the K-edge yields. Fortunately, the background signal from Compton scattering is small at L-edge energies. Although the overall experimental sensitivity may be lower, the signal-tc .1oise requirements for edge analysis are less stringent than for EXAFS, and as the technology improves, obtaining these spectra will no doubt eventually become routine.

Compared to the broad K-edge features, the sharper and richer L$_{2,3}$-edge multiplet structure appears more amenable to resolving the presence of mixtures of oxidation states, although this remains to be proven. For spectroscopic determination of interatomic distances, K-edge EXAFS is not challenged by 3d metal L-edge EXAFS, because several hundred volts of uninterrupted oscillations are generally required, and too many overlapping and interfering edges occur in the soft X-ray region. However, for detecting small changes in the transition-metal site symmetry, the sharper L$_{2,3}$ edge spectra may be more sensitive and more quantitatively interpretable than the K-edge data. The confluence of better sources, monochromators, detectors, and theoretical procedures makes soft X-ray spectroscopy a promising new tool for bioinorganic problems.

(31) Krause, M. O. *J. Chem. Phys. Ref. Data* **1979**, *8, 1979*, 307–327.
(32) Lynch, D. W.; Cowan, R. *Phys. Rev.* **1987**, *B36*, 9228.

From 1-D to 3-D Ferrimagnets in the EDTA Family: Magnetic Characterization of the Tetrahydrate Series M^{t}M(M′EDTA)$_2$·4H$_2$O [M^t, M, M′ = Co(II), Ni(II), Zn(II)]

F. Sapiña,[*,†] **E. Coronado,**[*,†] **D. Beltrán,**[†] **and R. Burriel**[‡]

Contribution from the Departamento de Quimica Inorgánica, Facultad de Ciencias Quimicas, Universidad de Valencia, 46100 Burjassot, Spain, and Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain. Received March 22, 1991

Abstract: We report on the magnetic behavior of the compounds M^{t}M(M′EDTA)$_2$·4H$_2$O (in short [M^{t}MM′]) in the very low temperature range. The structure of these compounds can be formally regarded as ordered bimetallic layers of alternating chelated and hydrated octahedral sites M and M′, with tetrahedral sites M^t connecting different MM′ layers. We have obtained the compounds [ZnZnNi], [ZnNiNi], [CoNiNi], [CoCoNi], and [CoCoCo]. While the compound [ZnNiNi] may support a 2-D magnetic lattice of Ni(II), since Zn(II) occupies tetrahedral sites, in the compounds without Zn the layers are connected through Co(II), increasing the dimensionality of the lattice to 3-D. A leveling of the magnetic susceptibility has been observed in [ZnNiNi], which has been attributed to zero-field splitting effects of the chelated Ni(II) ions. On the other hand, as expected on the basis of the structure, the substitution of Zn(II) by Co(II) in the tetrahedral site leads to the appearance of 3-D ferrimagnetic interactions in the compounds [CoNiNi], [CoCoNi], and [CoCoCo]. This is clearly noticeable from the sharp transition temperatures in the first two compounds at T_c = 0.44 and 0.10 K, respectively, with an out-of-phase susceptibility signal below T_c. In [CoCoNi], there is a rounded maximum in the $\chi_m T$ plot at T = 0.40 K. The magnetic data in the low-dimensional region have been analyzed for the compounds [CoCoCo] and [CoCoNi] by means of an anisotropic (Ising-type) model that assumes three different magnetic sublattices exchange-coupled by two magnetic interactions, as well as the local anisotropies of tetrahedral Co(II) and chelated Ni(II) ions.

Introduction

Major progress is being made by chemists in preparing novel low-dimensional magnetic materials in which two magnetic sublattices of unequal magnitude are structurally ordered. Thus, there are a variety of new bimetallic materials in which the different metal ions are chemically ordered, in particular the so-called ferrimagnetic chains or 1-D ferrimagnets. These compounds are desirable because they may have distinctive magnetic properties associated with the inability of the antiferromagnetic interaction to cancel the opposing unequal moments.[1] Further, they provide starting blocks from which to synthesize molecular-based ferromagnets, i.e., compounds having spontaneous magnetization below a critical temperature. This has been found when 1-D ferrimagnets are assembled in a ferromagnetic fashion taking advantage of the dipolar interchain interactions.[2,3] Such an approach is clearly limited by the chemical inability to control the relative positions of chains on the lattice scale, as well as by the weakness of the interchain interactions. A much more promising approach consists of connecting the chains by covalent bonds (instead of hydrogen bonds) in order to obtain 2-D or 3-D ordered bimetallic lattices.

Our own contribution in this area has dealt with the synthesis and magneto–structural chemistry of an extensive series of ordered bimetallic materials, namely the EDTA family.[4] We have shown the usefulness of EDTA and EDTA-like ligands in the preparation

† Universidad de Valencia.
‡ CSIC-Universidad de Zaragoza.

(1) Landee, C. P. In *Organic and Inorganic Low Dimensional Crystalline Materials*; Delhaes, P., Drillon, M., Eds.; NATO ASI Series 168; Plenum Press: New York, 1987; p 75.
(2) Kahn, O. In *Organic and Inorganic Low Dimensional Crystalline Materials*; Delhaes, P., Drillon, M., Eds.; NATO ASI Series 168; Plenum Press: New York, 1987; p 93.
(3) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, *22*, 392.
(4) Coronado, E. In *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; NATO ASI Series 198; Kluwer Academic Publishers, 1991; p 267.

Magnetic Behavior of $M^tM(M'EDTA)_2\cdot 4H_2O$ Complexes

J. Am. Chem. Soc., Vol. 113, No. 21, 1991 7941

Table I. Metal Analysis of the Heterometallic Compounds of the $M^tM(M'EDTA)_2\cdot 4H_2O$ Series

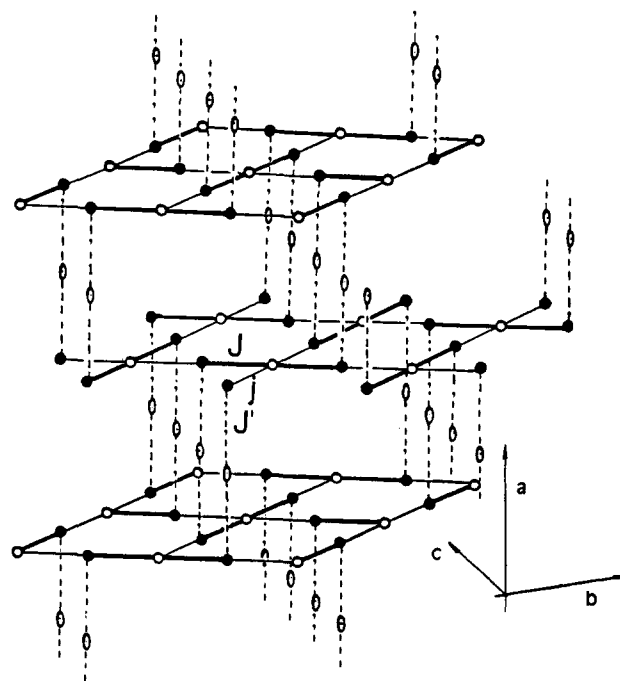| compd	% M obs (calc)	% Ni obs (calc)	$r_{M/Ni}$ obs (calc)[a]
[CoCoNi]	13.3 (13.34)	12.4 (13.29)	1.07 (1)
[CoNiNi]	6.9 (6.67)	19.5 (19.93)	0.35 (0.33)
[ZnNiNi]	7.5 (7.34)	19.1 (19.78)	0.36 (0.33)
[ZnZnNi]	14.0 (14.57)	12.2 (13.08)	1.02 (1)

[a] $r_{M/Ni}$ is the molar ratio between M (Co or Zn) and Ni.

of several families of isostructural bimetallic compounds, providing an ideal structural support to isolate ferrimagnetic systems of variable dimensionality. Thus, the ability of EDTA to selectively chelate one metal atom, e.g. M', to form the stable dianion $[M'(EDTA)^{2-}]$, while still providing bridging carboxylate groups to a second (hydrated) metallic cation, e.g. M^{2+}, results in the formation of ordered bimetallic solids. In this way, when two of the four carboxylates of EDTA act as bridges, one obtains the hexahydrate series of ferrimagnetic chains $MM'(EDTA)\cdot 6H_2O$ (M, M'= M(II), Co(II), Ni(II), Cu(II), Zn(II)).[5–9] In this series, the different metal ions can be easily accommodated at different sites, with the consequent control in strength and anisotropy of the exchange interactions. In this sense, the EDTA family provides the possibility of investigating a wide variety of 1-D ferrimagnets; and hence, much theoretical work has been developed in order to explain their distinctive magnetic properties.[10–13]

On the other hand, by conducting the synthesis under conditions of high temperature and pressure, one can obtain 3-D crystalline polymers in which the elimination of some water from the parent hexahydrates results in an increase in the number of carboxylate bridges, with the consequent intercrossing of the chains.[14–18] In this paper, we present the magnetochemistry of this series, formulated as $M^tM(M'EDTA)_2\cdot 4H_2O$ (in short $[M^tMM']$), paying particular attention to both the low-dimensional magnetic behavior and the 3-D magnetic ordering.

Experimental Section

Preparation of the Complexes. The compounds were prepared by a previously reported procedure,[14] which involves a hydrothermal treatment, either from supersaturated aqueous solutions of the corresponding hexahydrates or from aqueous solutions containing stoichiometric quantities of the tetrasodium salt of EDTA in concentrations of 0.2–0.4 M and metallic nitrates. The solutions were heated to 80–180 °C in sealed Pyrex vials under pressure. Crystalline solids were obtained after several hours of heat treatment. X-ray powder diffraction patterns were obtained by means of a Siemens Kristalloflex D500 diffractometer using Cu $K\alpha$ radiation. Powder diffractograms of these solids are identical within

(5) Coronado, E.; Drillon, M.; Fuertes, A.; Beltrán, D.; Mosset, A.; Galy, J. *J. Am. Chem. Soc.* **1986**, *108*, 900.

(6) Drillon, M.; Coronado, E.; Beltrán, D.; Curely, J.; Georges, R.; Nugteren, P. R.; de Jongh, L. J. *J. Magn. Magn. Mater.* **1986**, *54*, 1507.

(7) Coronado, E.; Drillon, M.; Nugteren, P. R.; de Jongh, L. J.; Beltrán D. *J. Am. Chem. Soc.* **1988**, *110*, 3907.

(8) Coronado, E.; Drillon, M.; Nugteren, P. R.; de Jongh, L. J.; Beltrán D.; Georges R. *J. Am. Chem. Soc.* **1989**, *111*, 3874.

(9) Coronado, E.; Sapiña, F.; Drillon, M.; de Jongh, L. J. *J. Appl. Phys.* **1990**, *67*, 6001.

(10) Drillon, M.; Coronado, E.; Beltrán, D.; Curely, J.; Georges, R. *Chem. Phys.* **1983**, *79*, 449.

(11) Sapiña, F.; Coronado, E.; Drillon, M.; Georges, R.; Beltrán, D. *J. Phys. (Paris)* **1988**, 48–49, 1423.

(12) Drillon, M.; Coronado, E.; Gianduzzo, J. C.; Curely, J.; Georges, R. *Phys. Rev. B* **1989**, *40*, 10992.

(13) Coronado, E. Ph.D. Thesis, University of Strasbourg, France, 1990. Curely, J. Ph.D. Thesis, University of Bordeaux, France, 1990.
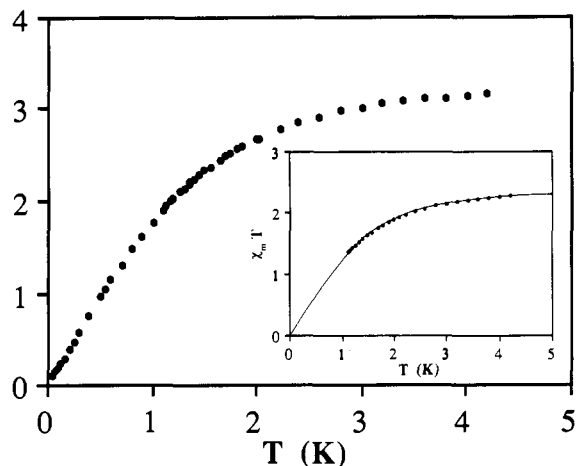
(14) Gomez-Romero, P.; Jameson, G. B.; Casañ-Pastor, N.; Coronado, E.; Beltrán, D. *Inorg. Chem.* **1986**, *25*, 3171.

(15) Coronado, E.; Barba, A.; Beltrán, D.; Burriel, R.; Carlin, R. L. In *Organic and Inorganic Low Dimensional Crystalline Materials*; Delhaes, P., Drillon, M., Eds.; NATO ASI Series 168; Plenum Press: New York, 1987; p 401.

(16) Coronado, E.; Sapiña, F.; Gomez-Romero, P.; Beltrán, D.; Burriel, R.; Carlin, R. L. *J. Phys. (Paris)* **1988**, 48–49, 853.

(17) Coronado, E.; Sapiña, F.; Beltrán, D.; Carlin, R. L. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 507.

(18) Sapiña, F.; Coronado, E.; Gomez-Romero, P.; Beltrán, D.; Burriel, R.; Carlin, R. L. *J. Appl. Phys.* **1990**, *67*, 6003.

Figure 1. Schematic diagram of the magnetic lattice in M^tM-$(M'EDTA)_2\cdot 4H_2O$, showing the layers of alternating octahedral sites (M', filled circles; M, open circles) and the tetrahedral sites connecting them (M^t, ellipses).

experimental error. Metals were determined by atomic absorption spectroscopy using a Perkin-Elmer Model 300 spectrophotometer. The corresponding metal analyses are summarized in Table I.

Magnetic Meausurements. The complex differential susceptibilities of powdered samples were measured between 0.04 and 4.2 K from the change in the mutual inductance between a primary and a secondary coil resulting from a change in the magnetization of the samples.

Measurements in the temperature interval 1.1–4.2 K were made with each data point calibrated against cerium(III) magnesium nitrate (CMN). Temperatures down to 40 mK were obtained by using an SHE Model DRI-40/4000 ^{3}He–^{4}He dilution refrigerator. The detection of the mutual inductance between 0.04 and 2 K is achieved through the use of a low-impedance ac bridge in which a superconducting quantum interference device (SQUID) is used as a null detector. The measurements presented here were obtained by using an excitation frequency of 16 Hz and a maximum oscillating field of 10 mOe. The data were converted from bridge readings to susceptibility values (emu mol^{-1}) by matching of the data between 1.1 and 2 K with those obtained independently in the liquid-^{4}He apparatus.

Results and Discussion

Chemical Design of the Magnetic Lattice. The structure of this series has been determined in the compound [CoCoCo].[14] There are three crystallographically independent metal sites. One of them is coordinated to two bridging and two nonbridging carboxylate groups from neighboring EDTA molecules [M^t-$(OOCR)_2(OOCR')_2$] (tetrahedral site). Another metal atom is coordinated to two molecules of water and four carboxylate bridges [$M(OOCR)_4(H_2O)_2$] (octahedral "hydrated" site). The last metal atom is chelated by EDTA and one molecule of water [M'-$(EDTA)(H_2O)$] (octahedral "chelated" site). The polymeric nature of the structure can be formally regarded as ordered bimetallic layers of alternating octahedral sites M and M', with tetrahedral sites M^t connecting different MM' layers (see Figure 1). The configurations of the three carboxylate bridges from EDTA are of the anti-syn type. These are nonequivalent, leading in the [CoCoCo] compound to intermetallic separations MM' = 5.512 (1), MM' = 5.324 (1), and $M'M^t$ = 5.240 (1) Å. From a magnetic point of view, this implies that there should be two different exchange couplings in the layer with double alternation, noted as J and j in Figure 1, and a third one between M^t and M', noted as J'.

In this structure, the possible combinations of metals are determined by the preferential occupations of the three sites. Thus,

Figure 2. Magnetic behavior of [ZnNiNi]. The inset shows the magnetic behavior of [ZnZnNi], along with the best fit.

Figure 3. Magnetic behavior of [CoNiNi]. The inset shows the out-of-phase component of the ac susceptibility.

the greater affinity of the EDTA ligand for Ni(II) with respect to Co(II) and Zn(II) ions forces Ni(II) to occupy preferentially the chelated position, M', while Zn(II) and Co(II), which show similar affinities, are left to occupy the two remaining positions. On the other hand, we have found that the tetrahedral site can only be occupied by Co(II) and Zn(II); Ni(II) shows a marked tendency to occupy the octahedral sites only. Finally, attempts to obtain tetrahydrated compounds containing other divalent ions, for example Cu(II) and Mn(II), have been unsuccessful. In such cases, there is a reduction of Cu(II) to metallic copper with the subsequent EDTA decarboxylation[19] or an oxidation of Mn(II) to Mn(IV) at the working temperatures (80–180 °C). With the above considerations in mind, a wise choice of metallic compositions has allowed us to design ordered metallic systems of magnetic dimensionality between 2 and 3. In this way, we have obtained the compounds [ZnZnNi], [ZnNiNi], [CoNiNi], [Co-CoNi], and [CoCoCo]. While the [ZnNiNi] compound may support a 2-D magnetic lattice of Ni(II), since Zn(II) occupies tetrahedral sites, in the others the layers are connected through Co(II) ions, increasing the dimensionality of the lattice.

Magnetic Susceptibility Results. The low-temperature data of the four compounds are illustrated in Figures 2–5 through plots of $\chi_m T$ vs T. For [ZnNiNi], $\chi_m T$ decreases continuously as the temperature is lowered (Figure 2). In view of the type of magnetic lattice involved, such antiferromagnetic-like behavior is rather surprising. Thus, since each layer contains two times as many chelated sites as hydrated sites, an antiferromagnetic coupling should be unable to compensate the two magnetic sublattices and so a ferrimagnetic-like behavior with a $\chi_m T$ minimum would appear. The observed behavior may be due to the existence of a relatively large zero-field splitting in the nickel ions. In fact, a value of $D/k_B = -3.8$ K can be estimated for "chelated" Ni(II) in [ZnZnNi] from magnetic measurements between 1.5 and 4 K (see the inset of Figure 2). Negative values of D mean that the Ni(II) ground state is a singlet $M_S = 0$. In view of the two nonequivalent exchange pathways between M and M', the magnetic behavior of [ZnNiNi] suggests that, at least, one of these couplings is (in absolute value) smaller than $|D|$; in such a case, the ferrimagnetic layer would reduce at the low-temperature limit to trimers of Ni(II) antiferromagnetically coupled, and so the observed behavior could result from the zero-field splitting of the triplet ground state of the trimer.

In the other three compounds, the product $\chi_m T$ shows, upon cooling, the typical features of low-dimensional ferrimagnets, with a minimum in the range 0.3–1.1 K. At a critical temperature (T_c), a sharp peak is observed, suggesting a transition to long-range magnetic ordering. These features are summarized in Table III. The occurrence of an out-of-phase signal below T_c in the ac
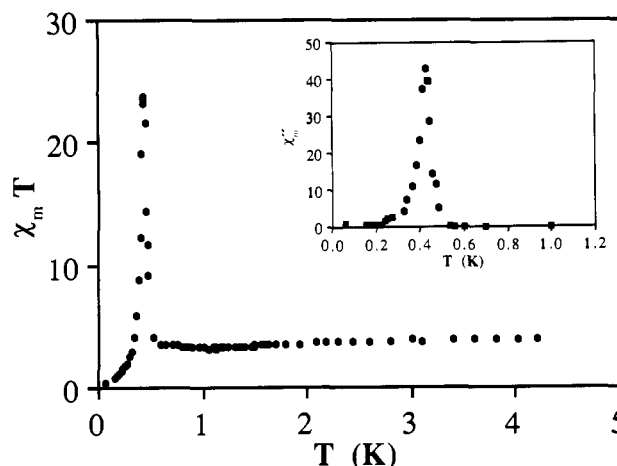
Table II. Best Fit Parameters of [CoCoCo] and [CoCoNi] from Magnetic Susceptibility

compd	fit	g_a	g_b	g_c	J/k, K	J'/k, K	D/k, K
[CoCoCo]	I	2.2	4.1	4.8	−6	−0.6	−10
	II	4.2	6.9	5.3	−1.5	−9	−10
[CoCoNi]	I	1.6	9.0	1.6	−2	−9	−3.7
	II	2.9	10.6	2.8	−10	−10	−8

susceptibility data indicates the presence of uncompensated moments in the ordered state. In fact, the structure of this series supports a 3-D ferrimagnetic ordering. Thus, the presence of an exchange coupling of tetrahedral Co(II) with its two nearest neighbors (M') would determine a parallel orientation of the noncompensated moments in the different ferrimagnetic layers, so as to give a 3-D ferrimagnetic arrangement of the magnetic moments. Notice that such an arrangement is independent of the sign of the exchange. Both ferro- and antiferromagnetic couplings would guarantee a parallel spin orientation on the two M' ions. The nature of the exchange between Co^t and M' can be obtained from an analysis of the magnetic data in the low-dimensional region.

Analysis of the Low-Dimensional Behavior of [CoCoCo] and [CoCoNi]. General Considerations. In discussing the magnetic properties of these compounds, one notices that the 3-D magnetic lattice derived from the structure is too complex to be modeled and some simplifications need to be introduced. As noted above, three different exchange couplings are to be expected. If it is assumed that one of the exchange couplings within the layer is much smaller than the other two, the magnetic lattice is reduced to a chain formed by three sublattices, which are ordered according to the sequence --A--C-B-C--A--C-B-C--A--, where A, B, and C refer to the sites M^t, M, and M', respectively, and dotted and full lines to the two different nonnegligible exchange couplings, J' and J. The sequence of magnetic moments along the chain may be sketched as

$$--S_a(g_a)--S_c(g_c)-S_b(g_b)-S_c(g_c)--S_a(g_a)--$$
$$S_c(g_c)-S_b(g_b)-S_c(g_c)--S_a(g_a)--$$
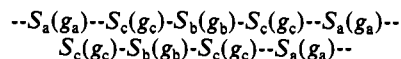
where S_a, S_b, and S_c are the spin quantum numbers for magnetic moments at sites A, B, and C and g_a, g_b, and g_c are the corresponding Landé factors at these sites. This assumption may be justified by the strong exchange alternation observed in the related bimetallic chain compounds containing Co(II). In fact, the compounds CoM'(EDTA)·6H$_2$O (M' = Co, Ni, Cu) behave as quasi-isolated dimers, showing interdimer to intradimer exchange coupling ratios of around 0.01.[7,9]

Dealing with the exchange model, it is to be noticed that the combined effect of spin–orbit coupling and distortion causes octahedral high-spin Co(II) to behave at sufficiently low temperatures ($T < 30$ K) as an anisotropic Kramers doublet ($g_\parallel \gg g_\perp$) with effective spin $S = {}^1/_2$.[20] Thus, an Ising-type model is

(19) Motekaitis, R. J.; Martell, A. E.; Hayes, D.; Frenier, W. W. *Can. J. Chem.* **1980**, *58*, 1999.

Table III. Magnetic Characterization of the $M^IM(M'EDTA)_2\cdot4H_2O$ Series

compd	S^I–S–S'	exchange $-J/k$	comments
[ZnNiNi]	0–1–1		χ_m data to 0.05 K; no T_c; 2-D ferrimagnet; $|J_{NiNi'}(min)| < D_{Ni'} \approx 3.9$ K
[CoNiNi]	$^3/_2$–1–1		χ_m data to 0.05 K; $T_m = 1.0$ K; $T_c = 0.44$ K; 3-D ferrimagnet
[CoCoCo]	$^3/_2$–$^1/_2$–$^1/_2$	$J_{CoCo'} = 2$–10 K $J_{Co'Co'} = 0.6$ K	χ_m data to 0.05 K; $T_m = 0.3$ K; $T_c = 0.10$ K; 3-D ferrimagnet
[CoCoNi]	$^3/_2$–$^1/_2$–1	$J_{CoNi'} = 2$–6.5 K $J_{Co'Ni'} = 9.5$ K	χ_m data to 0.05 K; $T_m = 1.1$ K; $T_c \simeq 0.40$ K; 3-D ferrimagnet

expected to describe conveniently the magnetic properties of [CoCoCo] and [CoCoNi]. We assume also that the external magnetic field is applied along the z axis. With the above considerations in mind, exact expressions of the zero-field parallel magnetic susceptibilities $(\chi_{||})$ can be obtained by using the transfer-matrix method.[17,18,21] This procedure also allows one to introduce a uniaxial anisotropy along the quantization axis for ions with spin values larger than $^1/_2$ (tetrahedral Co(II) and octahedral Ni(II)).

In the cases considered, the expressions for the perpendicular susceptibility cannot be determined by the same procedure. However, it is reasonable to assume that the experimental powder data may be accounted for by the parallel component of the susceptibility, since the perpendicular contribution remains weak and decreases toward zero upon cooling. Notice that such an approximation may lead to somewhat unrealistic Landé factors; only the ratio between them can be considered to be relevant.

The [CoCoCo] Compound. We consider that $S_b = S_c = ^1/_2$ for Co(II) in octahedral sites and $S_a = ^3/_2$ for Co(II) in tetrahedral sites. The full Hamiltonian is written as

$$\hat{H} = \sum_i (-J\hat{S}^z_{4i}\hat{S}^z_{4i+1} - J\hat{S}^z_{4i+1}\hat{S}^z_{4i+2} - J'\hat{S}^z_{4i+2}\hat{S}^z_{4i+3} -$$
$$J'\hat{S}^z_{4i}\hat{S}^z_{4i-1} - g_{4i}\mu_B H\hat{S}^z_{4i} - g_{4i+1}\mu_B H\hat{S}^z_{4i+1} - g_{4i+2}\mu_B H\hat{S}^z_{4i2} -$$
$$g_{4i+3}\mu_B H\hat{S}^z_{4i+3} - D_{Co'}(\hat{S}^z_{4i+3})^2)$$

where $g_{4i} = g_{4i+2} = g_c$, $g_{4i+1} = g_b$, $g_{4i+3} = g_a$, and $D_{Co'}$ deals with the zero-field splitting (ZFS) parameter of tetrahedral cobalt(II). The expressions for the elements of the 2 × 2 transfer matrix T are given as supplementary material, from which an analytical formula for the parallel magnetic susceptibility is obtained.

The low-temperature data are illustrated in Figure 4 along with the best fit curves. The fitting procedure has not been straightforward, due to the large number of parameters. In order to reduce this number, we have set a ZFS value on the tetrahedral cobalt site greater than 10 K, as commonly found in similar environments.[22] In this way, only the doublet state is appreciably populated in the temperature range of interest ($T < 4$ K). Several sets of parameters giving close agreement with the experimental values were found. A large interdependence among the three Landé parameters was found. Two different cases arise from considering the relative magnitude of J and J'. The best fits are reported in Figure 4 and Table II.

Notice that, due to the alternation of A and B in central positions between two C sites, there are two additional equivalent fits resulting from interchanging g_a with g_b and J with J'. Despite this wide variety of sets of parameters, it has been noticed that the position of the minimum of $\chi_m T$ is only dependent on the smallest exchange value. Then, a reliable value of this parameter can be obtained from the fitting procedure. In turn, the strongest exchange shows a large variability, with J/k values ranging between −2 and −10 K in case I and between −4 and −11 K in case II. Furthermore, the assignment of these values to the two exchange pathways is not unambiguous. To rule out this ambiguity, we have focused on the values obtained for the (g_a, g_b, g_c) sets. Thus, in view of the range of values commonly found for Co(II) ions in similar environments (ranging from 1 to 10 K in octahedral
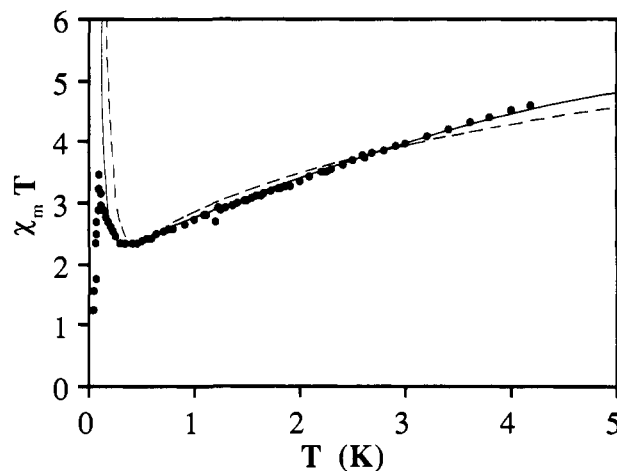

Figure 4. Magnetic behavior of [CoCoCo]. Circles indicate experimental points. Full and dashed lines correspond to fits I and II, respectively.
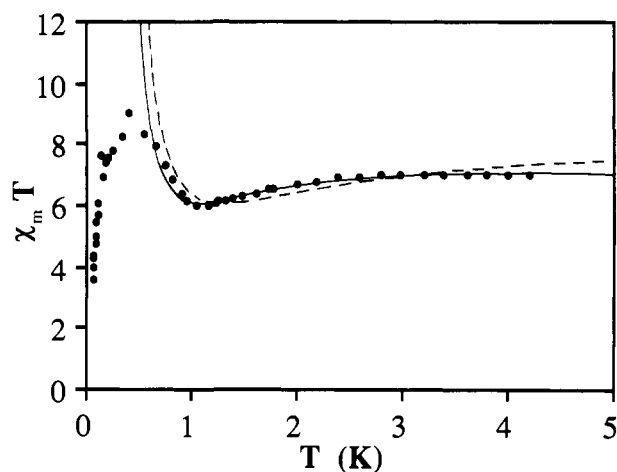

Figure 5. Magnetic behavior of [CoCoNi]. Circles indicate experimental points. Dashed and full lines correspond to fits I and II, respectively.

sites and from 2 to 2.5 in tetrahedral ones), we have noticed that only in the first set of parameters (fit I) is the tetrahedral g_a value reasonable. Accordingly, we can assign unambiguously the largest J value to the MM' interaction within the layer and the smallest one to the M'M^I interaction. The fact that the MM' interaction within the layer is of the same order of magnitude as that previously found in the chain CoCo(EDTA)·6H_2O may support this assignment.

The [CoCoNi] Compound. In this system, $S_c = 1$ for Ni(II), $S_b = ^1/_2$ for Co(II) in an octahedral site, and we assume that the tetrahedral Co(II) ion can be described below 4 K as a spin doublet, since its zero-field splitting is expected to be larger than −10 K, as in [CoCoCo]; in this way, the transfer matrix reduces again to 2 × 2, and hence, closed formulas for the parallel magnetic susceptibility can be deduced. Now, the full Hamiltonian is written as

$$\hat{H} = \sum_i (-J\hat{S}^z_{4i}\hat{S}^z_{4i+1} - J\hat{S}^z_{4i+2} - J'\hat{S}^z_{4i+2}\hat{S}^z_{4i+3} - J'\hat{S}^z_{4i}\hat{S}_{4i-1} -$$
$$g_{4i}\mu_B H\hat{S}^z_{4i} - g_{4i+1}\mu_B H\hat{S}^z_{4i+1} - g_{4i+2}\mu_B H\hat{S}^z_{4i+2} -$$
$$g_{4i+3}\mu_B H\hat{S}^z_{4i+3} - D_{Ni}[(\hat{S}^z_{4i})^2 + (\hat{S}^z_{4i+2})^2])$$

(20) Carlin, R. L.; de Jongh, L. J. *Chem. Rev.* **1986**, *86*, 659.

(21) Kramers, H. A.; Wannier, C. H. *Phys. Rev.* **1941**, *60*, 252.

(22) Carlin, R. L. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; NATO ASI Series 140; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1985; p 127.

where $g_{4i} = g_{4i+2} = g_c$, $g_{4i+1} = g_b$, and $g_{4i+3} = g_a$; J and J' deal with the coupling of Ni(II) with octahedral and tetrahedral Co(II), respectively, and D_{Ni} is the zero-field-splitting parameter of Ni(II) in the chelated site. The expressions for the elements of the transfer matrix are reported as supplementary material, as well as the formula of the parallel magnetic susceptibility.

The low-temperature data are illustrated in Figure 5. As for [CoCoCo], several sets of parameters giving close agreement with the experimental results can be found. Two different families of fits arise from considering the relative magnitude of the ZFS value of Ni(II) with respect to the exchange parameters. By setting $D_{Ni}/k_B = -3.8$ K and keeping g_{Ni} (g_c) and g_{Co} (g_a) around 2, we obtain reasonable fits with J' staying nearly constant and equal to -9.5 K and J varying from -2 to -6.5 K. On the other hand, keeping free D_{Ni}, we obtain good fits when $D_{Ni}/k_B = -8$ K and J varies between -6.5 and -10 K; again, J' stays close to -10 K. The best fits for each one of these families are reported in Figure 5 and Table II. We notice that these fits lead to obtaining reliable values for the exchange interaction between chelated Ni(II) and tetrahedral Co(II). In turn, these fits result in a large uncertainty in the value of the exchange within the layer. Since the second set of fits is not compatible with the experimental value of D_{Ni}, the only conclusion that seems apparent from these results is that the Co–Ni exchange within the layer is weaker than that with tetrahedral Co(II). Further experimental measurements, for example specific heat measurements, are now required in order to better determine the exchange interactions.

Summary and Conclusions

In this paper, we have reported the low-temperature magnetic susceptibility results of the isostructural series M^{t}M-(M'EDTA)$_2$·4H$_2$O (M^t = Zn(II), Co(II); M = Zn(II), Co(II), Ni(II); M' = Co(II), Ni(II)), which may be viewed as ferrimagnetic layers MM' connected through tetrahedral sites, M^t. By introducing Zn(II) in M^t, we have been able to obtain the 2-D ferrimagnet [ZnNiNi], which shows an antiferromagnetic-like behavior due to Ni(II) zero-field-splitting effects. On the other hand, the connection of the layers through Co(II) leads to compounds showing a 3-D ferrimagnetic ordering at a critical temperature T_c, clearly noticeable in both in-phase and out-of-phase ac susceptibility data. Above T_c, these compounds exhibit the characteristic magnetic behavior of low-dimensional ferrimagnets. These features are summarized in Table III.

In the low-dimensional regime, the magnetic data have been discussed in terms of a 1-D anisotropic (Ising) model. The model takes into account three different magnetic sublattices exchange-coupled with two interaction constants, as well as the local anisotropies of tetrahedral Co(II) and chelated Ni(II) ions. The resulting exchange parameters are summarized in Table II. As expected, there is a coupling between tetrahedral Co(II) and chelated ions [Co(II) or Ni(II)] belonging to two neighboring layers. This interaction is antiferromagnetic.

Remarkably, the ordering temperatures of these compounds are much enhanced when compared to those of the parent hexahydrates. Although the magnitudes of the "intrachain" interactions are similar in both series, the ordering temperatures are, at least, 1 order of magnitude larger in the tetrahydrates. Thus, while in [CoNiNi] the transition occurs at 0.44 K, no T_c is detected in the [CoNi] bimetallic chain down to 0.07 K.[9] Obviously, such a difference reflects the increase in the dimensionality of the lattice. In fact, a comparison between J and T_c values in tetrahydrate compounds suggests that the third exchange coupling is 1 order of magnitude smaller than J, while in the hexahydrate series j/J < 10^{-3}. From this trend, values of T_c above the temperature of liquid helium are expected for manganese-containing tetrahydrates.

The family reported in this work evidences the capability of the strategy followed: intercrossing bimetallic chains through covalent bonds in order to obtain 2- or 3-D ordered bimetallic lattices. This leads to a significant increase of the ordering temperature and provides a better control of the nature of the magnetic transition. Obviously, the low strength of antiferromagnetic exchange interactions determined by the type of carboxylate bridges forces these compounds to order at very low temperatures. Extending this strategy to compounds containing bridges with a better ability to transmit exchange interactions may provide a suitable way to obtain high-temperature magnets.

Supplementary Material Available: Expressions for the transfer matrix elements for the models developed to analyze the low-dimensional magnetic behavior of the [CoCoCo] and [CoCoNi] compounds (3 pages). Ordering information is given on any current masthead page.