A Novel Series of Heterotrinuclear Complexes Involving Imidazolate Bridging Schiff's Base Ligands. Synthesis, Crystal Structure, and Magnetic Properties

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Mononuclear copper(II) complexes with an unsymmetrical tridentate Schiff's base involving two imidazole moieties, $[Cu(HL)(H_2O)](ClO_4)_2$ (**1**) and [Cu(L)(hfac)] (**3**), have been prepared and characterized, where HL stands for the 1:1 condensation product of 2-imidazolecarboxaldehyde and histamine. Under basic conditions, **1** easily undergoes a self-assembly process affording an insoluble imidazolate-bridged polymeric species $\{[Cu(L)(H_2O)](ClO_4)\}_n$ (**2**). By using **1** and **3** as "ligand complexes" toward $M(hfac)_2$ (hfac = hexafluoroacetylacetonate) a series of imidazolate-bridged heterometal trinuclear complexes with the formula $[Cu(L)(hfac)M(hfac)_2Cu(hfac)(L)]$ (M = Zn^{II}, Cu^{II}, Ni^{II}, Mn^{II}) (**4**−**7**) can be prepared. The structures of these complexes have been solved by X-ray crystallographic methods. All the trinuclear complexes are isostructural and consist of trinuclear molecules with a V-shaped conformation, which are formed by two CuL(hfac) "ligands" bonded through imidazolate bridges to the central metal in cis-position. The ligand environment about the central metal atom can be described as a distorted octahedron, with the nitrogen atoms from the imidazolate groups and two oxygen atoms of the hfac ligands in the equatorial plane and the remaining two oxygen atoms from the hfac ligands filling the axial positions at longer distances. The coordination geometry of the copper(II) ion is very close to a square pyramid with one oxygen atom from the hfac in a more distant axial position. The magnetic susceptibility data (2−300 K) revealed antiferromagnetic interactions between copper(II) ions and the central metal. The magnetic susceptibility data were quantitatively analyzed using the theoretical expressions deduced from the spin Hamiltonian for a symmetrical three-spin system $H = -J_{CuM}(S_{Cu1}\cdot S_M + S_M\cdot S_{Cu2})$ to give the coupling parameters $J_{CuCu} = -60.6$ cm^{-1}, $J_{CuNi} = -21.6$ cm^{-1}, and $J_{CuMn} = -3.2$ cm^{-1}. These magnetic behaviors are discussed on the basis of the localized-orbital model of exchange interactions.

Introduction

Heteropolymetallic complexes are of current interest due to their importance in the study of magnetic exchange and charge transfer between metal ions, as models for biological systems, and in the designing of new magnetic materials, such as molecular-based magnets.[1−7]

The most successful and usual strategy for preparing heteronuclear complexes is that of using metal complexes as "ligands", that is to say, metal complexes containing potential donor groups for another metal ion or metal complex with empty coordination sites. Following this rational synthetic approach a great variety of heterometallic complexes, ranging from discrete entities to 3D extended structures can be obtained.[5] Typical examples of paramagnetic ligands, which can be used as building blocks for the design of heteropolymetallic systems are oxalate, oxamidate, oximate, cyano, and carboxylate metal complexes.[4,5] All of them have been widely investigated, in the past few years, for their use in the design of molecular-based magnets. Although most of the precursors act as chelate agents toward a second metal ion, monodentate precursors have also been successfully used for this end. Good examples of this kind of precursors are metal complexes containing an imidazole moiety, which after deprotonation can coordinate to another metal ion, leading to imidazolate-bridged heterometallic complexes.[7−12] Because the imidazolate anion is known to act as a bridging ligand between copper and zinc in bovine erythrocyte superoxide dismutase (BESOD)[13] and because the imidazole moiety of histidyl

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residues in a large number of metalloproteins constitutes all or part of the binding sites of various transition metal ions, the study of the bonding between imidazole derivatives and transition metal ions is of additional interest.

Despite this, as far as we know, only a small number of known and structurally fully characterized imidazolate-bridged heteronuclear complexes have been reported so far,[7,10−12,14] probably due to the difficulty in preparing and crystallizing them. With the exception of a trinuclear $Cu^{II}-Fe^{III}-Cu^{II}$ complex[14] all of them are dinuclear systems.

In view of this, we decided to prepare new imidazolate-bridged trinuclear complexes with a systematic combination of metal ions. It should be noted that studies on heterotrinuclear complexes are limited to a small number of known and fully characterized complexes.[15−27]

We report here on the synthesis, crystal structure, and magnetic properties of a series of imidazolate-bridged trinuclear complexes with the formula [Cu(L)(hfac)M(hfac)$_2$Cu(hfac)(L)] (M = Zn^{II}, Cu^{II}, Ni^{II}, Mn^{II}; HL is the tridentate Schiff base and hfac is the hexafluoroacetylacetonate anion).

Experimental Section

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 SQUID-based sample magnetometer on a Quantum Design model MPMS instrument. 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.

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

Preparation of the Compounds. [Cu(HL)(H$_2$O)](ClO$_4$)$_2$ (1). This complex was prepared by refluxing 2-imidazolecarboxaldehyde (0.2 g, 2.08 mmol) and histamine (0.23 g, 2.08 mmol) for 1 h in 30 mL of a MeOH/H_2O mixture (3/1, v/v). To the filtered and cold yellow solution was added $Cu(ClO_4)_2 \cdot 6H_2O$ (0.77 g, 2.08 mmol) in 30 mL of MeOH dropwise with stirring. After standing for several hours, a blue powder precipitated, which was collected by filtration, washed successively with methanol and diethyl ether, and dried in air. Yield: 70%. Anal. Calcd for $C_9H_{13}N_5Cl_2CuO_9$: C, 23.02; H, 2.79; N, 14.91. Found: C, 23.09; H, 2.81; N, 14.96. IR (KBr, cm^{-1}): $\upsilon(N_{his}-H)$ 3337; $\upsilon(N_{im}-H)$ 3150; $\upsilon(Cl-O)$ 1084, 1120, 1144.

{[Cu(L)(H$_2$O)](ClO$_4$)}$_n$ (2). To a solution of **1** in MeOH/H_2O mixture (3/1, v/v) was added KOH in methanol. A green-violet microcrystalline material immediately precipitated, which was filtered off, washed with methanol and diethyl ether, and dried in air. Yield: 80%. Anal. Calcd for $C_9H_{12}N_5ClCuO_5$: C, 29.35; H, 3.29; N, 19.03. Found: C, 29.83; H, 3.51; N, 19.06. IR (KBr, cm^{-1}): $\upsilon(N_{his}-H)$ 3350.

[Cu(L)(hfac)] (3). A filtered yellow solution of the HL ligand (0.39 g, 2.08 mmol), prepared by using the procedure described above, was added to a solution of Cu(hfac)$_2$ (1 g, 2.08 mmol) in 30 mL of methanol. The resulting blue solution was kept at room temperature for 2 days and provided a microcrystalline blue powder, which was filtered and washed with methanol and diethyl ether. Yield: 50%. Anal. Calcd for $C_{14}H_{11}N_5CuO_2F_6$: C, 36.63; H, 2.40; N, 15.26. Found: C, 36.23; H, 2.67; N, 15.04. IR (KBr, cm^{-1}): $\upsilon(N_{his}-H)$ 3308; $\upsilon(C=O)$ 1662, 1624; $\upsilon(F-C)$ 1255, 1204, 1143.

[Cu(hfac)(L)M(hfac)$_2$(L)(hfac)Cu] (4−7) (M = Zn^{II}, Cu^{II}, Ni^{II}, Mn^{II}). These trinuclear complexes were prepared in a similar way following methods (a) and (b) below. The synthetic procedures of **5** are described in detail as an example.

(a) To a solution of **3** (0.15 g, 0.33 mmol) in 30 mL of MeOH was added with continuous stirring a solution of Cu(hfac)$_2$ (0.08 g, 0.17 mmol) in 15 mL of MeOH. The resulting green solution was kept at room temperature for 3 days and gave green needlelike crystals, which were filtered, washed with diethyl ether, and dried in air. Yield: 90%.

(b) To a solution of **1** (0.15 g, 0.32 mmol) in 20 mL of a MeOH/H_2O mixture (3:1 v/v) was added a solution of Cu(hfac)$_2$ (0.16 g, 0.32 mmol) in 15 mL of MeOH. A solution of 0.32 mmol of KOH in MeOH was added dropwise with stirring to the mixture and then filtered. From the resulting solution, after 2 days, green needlelike crystals were isolated. Yield: 40%.

Anal. Calcd for $C_{38}H_{24}N_{10}O_8F_{24}Cu_2Zn$ (**4**): C, 32.65; H,1.74; N, 10.08. Found: C, 32.61; H, 1.72; N, 10.25. IR (KBr, cm^{-1}): $\upsilon(N_{his}-H)$ 3298; $\upsilon(C=O)$ 1654, 1623; $\upsilon(F-C)$ 1254, 1216, 1144.

Anal. Calcd for $C_{38}H_{24}N_{10}O_8F_{24}Cu_3$ (**5**): C, 32.74; H,1.74; N,10.05. Found: C, 32.52; H, 1.58; N, 9.67. IR (KBr, cm^{-1}): $\upsilon(N_{his}-H)$ 3308; $\upsilon(C=O)$ 1654, 1621; $\upsilon(F-C)$ 1255, 1216, 1149.

Anal. Calcd for $C_{38}H_{24}N_{10}O_8F_{24}Cu_2Ni$ (**6**): C, 32.81; H, 1.72; N, 10.07. Found: C, 32.36; H, 1.76; N, 9.81. IR (KBr, cm^{-1}): $\upsilon(N_{his}-H)$ 3324; $\upsilon(C=O)$ 1652, 1621; $\upsilon(F-C)$ 1255, 1211, 1145.

Anal. Calcd for $C_{38}H_{24}N_{10}O_8F_{24}Cu_2Mn$ (**7**): C, 32.89; H, 1.73; N, 10.10. Found: C, 33.35; H, 1.66; N, 9.78. IR (KBr, cm^{-1}): $\upsilon(N_{his}-H)$ 3309; $\upsilon(C=O)$ 1653, 1623; $\upsilon(F-C)$ 1253, 1214, 1153.

Crystallography. Intensity data of compounds **4**, **5**, and **7** were collected with a Rigaku AFC-7S single-crystal diffractometer at 193(2) K; reflections with negative intensities were not collected. The data for compound **6** were collected with a Siemens P4 diffractometer at 293(2) K. In each case, Mo Kα radiation ($\lambda = 0.710\,73$ Å, graphite monochromator) was used and scan type was $\omega/2\theta$. The structure of compound **6** was solved by direct methods[28] combined with subsequent Fourier analysis.[29] For compounds **4**, **5**, and **7** coordinates of **6** were used as starting parameters and refinements were carried out using the SHELXL-93 program.[29] The compounds are isostructural and assume 2-fold symmetry with the central metal atom laying on the symmetry axis. In each compound three of the four CF_3 groups are disordered in the asymmetric unit. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed on calculated positions (riding model). For **5**−**7**, reflection power and statistics of reflections at high 2θ angles were very poor, and therefore data for **5**−**7** were limited to $2\theta_{max} = 45°$ in the calculations. The only difference in the refinements of **4**−**7** were the different number of restraints for the disordered CF_3 groups. Further details about crystal data collection and structure determination are given in Table 1.

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Table 1. Crystallographic Data for Complexes **4**−**7**

	4	**5**	**6**	**7**
empirical formula	$C_{38}H_{24}N_{10}O_8F_{24}Cu_2Zn$	$C_{38}H_{24}N_{10}O_8F_{24}Cu_3$	$C_{38}H_{24}N_{10}O_8F_{24}Cu_2Ni$	$C_{38}H_{24}N_{10}O_8F_{24}Cu_2Mn$
fw	1397.12	1395.29	1390.46	1386.69
T, K	193(2)	193(2)	293(2)	193(2)
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$
a, Å	25.048(4)	24.798(9)	23.305(5)	24.982(6)
b, Å	13.777(4)	13.667(4)	13.767(3)	13.999(4)
c, Å	17.773(5)	17.716(7)	17.928(4)	17.728(5)
β, deg	125.120(10)	123.57(4)	124.60(3)	125.30(3)
V, Å^3	5017(2)	5003(3)	4735(2)	5060(2)
Z	4	4	4	4
ρ_{calc}, g cm^{-3}	1.850	1.853	1.951	1.820
R(F^2)^a	0.0486	0.0771	0.0795	0.0841
Rw(F^2)^b	0.1158	0.1824	0.1336	0.1021

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 = $|[\Sigma w(|F_o|^2 - |F_c|^2)^2]/\Sigma w|F_o|^4|^{1/2}$.

Results and Discussion

To prepare imidazolate-bridged trinuclear complexes we have followed a strategy similar to that intensively used by Matsumoto's group.[8,12] For "ligand complexes", they used mononuclear complexes of unsymmetrical tetradentate Schiff's bases involving an imidazole moiety. However, in some cases, these "ligand complexes", after deprotonation, show a great ability to receive an imidazolate nitrogen donor atom from another ligand complex, then a self-assembly reaction occurs and homopolynuclear copper(II) complexes are obtained.[30] To overcome this problem, we used a mononuclear copper(II) complex with a tridentate Schiff's base as a "ligand complex", in which the two remaining positions on the pentacoordinated copper(II) ion are blocked by a bidentate hexafluoroacetylacetonate anion. This was prepared directly by the reaction between the tridentate base and bis(hexafluoroacetylacetonate) copper(II). Because the coordination positions on the copper(II) ion are in principle saturated the precursor should be prevented from the self-assembly reaction. The resulting heterotrinuclear complexes are expected to have high solubility and then to be easily crystallized.

As expected, this precursor acts as a monodentate ligand toward bis(hexafluoroacetylacetonate)metal(II) to give rise to a series of imidazolate-bridged trinuclear complexes with the formula [Cu(hfac)(L)M(hfac)$_2$(L)(hfac)Cu]. These compounds can also be prepared from the mononuclear complex [Cu(HL)(H$_2$O)](ClO$_4$)]$_2$ (**1**) and bis(hexafluoroacetylacetonate)metal(II). In this case, free hexafluoroacetylacetonate anions, from the partial dissociation of the bis(hexafluoroacetylacetonate)metal(II) complex in a methanol/water mixture, are used both to block two coordination positions on the copper ion as well as to deprotonate the imidazole moiety. It should be noted that **1**, under basic conditions, leads to the self-assembled imidazolate bridged polymeric Cu(II) complex {[Cu(L)(H$_2$O)](ClO$_4$)}$_n$ (**2**). The reaction of the ligand with an excess of Cu(hfac)$_2$ directly yields the trinuclear copper(II) complex, as expected. Under the used reaction conditions the N_{his}−H hydrogen atom of the histamine moiety does not dissociate. Thus the $\upsilon(N_{his}-H)$ vibration is observed at about 3300 cm^{-1}, whereas the $\upsilon(N_{im}-H)$ vibration (due to the N−H group of the 2-imidazolate part of the ligand) observed at 3150 cm^{-1} in the precursor **1** is absent in the IR spectra of the trinuclear and self-assembled complexes. Compound **2** is insoluble, in good agreement with its polynuclear structure, while trinuclear complexes are soluble in common organic solvents.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **4**−**7**^{a}

	4, M = Zn(1)	**5**, M = Cu(2)	**6**, M = Ni(1)	**7**, M = Mn(1)
Cu(1)−N(11)	1.946(4)	1.953(6)	1.947(7)	1.976(7)
Cu(1)−N(1)	1.967(4)	1.944(6)	1.976(7)	1.975(7)
Cu(1)−O(16)	1.994(3)	1.997(6)	1.867(5)	1.982(6)
Cu(1)−N(7)	2.031(4)	2.033(6)	1.857(7)	2.008(7)
Cu(1)−O(18)	2.226(3)	2.235(5)	2.220(5)	2.229(6)
M−N(3)	2.059(4)	1.982(6)	1.951(7)	2.162(8)
M−O(21)	2.137(3)	2.349(4)	2.081(5)	2.198(6)
M−O(23)	2.172(3)	2.019(5)	2.019(6)	2.220(6)
N(11)−Cu(1)−N(1)	170.0(2)	170.3(2)	170.2(2)	170.4(3)
N(11)−Cu(1)−O(16)	92.2(2)	91.9(2)	90.4(3)	91.2(3)
N(1)−Cu(1)−O(16)	92.8(2)	92.7(2)	94.0(3)	93.8(3)
N(11)−Cu(1)−N(7)	91.4(2)	91.1(2)	93.4(3)	91.5(3)
N(1)−Cu(1)−N(7)	81.2(2)	81.7(3)	79.5(3)	81.3(3)
O(16)−Cu(1)−N(7)	162.07(14)	159.2(2)	159.7(3)	162.6(3)
N(11)−Cu(1)−O(18)	96.67(14)	97.3(2)	96.2(2)	96.3(3)
N(1)−Cu(1)−O(18)	92.2(2)	91.3(2)	92.4(2)	92.0(3)
O(16)−Cu(1)−O(18)	88.02(13)	88.4(2)	92.4(2)	88.8(2)
N(7)−Cu(1)−O(18)	108.98(14)	111.7(2)	107.0(3)	108.0(3)
N(3)−M−N(3)$^{\mathrm{I}}$	97.7(2)	94.4(4)	92.1(4)	95.2(4)
N(3)−M−O(21)	99.12(14)	100.5(2)	94.5(2)	100.4(3)
N(3)$^{\mathrm{I}}$−M−O(21)	94.76(14)	93.8(2)	97.0(2)	96.9(2)
N(3)−M−O(21)$^{\mathrm{I}}$	94.76(14)	93.8(2)	97.0(2)	96.9(2)
N(3)$^{\mathrm{I}}$−M−O(21)$^{\mathrm{I}}$	99.12(14)	100.5(2)	94.5(2)	100.4(3)
O(21)−M−O(21)$^{\mathrm{I}}$	158.8(2)	158.9(3)	163.4(3)	154.1(3)
N(3)−M−O(23)	172.89(13)	174.6(2)	174.2(2)	175.1(3)
N(3)$^{\mathrm{I}}$−M−O(23)	88.64(13)	89.1(2)	91.8(3)	89.5(3)
O(21)−M−O(23)	83.44(12)	83.3(2)	89.2(2)	80.3(2)
O(21)$^{\mathrm{I}}$−M−O(23)	81.02(12)	81.5(2)	78.5(2)	80.8(2)
N(3)−M−O(23)$^{\mathrm{I}}$	88.64(13)	89.1(2)	91.8(3)	89.5(3)
N(3)$^{\mathrm{I}}$−M−O(23)$^{\mathrm{I}}$	172.89(13)	174.6(2)	174.2(2)	175.1(3)
O(21)−M−O(23)$^{\mathrm{I}}$	81.02(12)	81.5(2)	78.5(2)	80.8(2)
O(21)$^{\mathrm{I}}$−M−O(23)$^{\mathrm{I}}$	83.44(12)	83.3(2)	89.2(2)	80.3(3)
O(23)−M−O(23)$^{\mathrm{I}}$	85.2(2)	87.7(3)	84.6(3)	85.9(3)

^{a} Symmetry transformations used to generate equivalent atoms: I = $-x, y, -z + {}^3/_2$.

Atomic crystallographic coordinates are given as Supporting Information. Selected bond distances and angles are listed in Table 2. All the trinuclear complexes are isostructural and consist of trinuclear molecules with a V-shaped conformation, which are formed by two CuL(hfac) "ligands" bonded through imidazolate bridges to the central metal in cis-position (Figure 1). A similar structure has been previously reported for a trinuclear Ni(II) complex containing an imidazolate-bridging Schiff's base ligand.[31] Both halves of the molecule are related by a crystallographically imposed 2-fold axis. The ligand environment about the central metal atom can be described as

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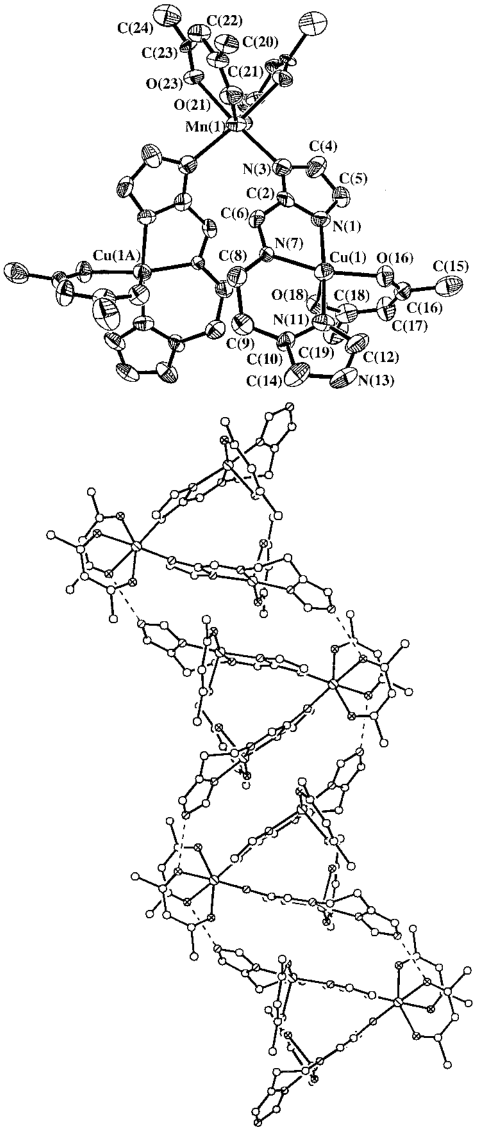

Figure 1. Perspective views of the molecular structure (F atoms omited for clarity) and packing of the isostructural trinuclear V-shaped complexes **4**–**7** (**7** shown).

a distorted octahedron, with the nitrogen atoms from the imidazolate groups and two oxygen atoms of the hfac ligands in the equatorial plane and the remaining two oxygen atoms from the hfac ligands filling the axial positions at longer distances. The coordination geometry of the copper(II) ion is very close to a square pyramid with one oxygen atom from the hfac in a more distant axial position. The copper(II) fragments are twisted away from the coordination plane, thus relieving close interligand contacts. In the unit cell, centrosymmetrically related molecules are linked by a pair of complementary hydrogen bonds involving the N(13)–H group from the histamine moiety and the O(23) atom of a neighboring molecule, ultimately leading to a chain of trinuclear molecules (Figure 1). These interactions stabilize the V-shaped structure instead of the less sterically hindered trans-linear conformation. As far as we know, this is the first time that the structural and magnetic properties of a Cu–Mn–Cu trinuclear complex have been reported.

The magnetic properties of the compounds are compared in Figure 2 in the form of $\chi_M T$ vs T. Those corresponding to the Cu–Zn–Cu complex have not been included because its $\chi_M T$ product is independent of the temperature with a value compatible with the spin value expected for two isolated Cu(II) ions,

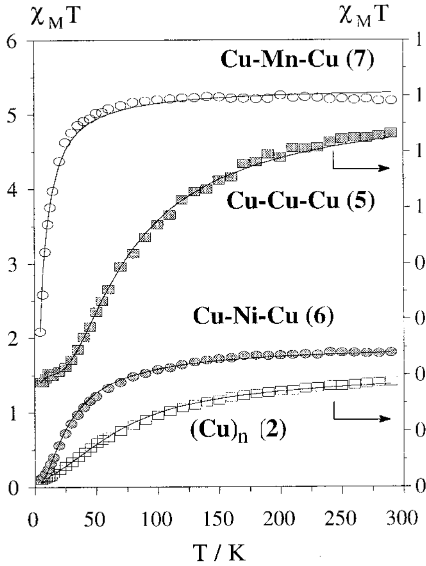

Figure 2. Magnetic properties, $\chi_M T$ (cm^3 mol^{-1} K) vs T, of complexes **2** (□), **5** (■), **6** (●), and **7** (○).

thus indicating that the J value between the terminal copper ions is negligible. The $\chi_M T$ product for compound **2** is 0.376 cm^3 mol^{-1} K at room temperature which is compatible with the spin-only value for $S = {}^1/_2$. As the temperature is lowered the $\chi_M T$ gradually decrease to 0.027 cm^3 mol^{-1} K at 5 K. The χ vs T curve shows a maximum at about 50 K. These facts clearly indicate that an 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 chain systems.[32] To take into account the tail of the magnetic susceptibility curve at low temperature a percentage of magnetic impurity (p) was included in the theoretical equation of the magnetic susceptibility. The best fitting led to $J = 61.1$ cm^{-1}, $g = 2.15$, and $p = 3\%$. The present J value suggests that an imidazolate group bridges two copper ions at their equatorial positions (J values normally are in the range from -40 to -100 cm^{-1}) rather than at their axial positions (J values ranging from -1 to -15 cm^{-1}).[30]

The $\chi_M T$ values at room temperature for the trinuclear complexes **5**–**7** are compatible with those expected for magnetically isolated three-spin systems (${}^1/_2$, S_M, ${}^1/_2$). On lowering the temperature the $\chi_M T$ product gradually decreases down to the values expected for the spin states ($S_M - 1$), thus indicating the existence of an antiferromagnetic interaction between the copper and central metal through the imidazolate group. The magnetic susceptibility data were quantitatively analyzed using the theoretical expressions deduced from the spin Hamiltonian for a symmetrical three-spin system $H = -J_{CuM}(S_{Cu1}{\cdot}S_M + S_M{\cdot}S_{Cu2}) - J'S_{Cu1}{\cdot}S_{Cu2}$, where the exchange interaction between terminal copper(II) ions was neglected and the corrections for intermolecular interactions (θ) and paramagnetic impurity were taken into consideration (p). Nevertheless, since the interaction between the terminal copper ions in the Cu–Zn–Cu complex is negligible, the J' value was assumed to be zero. The expression used is $\chi_M^{CuMCu} = (C/T - \theta)f(J,T) + p$, where $C = Ng^2\beta^2/4k$ and $f(J,T)$ is derived from the theoretical equations.[7] The results of the best fitting to the experimental data together with some structural parameters of the complexes are given in

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[32] Estes, W. E.; Gavel, D. P.; Hatfield, W. E.; Hodgson, D. *Inorg. Chem.* **1978**, *17*, 1415.

Table 3. Structural and Magnetic Data for Complexes **4**−**7**

compound	$\alpha_1\alpha_2$ (deg)[a]	$\theta_1\theta_2$ (deg)[b]	N−M (Å)	M···M (Å)	g(M)	J, nJ (cm^{-1})
4 (M = Zn)	146.8	10.0	2.026	5.868		
	165.7	40.0				
5 (M = Cu)[c]	145.6	11.7	1.983	5.808	g(Cu) = 2.19	−60.6
	166.3	41.6			g(Cu) = 2.20	−60.6
6 (M = Ni)[d]	147.7	12.9	1.953	5.848	g(Cu) = 2.11	−21.6
	167.4	43.2			g(Ni) = 2.12	−43.2
7 (M = Mn)	146.3	8.6	2.162	6.025	g(Cu) = 2.00	−3.2
	165.8	37.3			g(Mn) = 2.04	−16.0

[a] α is the angle between the Cu−N and N−N vectors. [b] θ is the dihedral angle between the plane of the magnetic orbital on the copper ions and the imidazolate plane. [c] With a Weiss constant $\theta = -0.6$ K. [d] With a paramagnetic impurity $p = 0.05$.

Table 3. It should be noted, first, the decrease of the exchange interaction on going from Cu(II) to Mn(II) and second that the J value for the Cu(II) trinuclear complex is compatible with those for di- and trinuclear copper(II) complexes, in which the imidazolate group bridges copper(II) at the equatorial positions,[33,34] and thus the antiferromagnetic exchange interaction is due to the σ overlap of the d_{xy} orbitals through the imidazolate bridge.

The decrease of the exchange interactions on going from Cu(II) to Mn(II) can be justified by the fact that the exchange coupling constant must be decomposed into a sum of individual contributions involving each pair of magnetic orbitals involved in the exchange interaction.[7] Given that a copper(II) ion in square pyramidal surroundings has one unpaired electron in a d_{xy} orbital (x and y axes are taken along the donor atoms), the exchange coupling constant can be expressed as $J = (1/n)\sum_p J_{xy,p}$ where n is the number of magnetic orbitals p on the central metal M. To deal with comparable values of the net antiferromagnetic interaction the nJ values should be taken into account. Furthermore, owing to the extended nature of the imidazolate bridge the ferromagnetic contributions should be negligible and then nJ would be almost equal to the antiferromagnetic interaction involving the d_{xy} magnetic orbitals, $J_{xy,xy}$. Therefore, the magnitude of $J_{xy,xy}$ in this family of symmetrical trinuclear complexes follows, as expected, the trend Cu > Ni > Mn. It has been concluded by EHMO calculations[35] that the extent of the antiferromagnetic exchange interaction in imidazolate-bridged complexes would be predominantly affected by the angle (α) between Cu−N_{Im} and N_{Im}−N_{Im} vectors and it would depend in some extent on the dihedral angle (θ) between coordination and imidazolate planes. Given the structural similarities in this series of complexes (α and θ angles are quite similar from each to other), the decrease of $J_{xy,xy}$ on going from Cu(II) to Mn(II) might be mainly attributed to the decrease of the spin delocalization on the bridge as the energy of their respective 3d orbitals increases. In close accordance with this and the increase of energy in the 3d orbitals with the ionic radius, a linear correlation can be established between $J_{xy,xy}$ and the ionic radius of the central metal ion.

The X-band powder and methanol solution EPR spectra of **4** at 100 K are very similar and only exhibit a quasi-isotropic signal centered at $g = 2.09$, which might indicate that the trinuclear structure is fully retained in solution. Nevertheless, since the negligible exchange interaction between the two copper ions of the trinuclear unit should not modify the EPR solution spectrum from that of the discrete copper(II) complexes, the presence of the latter in solution cannot be discarded.

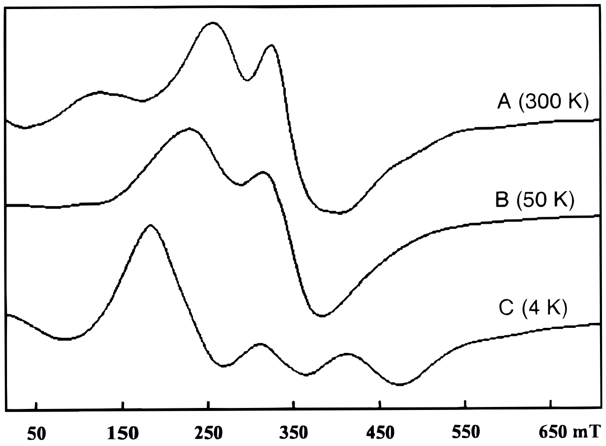

Figure 3. Powder X-band EPR spectra of complex **7** at (A) 300 K, (B) 50 K, and (C) 4 K.

The powder EPR spectrum of **5** at room temperature shows a quasi-isotropic signal centered at $g = 2.07$, which is devoid of any fine structure or half-field transition. No substantial change is observed on cooling to 100 K. At 4.2 K the spectrum looks like that associated with an axial doublet with $g_{\parallel} = 2.15$ and $g_{\perp} = 2.07$, as expected for transitions within the ground doublet state, the only populated state at this temperature. The frozen methanol solution spectrum seems to consist of two superimposed spectra: one with features centered at $g_{\parallel} = 2.15$ and $g_{\perp} = 2.06$, which is almost identical to that observed in the solid state and then should correspond to the trinuclear entity and another of lower intensity, exhibiting a well-resolved hyperfine structure in the $g_{\parallel}$ region, with $g_{\parallel} = 2.32$, $A_{\parallel} = 0.013$ cm^{-1}, and $g_{\perp} = 2.10$. This fact suggests that trinuclear structure is not completely retained in solution.

The X-band powder spectrum of **6** at room temperature exhibits a unique quasi-isotropic broad signal centered at $g = 2.06$. The spectrum broadens on cooling to 100 K and the feature moves toward lower field ($g = 2.12$). At 4.2 K the EPR spectrum is silent, as expected if the only populated state is the singlet ground state. The frozen methanol solution spectrum at 100 K exhibits a large and intense signal centered at $g = 2.06$ and a smaller and broad one at $g = 4.90$. This spectrum is more typical of Cu−Ni pairs with a moderately strong axial zero-field splitting of the excited quarted ground state,[36] thus indicating that the trinuclear structure is at least partially destroyed in solution to give Cu−Ni dinuclear species.

The polycrystalline powder EPR spectra of **7** recorded at X-band in the range 4.2−300 K are given in Figure 3. These

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

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(36) Colacio, E.; Dominguez-Vera, J. M.; Escuer, A.; Kivekäs, R.; Romerosa, A. *Inorg. Chem.* **1994**, *33*, 3914.

spectra show a marked temperature dependence, in agreement with the magnetic data that indicated the thermal population of all the spin states. At high temperature the spectrum is very complicated with several features spread out over the range 120−590 mT. It should be noted that a similar spectrum was reported for the compound Mn(hfac)$_2$(tempo)$_2$ (tempo = 2,2,6,6-tetramethylpiperidinyl-1-oxy), an electronically analogue of **7** also exhibiting an antiferromagnetic interaction between the manganese(II), $S_{mn} = {}^5/_2$, and the two radicals, $S_r = {}^1/_2$. On cooling to 50 K, the weak features at 120, 150, 500, and 590 mT markedly decrease in intensity whereas the intense feature at 257 mT becomes wider. At 4 K the spectrum is completely different with an intense feature at 226 mT and two weaker ones at 338 and 443 mT. At this temperature the first excited quintet state, which from the magnetic data is 8 cm^{-1} above the ground quartet state, is largely depopulated, so that the spectrum should be essentially that of the quartet ground state. Thus, the pattern observed at 4 K might be due to transitions within the quartet ground state, with a zero-field splitting ($D \approx 0.05$ cm^{-1}) that is smaller than the microwave quantum. The frozen methanol solution spectrum at 100 K exhibits an allowed hyperfine sextet centered at $g = 1.97$ with forbidden hyperfine lines corresponding to transitions between levels with different nuclear magnetic quantum numbers. This spectrum is typical of isolated Mn^{2+} species,[37] thus indicating that the structure is not retained in dilute methanol solution. The signal corresponding to the Cu^{2+} species appears superimposed at $g = 2.10$.

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Supporting Information Available: Listing of complete crystallographic data, atomic coordinates, bond distances and angles, anisotropic thermal parameters (Tables 4.1−7.6), linear correlation between *nJ* and ionic radius (Figure S1) (33 pages). An electronic file, in CIF format, is also available on the Internet only. Ordering and access information is given on any current masthead page.

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