text{H}_2\text{O}\}_n$  (**4**). Variable-temperature magnetic data are well reproduced for one-dimensional infinite regular chain systems with  $J = -60.3 \text{ cm}^{-1}$  and  $g = 2.02$  for **3** and  $J = -69.5 \text{ cm}^{-1}$  and  $g = 2.06$ , for **4**. When **1** is used as a "ligand complex" for  $[\text{M}(\text{hfac})_2]$  ( $\text{M} = \text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Zn}^{\text{II}}$ ) in a basic medium, only the imidazolate-bridged trinuclear complexes  $[\text{Cu}(\text{L})(\text{hfac})\text{M}(\text{hfac})_2\text{Cu}(\text{hfac})(\text{L})]$  ( $\text{M} = \text{Zn}^{\text{II}}, \text{Cu}^{\text{II}}$ ) (**5**, **6**) can be isolated. Nevertheless, the analogous complex containing  $\text{Mn}^{\text{II}}$  as the central metal (**7**) can be prepared from the precursor  $[\text{Cu}(\text{HL})\text{Cl}_2]$  (**2**). All the trinuclear complexes are isostructural. The structures of **5** and **6** have been solved by X-ray crystallographic methods and consist of well-isolated molecules with  $C_i$  symmetry, the center of symmetry being located at the central metal. Thus, the copper(II) fragments are in trans positions, leading to a linear conformation. The magnetic susceptibility data (2–300 K), which reveal the occurrence of antiferromagnetic interactions between copper(II) ions and the central metal, were quantitatively analyzed for symmetrical three-spin systems to give the coupling parameters  $J_{\text{CuCu}} = -37.2$  and  $J_{\text{CuMn}} = -3.7 \text{ cm}^{-1}$  with  $D = \pm 0.4 \text{ cm}^{-1}$  for **6** and **7**, respectively. These magnetic behaviors are compared with those for analogous systems and discussed on the basis of a localized-orbital model of exchange interactions.

## Introduction

Imidazole is a ligand that plays an important role in biological systems, since the imidazole moiety of the histidyl residues in a large number of metalloproteins constitutes all or part of the binding sites of various transition metal ions.<sup>1–3</sup> For instance, its conjugate base, the imidazolate anion, is known to act as a bridging ligand between copper(II) and zinc(II) in bovine erythrocyte superoxide dismutase (BESOD).<sup>4</sup> Furthermore, from ESEEM <sup>14</sup>N/<sup>15</sup>N-labeling studies and <sup>15</sup>N ENDOR spectroscopy, it has been suggested that a histidyl residue might bridge two manganese atoms in photosystem II (PSII),<sup>5</sup> whose function is

to facilitate the four-electron oxidation of water to dioxygen. It is of interest that polydentate ligands including an imidazole moiety can be used to synthesize metal complexes that are capable of undergoing reversible interconversions between a monomer and a self-assembled oligomer by inputting external information, specifically a change of pH.<sup>6</sup> By controlling the pH, it is then possible to interconvert a protonated monomer into an imidazolate-bridged deprotonated oligomer and vice

<sup>†</sup> Universidad de Granada.

<sup>‡</sup> University of Helsinki.

<sup>§</sup> Universitat de València.

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versa, thus affording new functional materials with potential switching ability. In view of all this, studies aimed at characterizing the bonding between imidazole and transition metal ions are of considerable interest. From the magnetochemical point of view, imidazolate-bridged transition metal complexes have also been actively studied to understand the factors determining the extent of the exchange coupling through the imidazolate bridge. Consequently, there are numerous examples of structurally and magnetically characterized imidazolate-bridged complexes,<sup>6–9</sup> but only a few of them are trinuclear systems.<sup>8,9</sup> We recently reported a series of imidazolate-bridged trinuclear complexes with the formula  $[\text{Cu}(\text{L}^1)(\text{hfac})\text{M}(\text{hfac})_2\text{Cu}(\text{hfac})(\text{L}^1)]$  ( $\text{M} = \text{Zn}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Mn}^{\text{II}}$ ;  $\text{HL}^1$  is the tridentate Schiff base from the 1:1 condensation of 2-imidazolecarboxaldehyde and histamine (Scheme 1), and hfac is the hexafluoroacetylacetonate anion),<sup>9</sup> prepared from imidazole-containing mononuclear complexes and  $[\text{M}(\text{hfac})_2]$  as building blocks, which represent new examples of the scarce structurally and magnetically characterized heterotrimeric complexes. These complexes have the imidazolate bridges in cis positions and adopt a V-shaped conformation. It seems that the hydrogen bonds involving the amino group of the histamine residue favor the observed conformation instead of the less sterically hindered trans-linear structure. With the aim of obtaining the latter type of imidazolate-bridged trinuclear molecules and comparing their magnetic properties with those of the corresponding cis molecules, we have extended this study by using the tridentate Schiff base HL (Scheme 1), which has no active hydrogen atom that might be involved in the formation of hydrogen bonds. We report here the mononuclear precursors  $[\text{Cu}(\text{HL})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Cu}(\text{HL})\text{Cl}_2]$  (**2**), their deprotonated and self-assembled complexes  $\{[\text{Cu}(\text{L})(\text{H}_2\text{O})](\text{ClO}_4)_2\}_n$  (**3**) and  $\{[\text{Cu}(\text{L})\text{Cl}]\cdot 2\text{H}_2\text{O}\}_n$  (**4**), the trans-linear trinuclear complexes  $[\text{Cu}(\text{L})(\text{hfac})\text{M}(\text{hfac})_2\text{Cu}(\text{hfac})(\text{L})]$  ( $\text{M} = \text{Zn}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Mn}^{\text{II}}$ ) (**5–7**), and the mononuclear complex  $[\text{Ni}(\text{HL})_2(\text{hfac})(\text{H}_2\text{O})](\text{hfac})$  (**8**). The magnetic properties of the self-assembled and trinuclear complexes are interpreted.

## Experimental Section

**Physical Measurements.** Elemental analyses were carried out at the Centro de Instrumentación Científica of the University of Granada on a Fisons-Carlo Erba model EA 1108 analyzer. 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 operating in the 300–4.2 K range and a Drusch EAF 164E electromagnet, whereas those of **7** were collected with the use of a SQUID-based sample magnetometer on a Quantum Design model MPMS instrument. The magnetic field was approximately 15 000 G. Data were corrected for the diamagnetism of the ligands using Pascal's constants.

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

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**Preparations of the Compounds.**  $[\text{Cu}(\text{HL})(\text{H}_2\text{O})(\text{ClO}_4)](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$  (**1**). This complex was prepared by refluxing 2-imidazolecarboxaldehyde (0.19 g, 2 mmol) and 2-(aminoethyl)pyridine (0.24 g, 2 mmol) for 1 h in 30 mL of an MeOH/H<sub>2</sub>O mixture (3:1, v/v). To the filtered and cold yellow solution was added dropwise with stirring  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.74 g, 2 mmol) in 30 mL of MeOH. After several hours of standing, a blue powder precipitated, which was collected by filtration, washed successively with methanol and diethyl ether, and dried in air. Yield: 73%. Anal. Calcd for  $\text{C}_{11}\text{H}_{18}\text{N}_4\text{Cl}_2\text{CuO}_{11}$ : C, 25.63; H, 3.52; N, 10.88. Found: C, 25.67; H, 3.04; N, 10.85. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{N}_{\text{im}}-\text{H})$  3111;  $\nu(\text{Cl}-\text{O})$  1089, 1120, 1144;  $\nu(\text{C}=\text{N})$  1606;  $\nu(\text{CH})$  2916, 2847.

$[\text{Cu}(\text{HL})\text{Cl}_2]$  (**2**). Green crystals of this compound were obtained by following the procedure described for **1**, but using  $\text{CuCl}_2$  instead of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ . Yield: 80%. Anal. Calcd for  $\text{C}_{11}\text{H}_{12}\text{N}_4\text{Cl}_2\text{Cu}$ : C, 39.45; H, 3.59; N, 16.73. Found: C, 39.30; H, 3.51; N, 17.10. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{N}_{\text{im}}-\text{H})$  3124;  $\nu(\text{C}=\text{N})$  1607;  $\nu(\text{CH})$  2920, 2866.

$\{[\text{Cu}(\text{L})(\text{H}_2\text{O})](\text{ClO}_4)_2\}_n$  (**3**). To a solution of **1** in an MeOH/H<sub>2</sub>O mixture (3:1, v/v) was added KOH in methanol. A green-violet microcrystalline material immediately precipitated, which was filtered off, washed successively with methanol and diethyl ether, and dried in air. Yield: 90%. Anal. Calcd for  $\text{C}_{11}\text{H}_{13}\text{N}_4\text{ClCuO}_5$ : C, 34.83; H, 3.46; N, 14.78. Found: C, 35.20; H, 3.02; N, 14.38. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{Cl}-\text{O})$  1090, 1115, 1144;  $\nu(\text{C}=\text{N})$  1606;  $\nu(\text{CH})$  2917, 2857.

$\{[\text{Cu}(\text{L})\text{Cl}]\cdot 2\text{H}_2\text{O}\}_n$  (**4**). Green microcrystals were obtained by following the same procedure as that for **3**, but using **2** as the starting compound. Yield: 80%. Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_2\text{ClCu}$ : C, 39.39; H, 4.17; N, 16.71. Found: C, 39.13; H, 3.73; N, 16.63. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$  1607;  $\nu(\text{CH})$  2924, 2852.

$(\text{hfac})\text{Cu}(\mu\text{-L})\text{M}(\text{hfac})_2(\mu\text{-L})\text{Cu}(\text{hfac})$  ( $\text{M} = \text{Zn}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Mn}^{\text{II}}$ ) (**5–7**). Complexes **5** and **6** were prepared similarly. The synthetic procedure for **6** is described in detail as an example.

To a solution of **1** (1.03 g, 2 mmol) in 20 mL of an MeOH/H<sub>2</sub>O mixture (3:1, v/v) was added a solution of  $[\text{Cu}(\text{hfac})_2]\cdot\text{H}_2\text{O}$  (0.99 g, 2 mmol) in 15 mL of MeOH. A solution of 2 mmol of KOH in MeOH was added dropwise with stirring to the mixture, followed by filtration. From the resulting solution, after 2 days, were obtained green needlelike crystals, which were filtered off, washed with methanol, and air-dried. Yield: 55% (based on **1**).

Complex **6** could also be prepared by treating a methanolic solution of the ligand (1.03 g, 2 mmol) with an excess of  $[\text{Cu}(\text{hfac})_2]\cdot\text{H}_2\text{O}$  (1.98 g, 4 mmol). Yield: 60%.

Complex **7** was prepared from **2** by a procedure similar to that described above for **5** and **6** (these complexes could also be obtained from **2**). All attempts to obtain **7** from **3** were unsuccessful.

**5** was prepared in 60% yield. Anal. Calcd for  $\text{C}_{42}\text{H}_{26}\text{N}_8\text{O}_8\text{F}_{24}\text{Cu}_2\text{Zn}$ : C, 35.53; H, 1.83; N, 7.89. Found: C, 35.43; H, 1.98; N, 8.09. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{O})$  1654, 1613;  $\nu(\text{F}-\text{C})$  1257, 1218, 1151;  $\nu(\text{C}=\text{N})$  1611;  $\nu(\text{CH})$  2930, 2864.

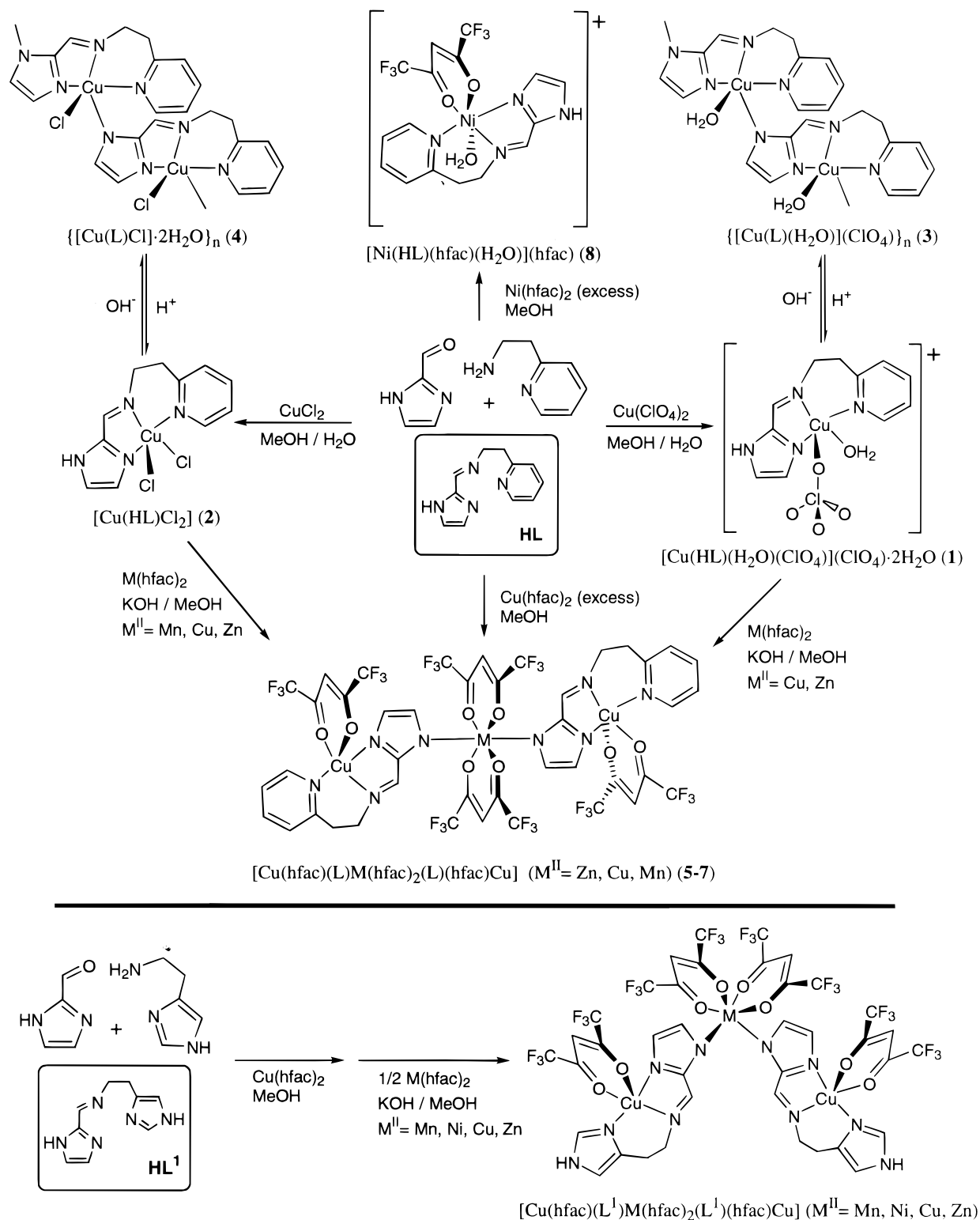
**6** was prepared in 55% yield. Anal. Calcd for  $\text{C}_{42}\text{H}_{26}\text{N}_8\text{O}_8\text{F}_{24}\text{Cu}_3$ : C, 35.57; H, 1.83; N, 7.91. Found: C, 35.50; H, 1.83; N, 8.31. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{O})$  1654, 1612;  $\nu(\text{F}-\text{C})$  1257, 1218, 1150;  $\nu(\text{C}=\text{N})$  1611;  $\nu(\text{CH})$  2929, 2863.

**7** was prepared in 45% yield. Anal. Calcd for  $\text{C}_{42}\text{H}_{26}\text{N}_8\text{O}_8\text{F}_{24}\text{Cu}_2\text{Mn}$ : C, 35.75; H, 1.84; N, 7.95. Found: C, 35.50; H, 1.92; N, 8.15. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{O})$  1654, 1612;  $\nu(\text{F}-\text{C})$  1257, 1218, 1151;  $\nu(\text{C}=\text{N})$  1612;  $\nu(\text{CH})$  2930, 2863.

$[\text{Ni}(\text{HL})(\text{hfac})(\text{H}_2\text{O})](\text{hfac})$  (**8**). To a filtered solution of HL (1.03 g, 2 mmol) in 20 mL of an MeOH/H<sub>2</sub>O mixture (3:1, v/v), prepared by using the procedure described above, was added with continuous stirring a solution of  $[\text{Ni}(\text{hfac})_2]$  (1.90 g, 4 mmol) in 15 mL of MeOH. The resulting cloudy solution was filtered to eliminate a small amount of green precipitate. The filtrate kept at room temperature for 2 days produced green needlelike crystals, which were filtered off, washed with methanol, and air-dried. Yield: 63%. Anal. Calcd for  $\text{C}_{21}\text{H}_{15}\text{N}_4\text{O}_5\text{F}_{12}\text{Ni}$ : C, 36.57; H, 2.19; N, 8.13. Found: C, 36.28; H, 2.15; N, 8.27. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{N}_{\text{im}}-\text{H})$  3124;  $\nu(\text{C}=\text{O})$  1663, 1647;  $\nu(\text{F}-\text{C})$  1262, 1212, 1151;  $\nu(\text{C}=\text{N})$  1608;  $\nu(\text{CH})$  2937, 2860.

**Crystallography.** Crystallographic data are listed in Table 1. The unit cell parameters were determined and the data collected with a Siemens STADI4 diffractometer for **2**, a Siemens P4 for **8**, a Rigaku

Scheme 1



AFC7S for **5**, and a Rigaku AFC5S5 for **6**. The data were corrected for Lorentz-polarization effects and for dispersion, and an empirical absorption correction was applied. The structures were solved by direct methods using the SHELXTL V5 package<sup>10</sup> for **2** and **8** and the SHELXS-97 program<sup>11</sup> for **5** and **6**; they were refined (full-matrix least-squares on  $F^2$ ) by using respectively the SHELXTL V5 package<sup>10</sup> and the SHELXL-97 program.<sup>11</sup> All non-hydrogen atoms were refined

anisotropically, except the F atoms in **8**, which were refined isotropically, while the H atoms were included in calculated positions and treated as riding atoms. In **5**, **6**, and **8**, the  $\text{CF}_3$  groups are disordered and were refined by assuming two orientations.

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**Table 1.** Crystal Data and Structure Refinement Details for **2**, **5**, **6**, and **8**

	<b>2</b>	<b>5</b>	<b>6</b>	<b>8</b>
empirical formula	C <sub>11</sub> H <sub>12</sub> Cl <sub>2</sub> CuN <sub>4</sub>	C <sub>42</sub> H <sub>26</sub> Cu <sub>2</sub> F <sub>24</sub> N <sub>8</sub> O <sub>8</sub> Zn	C <sub>42</sub> H <sub>26</sub> Cu <sub>3</sub> F <sub>24</sub> N <sub>8</sub> O <sub>8</sub>	C <sub>21</sub> H <sub>16</sub> F <sub>12</sub> N <sub>4</sub> NiO <sub>5</sub>
fw	334.69	1419.16	1417.33	691.09
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> (Å)	8.303(2)	10.986(2)	11.057(2)	9.607(5)
<i>b</i> (Å)	13.382(3)	12.778(3)	12.864(3)	12.327(5)
<i>c</i> (Å)	11.876(2)	9.925(2)	9.985(5)	12.690(5)
$\alpha$ (deg)	90	107.84(3)	107.50(3)	115.211(5)
$\beta$ (deg)	90.96(3)	101.13(3)	101.18(2)	93.846(5)
$\gamma$ (deg)	90	75.17(3)	75.16(2)	91.799(5)
<i>V</i> (Å <sup>3</sup> )	1319.4(5)	1272.1(5)	1298.8(8)	1353.6(10)
<i>Z</i>	4	1	1	2
<i>d</i> <sub>calcd</sub> (Mg m <sup>-3</sup> )	1.685	1.852	1.812	1.696
temperature (K)	293(2)	193(2)	294(2)	293(2)
wavelength (Å)	0.710 73	0.710 73	0.710 69	0.710 69
abs coeff (mm <sup>-1</sup> )	2.046	1.444	1.362	0.839
final <i>R</i> indices <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]: <i>R</i> 1, <i>wR</i> 2	0.0375, 0.0841	0.0492, 0.1345	0.0434, 0.1041	0.0330, 0.0802

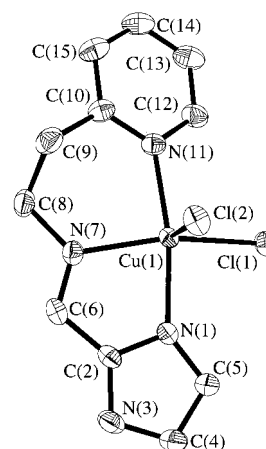
$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

## Results and Discussion

The reaction of HL, a tridentate ligand from the condensation of 2-imidazolecarboxaldehyde and 2-(aminoethyl)pyridine, with either Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O or CuCl<sub>2</sub> in a 1:1 molar ratio gives [Cu(HL)(H<sub>2</sub>O)(ClO<sub>4</sub>)](ClO<sub>4</sub>)·2H<sub>2</sub>O (**1**) or [Cu(HL)Cl<sub>2</sub>] (**2**), in which the NH group of the imidazole moiety remains protonated.

Complexes **1** and **2**, after deprotonation, show a great tendency to accept an imidazole nitrogen donor atom from a neighboring molecule and to form, through a self-assembly process, polynuclear copper(II) complexes of formula [Cu(L)X]<sub>*n*</sub> (X = H<sub>2</sub>O, Cl<sup>-</sup>). The reversible disassembling process from polynuclear to mononuclear systems can be achieved in an acid medium.

To obtain trinuclear complexes, we used the mononuclear complexes **1** and **2** as ligands for bis(hexafluoroacetylacetonato)metal(II) (see Scheme 1). When **1** is allowed to react with an excess of [M(hfac)<sub>2</sub>] (M = Cu<sup>II</sup>, Ni<sup>II</sup>, Mn<sup>II</sup>, Zn<sup>II</sup>) in a basic medium, only the trinuclear complexes [(hfac)Cu(L)M(hfac)<sub>2</sub>-(L)Cu(hfac)] (M = Zn<sup>II</sup>, Cu<sup>II</sup>) can be isolated. It should be noted that free hexafluoroacetylacetonato anions, from the partial dissociation of [M(hfac)<sub>2</sub>] complexes in a methanol/water mixture, block two coordination positions on the copper ion. Thus, the copper(II) coordination sphere is in principle saturated and precursor **1** may be prevented from undergoing the self-assembly reaction. The fact that the trinuclear analogues containing Mn<sup>II</sup> and Ni<sup>II</sup> could not be obtained is a consequence of the great tendency of the complexes to undergo self-assembly, so that only the most stable Zn<sup>II</sup> and Cu<sup>II</sup> complexes are formed. When [Cu(HL)Cl<sub>2</sub>] (**2**) is used, however, complexes **5–7** are obtained, while all attempts to prepare the corresponding Ni(II) complex yielded a mixture of products, including the self-assembled and the trinuclear Cu–Ni–Cu complexes. Thus, in this case, the formation of **4** through the self-assembly process is likely to be thermodynamically/kinetically less favored than that of **3**, allowing the coordination of the deprotonated precursor to the [Mn(hfac)<sub>2</sub>] unit. It should be pointed out that the reaction of the ligand with [Cu(hfac)<sub>2</sub>] in a 1:2 molar ratio leads to the trinuclear copper(II) complex. In this case, free hfac<sup>-</sup> anions also deprotonate the imidazole moiety. In view of this, we attempted to prepare, by following the same method, a linear Ni<sub>3</sub> trinuclear complex, which would exhibit an irregular spin state distribution and ferrimagnetic behavior.<sup>12</sup> However, the direct reaction between HL and an excess of [Ni(hfac)<sub>2</sub>] in a methanol/water mixture yielded the mononuclear complex



**Figure 1.** Perspective view of the mononuclear precursor **2**.

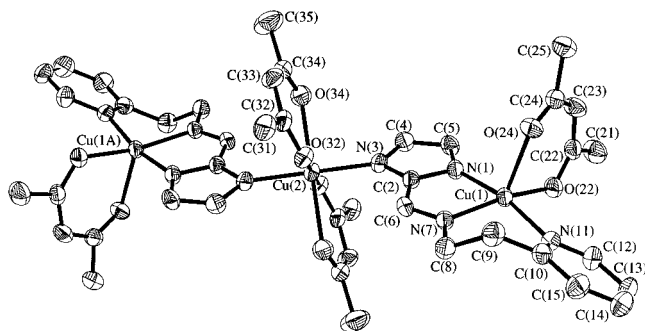
[Ni(HL)(hfac)(H<sub>2</sub>O)](hfac) (**8**), in which the ligand remains deprotonated. In this case, the coordination of the ligand to the Ni<sup>II</sup> ion may reduce the acidity of the N<sub>im</sub>–H group to such an extent that the hexafluoroacetylacetonate base cannot bring about its deprotonation. It should be noted that all attempts to obtain bimetallic trinuclear species of the type Ni–M–Ni from **8** and [M(hfac)<sub>2</sub>] as precursors in a basic medium were unsuccessful.

The IR spectra of the precursors **1** and **2** exhibit  $\nu$ (N<sub>im</sub>–H) stretching vibration bands at 3111 and 3124 cm<sup>-1</sup>, respectively, which are absent in the IR spectra of the trinuclear and self-assembled complexes. Complex **8** exhibits that band at 3124 cm<sup>-1</sup>. Compounds **1** and **2** are insoluble, in good accord with their polynuclear structures, while trinuclear complexes and the mononuclear complex **8** are soluble in common organic solvents. IR and powder X-ray diffraction results indicate that complex **7** is isostructural with **5** and **6**.

**Crystal Structures.** The structure of precursor **2** consists of discrete mononuclear [Cu(HL)Cl<sub>2</sub>] molecules. A perspective view of the structure together with the atom-labeling scheme is shown in Figure 1. Selected bond distances and angles are given in Table 2. The copper(II) ion is pentacoordinated with a geometry that is intermediate between a trigonal bipyramid (*C*<sub>3*v*</sub>) and a square-based pyramid (*C*<sub>4*v*</sub>). According to the procedure described by Addison,<sup>13</sup> the copper(II) atom has a  $\tau$  value of

(12) Kahn, O. *Molecular Magnetism*; VCH Publishers: Weinheim, Germany, 1993.





**Figure 2.** Molecular structure of the trans trinuclear complexes **5** and **6** (shown). F atoms are omitted for clarity.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **2**

Cu(1)–N(1)	2.012(2)	Cu(1)–N(7)	2.047(2)
Cu(1)–N(11)	2.065(2)	Cu(1)–Cl(1)	2.2929(9)
Cu(1)–Cl(2)	2.5404(8)		
N(1)–Cu(1)–N(7)	79.64(9)	N(1)–Cu(1)–N(11)	166.88(9)
N(7)–Cu(1)–N(11)	91.36(9)	N(1)–Cu(1)–Cl(1)	88.70(7)
N(7)–Cu(1)–Cl(1)	159.41(7)	N(11)–Cu(1)–Cl(1)	96.91(7)
N(1)–Cu(1)–Cl(2)	94.92(7)	N(7)–Cu(1)–Cl(2)	95.83(7)
N(11)–Cu(1)–Cl(2)	95.48(7)	Cl(1)–Cu(1)–Cl(2)	102.07(3)

0.12 ( $\tau = (\theta_1 - \theta_2)/60^\circ$ , where  $\theta_1$  and  $\theta_2$  are the largest angles in the coordination sphere), thus indicating that the  $\text{CuN}_3\text{Cl}_2$  coordination polyhedra can be better described as distorted square-based pyramids. In this description, the basal coordination sites are occupied by the three donor nitrogen atoms of the tridentate ligand, with bond distances in the range 2.012(2)–2.065(2) Å, and one of the chloride atoms at a distance of 2.2929(9) Å, whereas the apical site is occupied by the other chloride ligand at a longer distance of 2.5404(8) Å. The latter atom, Cl(2), is involved in a hydrogen-bond interaction with the imidazole moiety of an adjacent molecule,  $\text{N}(3)\text{---H}\cdots\text{Cl}(2)^i$  with values of 3.130(3) Å and  $173.4(2)^\circ$  ( $i = x - 1/2, 1/2 - y, 1/2 + z$ ).

The trinuclear complexes **5** and **6** are isostructural and consist of well-isolated  $[\text{hfac}]\text{Cu}(\text{L})\text{M}(\text{hfac})_2(\text{L})\text{Cu}(\text{hfac})$  molecules with  $C_i$  symmetry, the center of symmetry being located at the central metal. Thus, the  $[\text{Cu}(\text{L})(\text{hfac})]$  fragments are in trans positions, leading to a linear conformation with  $\text{Cu}^{\text{II}}\text{---Zn}^{\text{II}}$  and  $\text{Cu}^{\text{II}}\text{---Cu}^{\text{II}}$  distances of 5.809(2) and 5.782(3) Å, respectively. A perspective view of the structure of **6** is given in Figure 2 together with the atom-labeling scheme. Selected bond distances and angles for **5** and **6** are listed in Table 3. As described elsewhere, the related trinuclear complexes, containing the ligand from the 1:1 condensation of 2-imidazolecarboxaldehyde and histamine, adopt a V-shaped conformation.<sup>9</sup> This conformation was suggested to be a consequence of the hydrogen-bond interactions involving the amino group of the histamine residue and the oxygen atom of the hexafluoroacetylacetonate group from a neighboring molecule. In this case, however, the absence of active hydrogen atoms, which might be involved in hydrogen-bond interactions, leads to the less sterically hindered linear conformation. The central metal atom M ( $\text{Zn}^{\text{II}}$  or  $\text{Cu}^{\text{II}}$ ) adopts a minimally distorted  $\text{MO}_4\text{N}_2$  octahedral environment, with the nitrogen atoms from the imidazolate groups and two oxygen atoms of the hfac ligands occupying trans equatorial positions and the remaining two oxygen atoms from the hfac ligands filling the axial positions at a longer distance. The terminal copper(II) ions exhibit almost perfect square pyramidal coordination

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **5** and **6**

Complex <b>5</b>			
Cu(1)–N(1)	1.977(3)	Cu(1)–N(7)	2.001(2)
Cu(1)–N(11)	2.020(3)	Cu(1)–O(22)	1.978(2)
Cu(1)–O(24)	2.231(2)		
Zn(1)–N(3)	2.029(2)	Zn(1)–N(3) <sup>ii</sup>	2.029(2)
Zn(1)–O(32)	2.071(2)	Zn(1)–O(32) <sup>ii</sup>	2.071(2)
Zn(1)–O(34)	2.219(2)	Zn(1)–O(34) <sup>ii</sup>	2.219(2)
N(1)–Cu(1)–O(22)	91.11(10)	N(1)–Cu(1)–N(7)	81.75(10)
O(22)–Cu(1)–N(7)	163.53(9)	N(1)–Cu(1)–N(11)	168.52(9)
O(22)–Cu(1)–N(11)	92.58(10)	N(7)–Cu(1)–N(11)	91.81(10)
N(1)–Cu(1)–O(24)	97.74(9)	O(22)–Cu(1)–O(24)	87.73(8)
N(7)–Cu(1)–O(24)	107.86(9)	N(11)–Cu(1)–O(24)	93.27(9)
N(3) <sup>ii</sup> –Zn(1)–N(3)	180.0	N(3) <sup>ii</sup> –Zn(1)–O(32) <sup>ii</sup>	91.40(9)
N(3)–Zn(1)–O(32) <sup>ii</sup>	88.60(9)	N(3) <sup>ii</sup> –Zn(1)–O(32)	88.60(9)
N(3)–Zn(1)–O(32)	91.40(9)	O(32) <sup>ii</sup> –Zn(1)–O(32)	180.0
N(3) <sup>ii</sup> –Zn(1)–O(34) <sup>ii</sup>	91.11(9)	N(3)–Zn(1)–O(34) <sup>ii</sup>	88.89(9)
O(32) <sup>ii</sup> –Zn(1)–O(34) <sup>ii</sup>	87.05(8)	O(32)–Zn(1)–O(34) <sup>ii</sup>	92.95(8)
N(3) <sup>ii</sup> –Zn(1)–O(34)	88.89(9)	N(3)–Zn(1)–O(34)	91.11(9)
O(32) <sup>ii</sup> –Zn(1)–O(34)	92.95(8)	O(32)–Zn(1)–O(34)	87.05(8)
O(34) <sup>ii</sup> –Zn(1)–O(34)	180.0		
Complex <b>6</b>			
Cu(1)–N(1)	1.975(3)	Cu(1)–N(7)	2.007(3)
Cu(1)–N(11)	2.030(4)	Cu(1)–O(22)	1.979(3)
Cu(1)–O(24)	2.232(3)		
Cu(2)–N(3)	1.992(3)	Cu(2)–N(3) <sup>ii</sup>	1.992(3)
Cu(2)–O(32)	2.051(3)	Cu(2)–O(32) <sup>ii</sup>	2.051(3)
Cu(2)–O(34)	2.283(3)	Cu(2)–O(34) <sup>ii</sup>	2.283(3)
N(1)–Cu(1)–O(22)	91.20(14)	N(1)–Cu(1)–N(7)	81.57(14)
O(22)–Cu(1)–N(7)	163.62(14)	N(1)–Cu(1)–N(11)	167.99(14)
O(22)–Cu(1)–N(11)	92.62(14)	N(7)–Cu(1)–N(11)	91.74(14)
N(1)–Cu(1)–O(24)	98.32(14)	O(22)–Cu(1)–O(24)	87.39(12)
N(7)–Cu(1)–O(24)	108.12(13)	N(11)–Cu(1)–O(24)	93.22(13)
N(3) <sup>ii</sup> –Cu(2)–N(3)	180.0	N(3) <sup>ii</sup> –Cu(2)–O(32) <sup>ii</sup>	91.36(13)
N(3)–Cu(2)–O(32) <sup>ii</sup>	88.64(13)	N(3) <sup>ii</sup> –Cu(2)–O(32)	88.64(13)
N(3)–Cu(2)–O(32)	91.36(13)	O(32) <sup>ii</sup> –Cu(2)–O(32)	180.0
N(3) <sup>ii</sup> –Cu(2)–O(34) <sup>ii</sup>	91.01(13)	N(3)–Cu(2)–O(34) <sup>ii</sup>	88.99(13)
O(32) <sup>ii</sup> –Cu(2)–O(34) <sup>ii</sup>	86.31(12)	O(32)–Cu(2)–O(34) <sup>ii</sup>	93.69(12)
N(3) <sup>ii</sup> –Cu(2)–O(34)	88.99(13)	N(3)–Cu(2)–O(34)	91.01(13)
O(32) <sup>ii</sup> –Cu(2)–O(34)	93.69(12)	O(32)–Cu(2)–O(34)	86.31(12)
O(34) <sup>ii</sup> –Cu(2)–O(34)	180.0		

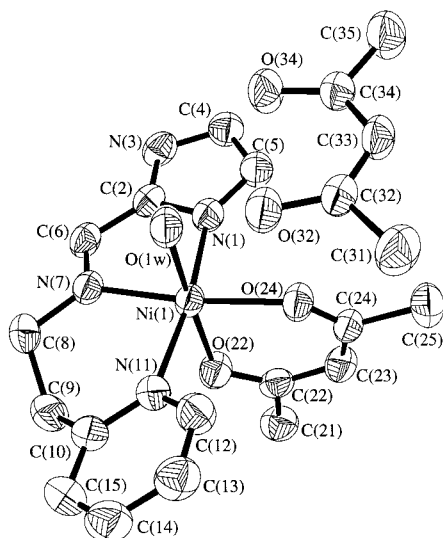
<sup>a</sup> ii =  $-x, -y, -z$ .

dination geometries ( $\tau = 0.08$  and  $0.07$  for **5** and **6**, respectively) for the  $\text{N}_3\text{O}_2$  donor set, where the basal coordination sites are occupied by one oxygen atom of the hfac ligand and the three donor atoms of the tridentate ligand at distances close to 2.0 Å, whereas the apical site is occupied for the remaining oxygen atom from the hfac ligand at a longer distance. As usual, the copper ions are raised from the mean basal plane toward the apical nitrogen atoms by 0.2228(11) and 0.2266(18) Å for **5** and **6**, respectively.

The structure of **8** consists of mononuclear  $[\text{Ni}(\text{HL})(\text{hfac})(\text{H}_2\text{O})]^+$  cations and  $\text{hfac}^-$  anions bonded by hydrogen bonds. A perspective view of the structure is given in Figure 3, and selected bond distances and angles are listed in Table 4. The  $\text{Ni}^{\text{II}}$  ion adopts a minimally distorted  $\text{NiN}_3\text{O}_3$  octahedral coordination environment, in which the three nitrogen atoms from the undeprotonated HL ligand as well as the three oxygen atoms from hfac and water ligands occupy mer positions. The free hfac ligand is planar, as expected for a  $\pi$  aromatic system, and forms two hydrogen bonds with water molecules, the  $\text{O}(34)\cdots\text{O}(1\text{W})$  and  $\text{O}(32)\cdots\text{O}(1\text{W})$  distances being 2.903(7) and 2.779(6) Å, respectively (iii =  $2 - x, 1 - y, 1 - z$ ).

**Magnetic Properties.** The  $\chi_{\text{M}}T$  products at room temperature for compounds **3** and **4** (0.34 and  $0.37 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , respectively) are compatible with the spin-only value for a system with  $S = 1/2$ . The  $\chi_{\text{M}}$  vs  $T$  plots show maxima at 55 and 65 K for **3** and **4**, respectively. These facts clearly indicate that an

(13) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.



**Figure 3.** Perspective view of complex **8**. F atoms are omitted for clarity.

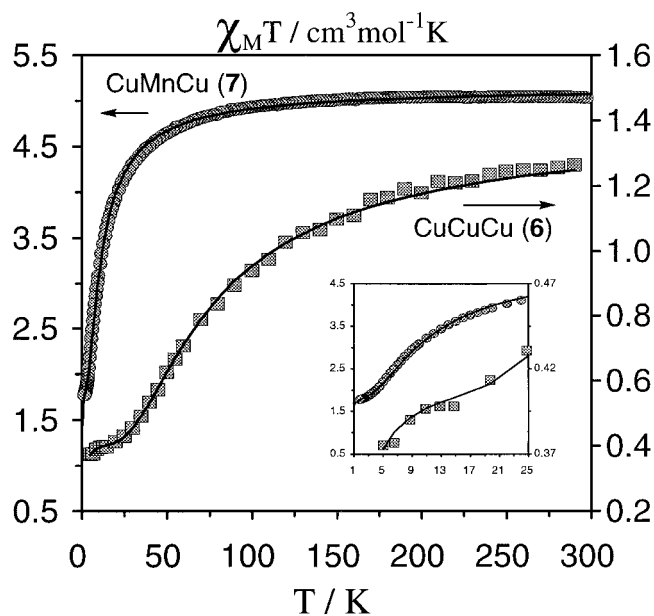
**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for **8**

Ni(1)–N(1)	2.093(2)	Ni(1)–N(7)	2.055(2)
Ni(1)–N(11)	2.091(2)	Ni(1)–O(22)	2.063(2)
Ni(1)–O(24)	2.032(2)	Ni(1)–O(1W)	2.064(2)
O(24)–Ni(1)–N(7)	172.37(8)	O(24)–Ni(1)–O(1W)	87.40(8)
N(7)–Ni(1)–O(1W)	92.60(8)	O(24)–Ni(1)–O(22)	89.46(8)
N(7)–Ni(1)–O(22)	90.79(8)	O(1W)–Ni(1)–O(22)	176.22(7)
O(24)–Ni(1)–N(1)	92.60(8)	N(7)–Ni(1)–N(1)	79.77(9)
O(1W)–Ni(1)–N(1)	92.27(9)	O(22)–Ni(1)–N(1)	89.96(9)
O(24)–Ni(1)–N(11)	95.69(8)	N(7)–Ni(1)–N(11)	91.94(9)
O(1W)–Ni(1)–N(11)	88.59(9)	O(22)–Ni(1)–N(11)	89.63(9)
N(1)–Ni(1)–N(11)	171.70(8)		

antiferromagnetic interaction operates between copper(II) ions. The magnetic susceptibility data were analyzed on the basis of the isotropic spin Hamiltonian  $H = -J\sum_i^{n-1} S_i \cdot S_{i+1}$  for one-dimensional infinite regular chain systems.<sup>12</sup> The best fitting led to  $J = -60.3$  and  $-69.5$   $\text{cm}^{-1}$  and  $g = 2.02$  and  $2.06$  for **3** and **4**, respectively. These  $J$  values suggest that, in both compounds, an imidazolate group bridges two copper ions at their equatorial positions ( $J$  values normally are in the range  $-40$  to  $-100$   $\text{cm}^{-1}$ ) rather than at their axial positions ( $J$  values ranging from  $-1$  to  $-30$   $\text{cm}^{-1}$ ).<sup>6</sup>

The temperature dependences of  $\chi_M T$  for compounds **6** and **7** are compared in Figure 4. A plot for the Cu–Zn–Cu complex **5** has not been included because its  $\chi_M T$  product is independent of temperature and has a value compatible with the spin value expected for two isolated  $\text{Cu}^{\text{II}}$  ions, thus indicating that the coupling between the terminal copper ions is negligible.

The  $\chi_M T$  values at room temperature for the trinuclear complexes **6** and **7** are compatible with those expected for magnetically isolated three-spin systems ( $1/2, S_M, 1/2$ ). When the temperature is lowered, the  $\chi_M T$  product gradually decreases down to the values expected for the spin states  $S = 1/2$  and  $S = 3/2$ , respectively, thus indicating the existence of an antiferromagnetic interaction between the copper and central metal through the imidazolate group. The magnetic susceptibility data for **6** were quantitatively analyzed using the theoretical expression deduced from the spin Hamiltonian for a symmetrical three-spin system,  $\mathbf{H} = -J_{\text{CuM}}(\mathbf{S}_{\text{Cu1}}\mathbf{S}_M + \mathbf{S}_M\mathbf{S}_{\text{Cu2}})$ ,<sup>12</sup> where the exchange interaction between terminal copper(II) ions was neglected. The parameters resulting from the best fitting of the magnetic data are  $J = -37.2$   $\text{cm}^{-1}$ ,  $g_{\text{Cu}} = 2.12$ ,  $g_{\text{Cu}}(\text{central}) = 2.19$ , and  $\Theta = -0.6$  K; the latter was included to account for

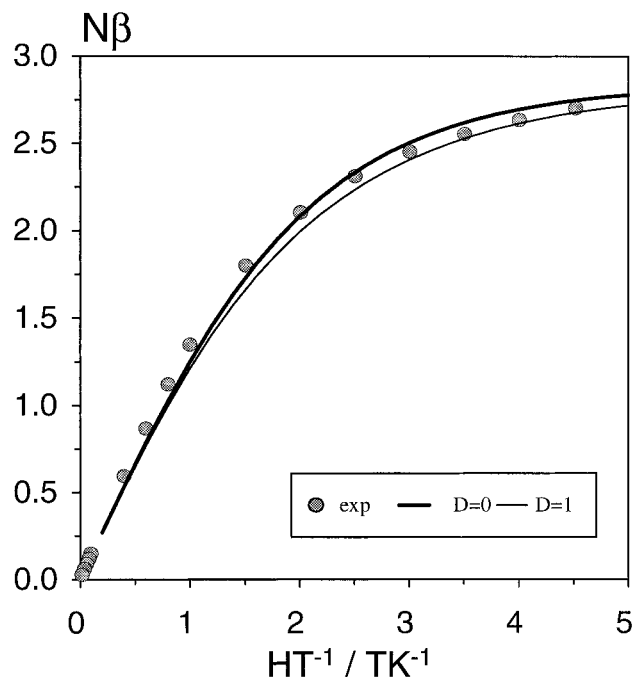


**Figure 4.** Magnetic properties,  $\chi_M T$  ( $\text{cm}^3 \text{mol}^{-1} \text{K}$ ) vs  $T$ , of complexes **6** (■) and **7** (●). Inset: amplification of the low-temperature range.

the intermolecular interactions. The  $J$  value for the  $\text{Cu}^{\text{II}}$  trinuclear complex is compatible with those for di- and trinuclear copper(II) complexes in which the imidazolate group bridges the copper(II) ions at their equatorial positions,<sup>6,9</sup> the antiferromagnetic exchange interaction thus being due to the  $\sigma$  overlap of the  $d_{xy}$  orbitals through the imidazolate bridge. In the case of **7**, the  $\chi_M T$  product slightly decreases at very low temperatures below the beginning of a plateau corresponding to the  $S = 3/2$  ground state. This is mainly due to a zero-field splitting within the quartet ground state that arises from both local anisotropy of  $\text{Mn}^{\text{II}}$  and the  $\text{Cu}^{\text{II}}\text{--Mn}^{\text{II}}$  anisotropic interaction. Then, the appropriate spin Hamiltonian for analyzing the magnetic data is  $\mathbf{H} = -J(\mathbf{S}_{\text{Cu1}}\mathbf{S}_{\text{Mn}} + \mathbf{S}_{\text{Cu2}}\mathbf{S}_{\text{Mn}}) + \mathbf{S}_{\text{Mn}}\mathbf{D}_{\text{Mn}}\mathbf{S}_{\text{Mn}} + \mathbf{S}_{\text{Cu1}}\mathbf{D}_{\text{Cu1Mn}}\mathbf{S}_{\text{Mn}} + \mathbf{S}_{\text{Cu2}}\mathbf{D}_{\text{Cu2Mn}}\mathbf{S}_{\text{Mn}}$ , where  $\mathbf{D}_{\text{Mn}}$  and  $\mathbf{D}_{\text{CuMn}}$  represent local anisotropy and anisotropic interactions, respectively. The best fitting to the theoretical expression obtained from the above spin Hamiltonian<sup>12</sup> (assuming that the zero-field splitting is axial and that  $D$  is the energy gap between the  $\pm 3/2$  and  $\pm 1/2$  Kramers doublets arising from the quartet ground state) led to  $J = -3.74$   $\text{cm}^{-1}$ ,  $|D| = 0.40$   $\text{cm}^{-1}$  (the sign of  $D$  could not be determined unambiguously from powder magnetic susceptibility data),  $g_{\text{Mn}} = 2.00$ , and  $g_{\text{Cu}} = 2.06$ .  $D$  is related to the local anisotropy and anisotropic interaction parameters by the expression<sup>12</sup>  $D = -7(\mathbf{D}_{\text{Cu1Mn}} + \mathbf{D}_{\text{Cu2Mn}})/30 + 28 \mathbf{D}_{\text{Mn}}/15$ .

Since  $\mathbf{D}_{\text{Mn}}$  is probably the main contribution to  $D$ ,  $\mathbf{D}_{\text{Mn}} = 15D/28 = \pm 0.2$   $\text{cm}^{-1}$ . Nevertheless, the  $D$  value obtained from the fitting is strongly correlated with the intermolecular magnetic interactions and should be considered as a limit value. Thus  $\mathbf{D}_{\text{Mn}} < \pm 0.2$   $\text{cm}^{-1}$ . The experimental magnetization data of **7** at 1.9 K (Figure 5) can be well fitted to the theoretical expression for an  $S = 3/2$  system with  $g_{3/2,1} = 1.98$  for  $D = 0$  as well as for  $D = 1$ . This result nicely supports the quartet nature of the ground state and a very small zero-field splitting within this state, in line with the magnetic susceptibility results. From the relationship between  $g_{3/2,1}$  and the local  $g$  factors,<sup>12</sup>  $g_{3/2,1} = (7g_{\text{Mn}} - 2g_{\text{Cu}})/5$ , with  $g_{\text{Mn}} = 2.0$ , a value for  $g_{\text{Cu}} = 2.05$  is obtained, which is in good agreement with that deduced from magnetic susceptibility measurements.

The above results indicate that, as expected, the  $J$  value for complex **7** is much smaller than that for complex **6**. Nevertheless, to deal with comparable values, the  $n_{\text{Cu}}n_{\text{M}}/|J|$  relation ( $n_{\text{Cu}}$



**Figure 5.** Theoretical plots of an  $S = 3/2$  system with  $g_{3/2,1} = 1.98$  and  $D = 0$  (thick line) or  $D = 1$  (thin line) and magnetization data for **7** at 1.9 K.

and  $n_M$  are the numbers of unpaired electrons on the copper(II) and central metal paramagnetic centers) should be taken into account. From the  $J$  values of **6** and **7** and the above relation, we see that  $|J_{Cu}|$  ( $-37.2 \text{ cm}^{-1}$ )  $\gg$   $5|J_{Mn}|$  ( $-3.74 \text{ cm}^{-1}$ ), thus illustrating the ability of  $\text{Cu}^{\text{II}}$  as compared to  $\text{Mn}^{\text{II}}$  to yield antiferromagnetic interactions, everything being equal. This can be attributed mainly to the decrease of the spin delocalization on the bridge as the energy of the 3d orbitals increases and to the presence of possible ferromagnetic contributions in the case of  $\text{Mn}^{\text{II}}$ .

Furthermore, the  $J$  value for the trans trinuclear copper(II) complex **6** ( $-37.2 \text{ cm}^{-1}$ ) is smaller than that observed previously by us for the analogous cis trinuclear  $\text{Cu}_3$  complex with a V-shape conformation ( $-60.6 \text{ cm}^{-1}$ ). This fact can be satisfac-

torily explained by applying the analysis made by Bencini et al.<sup>14</sup> of the exchange interaction mediated by an imidazolate bridge. They concluded, by using extended Hückel molecular orbital calculations, that the extent of the antiferromagnetic coupling would be predominantly affected by the  $\alpha$  angle between the Cu–N and N–N vectors and it would be depend, to some extent, on the  $\theta$  angle between the copper and imidazole coordination planes. Thus, the antiferromagnetic exchange interaction would increase with an increase of  $\alpha$  and  $\theta$  angles. To establish a correlation between the square of the energy gap of the singly occupied molecular orbitals ( $\Delta^2$ ), upon which the antiferromagnetic contribution depends, and the  $\alpha$  and  $\theta$  angles, we performed new EHMO calculations<sup>15</sup> on the dinuclear model compound  $[(\text{OH})_2(\text{NH}_3)\text{Cu}(\mu\text{-imidazolate})\text{Cu}(\text{NH}_3)(\text{OH})_2]$  with a square planar coordination environment around the copper(II) ions. The results agree well with those of Bencini et al. and indicate that, for the  $\theta$  values observed in the cis and trans complexes of about  $45^\circ$ , there is a marked decrease in  $\Delta^2$  on moving from  $166$  to  $162^\circ$ , the  $\alpha_2$  values for the cis and trans complexes, respectively ( $\alpha_1$ ,  $\theta_1$ , and  $\theta_2$  being quite similar for both compounds). Therefore, the difference in the magnitudes of the antiferromagnetic exchange interactions observed for the cis and trans  $\text{Cu}_3$  complexes can be attributed mainly to the difference in  $\alpha_2$  values.

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**Supporting Information Available:** Listings of structure refinement details, atomic coordinates, thermal parameters, and bond distances and angles for complexes **2**, **5**, **6**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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