According to this theory, high values of E_a have a better correspondence with an S_N2 mechanism while low values have a better correspondence with an S_N1 mechanism.

On the basis of a crystal field model, the formation of a seven-coordinate complex (pentagonal bipyramidal; S_N2 mechanism) requires $8.52Dq$[30] (Dq being close to 25 kJ mol^{-1} for the $[CoH_2O(NH_3)_5]^{3+}$ ion), which would be about 100 kJ mol^{-1}, similar to the E_a value found. In addition, the heptacoordination in the S_N2 reaction suggests the formation of a Schottky type defect in an ionic crystal. This process requires high energy ($E_{def} = 0.24U$; U = lattice energy);[32] consequently, the E_a value expected should be larger than 110–120 kcal mol^{-1}.

The mechanism, therefore, might be S_N1 (dissociative mechanism) with the formation of a square-base-pyramid activated complex, requiring only $4.0Dq$ (for a trigonal-bipyramidal activated complex it would require $11.49Dq$).[30] The transition state is, then, determined by the water loss and the formation of a nonionic Frenkel type defect.

The activation energy for this type of process in an isostructural family of compounds should be nearly constant, especially if they have a common cation and similar anions.

However, our experimental results show a significant variation in the E_a values for the deaquation–anation process (Table VII):

$$[CoH_2O(NH_3)_5][Co(CN)_5X] \rightarrow H_2O + [(NH_3)_5CoNCCo(CN)_4X]$$

$$X = CN, Cl, Br, I, NO_2, N_3$$

To explain the results we propose the concept of "lattice free space" as an important parameter to discuss these solid-state reactions. The ordering in E_a values is in good agreement with the "unit cell free space" (see X-ray powder diffraction results). In the cases where there is a large space between the cations and anions (as may be supposed in the I and N_3 compounds), the water molecule may be able to slip into an interstitial position causing little or no lattice distortion. In these situations low values of E_a are expected. On the other hand, where there is a smaller space between the ions (as may be supposed in the CN and Cl compounds), the water molecules can occupy an interstitial position only with considerable lattice expansion; consequently, larger E_a values should result.

It can be concluded that in an S_N1 process the activation energy is determined by the crystal field component as well as the lattice component as is evident in this paper. The lattice component can be envisaged as the "free space" in the crystalline structure. The importance of the lattice component has been pointed out by some of us in several families of double-complex salts such as $[CoH_2O(NH_3)_5]_2[M(CN)_4]_3$ (M = Ni, Pd, Pt)[33] and $[MH_2O(NH_3)_5][M'(CN)_6]$ (M = Co, Rh, Ir; M' = Cr).[34]

Acknowledgment. This work was supported by CAICYT grant 360/81. We are very grateful to A. Escuer from the University of Barcelona for allowing us to use his kinetics program.

Registry No. $[CoH_2O(NH_3)_5][Co(CN)_5Cl]$, 102976-81-8; $[CoH_2O(NH_3)_5][Co(CN)_5Br]$, 102941-69-5; $[CoH_2O(NH_3)_5][Co(CN)_5I]$, 102976-82-9; $[CoH_2O(NH_3)_5][Co(CN)_5N_3]$, 102941-70-8; $[CoH_2O(NH_3)_5][Co(CN)_5NO_2]$, 102941-71-9; $(NH_3)_5CoNCCo(CN)_4Cl$, 102941-72-0; $(NH_3)_5CoNCCo(CN)_4Br$, 102941-73-1; $(NH_3)_5CoNCCo(CN)_4I$, 102941-74-2; $(NH_3)_5CoNCCo(CN)_4N_3$, 102976-83-0; $(NH_3)_5CoNCCo(CN)_4NO_2$, 102976-84-1; $K_3[Co(CN)_5Cl]$, 14705-98-7; $K_3[Co(CN)_5Br]$, 14650-10-3; $K_3[Co(CN)_5I]$, 14650-11-4; $K_3[Co(CN)_5NO_2]$, 14854-72-9; $K_3[Co(CN)_5N_3]$, 14705-99-8; $[CoH_2O(NH_3)_5](ClO_4)_3$, 13820-81-0; $K_3[Co(CN)_6]$, 13963-58-1.

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Low-Dimensional Bimetallic Ordered Systems: Synthesis and Characterization of the Isomorphous Series $Co_xNi_{2-x}EDTA·2H_2O$. Crystal Structure of $Co_2EDTA·2H_2O$ and Preferential Site Occupation in $CoNiEDTA·2H_2O$

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Received February 12, 1986

Four members of the isomorphous series of empirical formula $Co_xNi_{2-x}EDTA·2H_2O$ have been prepared (x = 2.0, 1.5, 1.0, 0.7), and the crystal structure has been solved for $Co_2EDTA·2H_2O$ (space group $C2/c$, a = 26.967 (3) Å, b = 9.495 (1) Å, c = 11.154 (1) Å, β = 92.395 (8)°, Z = 8). These solids are crystalline polymers with three crystallographically independent metal centers corresponding to chromophores MN_2O_4, MO_4, and MO_6, bridged through carboxylate groups from EDTA. Metals in the MO_4 and MO_6 moieties occupy special positions (2 and $\bar{1}$, respectively). The electronic spectra of the complexes are consistent with preferential occupation of the MN_2O_4 site by Ni in the complex $CoNiEDTA·2H_2O$. Magnetic susceptibility measurements down to 4 K show no appreciable intermetallic magnetic interactions in $CoNiEDTA·2H_2O$, while some small antiferromagnetic coupling is detected for $Co_2EDTA·2H_2O$. According to their structural features these materials may be viewed as ferrimagnetic two-dimensional systems.

Introduction

The study of low-dimensional materials has been the subject of increasing interest over the past few years with linear chains having been the most extensively studied, both experimentally and theoretically.[1,2] While homometallic linear-chain systems are most frequently found in the literature, the coordination asymmetry present in the complex $Zn_2EDTA·6H_2O$[3] encouraged us to prepare an isomorphous series of heterometallic compounds of formula $[M(H_2O)_4O_IO_{II}][M'EDTA]·2H_2O$, where M = Mg,

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Table I. Chemical Analyses of the Series Compounds $Co_xNi_{2-x}EDTA{\cdot}2H_2O$

	% Co		% Ni		% C		% N		% H		
x	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	r^a
0.7	8.4	8.84	16.9	17.77	27.9	27.19	6.6	6.34	3.9	3.7	1.9
1.0	12.9	13.34	13.0	13.29	27.2	27.18	6.4	6.34	3.8	3.6	1.9
1.5	18.4	20.00	6.7	7.13	27.4	27.17	6.6	6.34	3.8	3.6	1.9
2.0	26.7	26.66			27.0	27.17	6.2	6.34	3.5	3.6	2.0

[a] *r* = total moles of M(II)/moles of EDTA.

Mn, Co, Zn, and Ni, M′ = Co, Zn, Ni, and Cu, and O_I and O_{II} denote carboxylate oxygen atoms from EDTA.[4] These materials all have the same crystal structure, featuring zigzag chains of alternating octahedral MN_2O_4 and MO_6 sites.[5] For many combinations of M and M′, a preferential site occupation gives rise to bimetallic ordered-chain systems (...M–M′–M–M′...)[4,6] that exhibit ferrimagnetic 1-D behavior due to the alternating magnetic moments located on M and M′.[6–10] Also we have reported very recently the local structure and magnetic behavior of some of these complexes in the amorphous state.[11–13]

We report here the study of a second isomorphous series based on a novel phase of bimetallic EDTA complexes, containing octahedral and tetrahedral sites leading to more complex magnetic behavior and at the same time being potentially more versatile for the design of low-dimensional systems.

Experimental Section

Preparation of the Complexes. The four members of the isomorphous series of hexahydrates $Co_xNi_{2-x}EDTA{\cdot}6H_2O$ (*x* = 2.0, 1.5, 1.0, and 0.5), used as starting materials, were prepared as reported previously.[4]

Each member of the isomorphous series $Co_xNi_{2-x}EDTA{\cdot}2H_2O$ (*x* = 2.0, 1.5, 1.0, and 0.7) was prepared by hydrothermal treatment from the corresponding hexahydrate $Co_xNi_{2-x}EDTA{\cdot}6H_2O$ (*x* = 2.0, 1.5, 1.0, and 0.5, respectively). Supersaturated aqueous solutions of these (0.5 g/mL of water) were heated up to 180 °C in sealed Pyrex vials under pressure. Purple-blue crystals of the title complexes were obtained after several hours. It should be noted that the coefficient *x* remains unchanged from one family of complexes to the other, except for the last member, with a Ni/Co molar ratio of 3 in the hexahydrate while only 2 in the dihydrate. Also, we were unable to crystallize $Ni_2EDTA{\cdot}2H_2O$ under the conditions used.[14] Chemical analyses are shown in Table I.

The water content of the complexes was determined from thermogravimetric analysis to be 2 mol of H_2O/mol of complex; in all cases water was lost through an endothermic process at temperatures between 239 and 265 °C (temperatures at half-loss; (systematically higher temperatures as the content of Ni in the complexes increases).[14]

Infrared spectra were recorded as KBr pellets in the range 4000–1000 cm^{-1} and were practically identical for all complexes[14] (ν_{as}(COO) 1617, 1587, 1560 (sh) cm^{-1}; ν_s(COO) 1406, 1380 cm^{-1}; ν(CN) 1120, 1103 cm^{-1}).

Powder diffractograms of all four members of the title series were identical within experimental error. Additionally, precession photographs taken on single crystals of $Co_2EDTA{\cdot}2H_2O$ and $CoNiEDTA{\cdot}2H_2O$ showed identical diffraction patterns and positively proved these complexes to be isostructural.[14]

Table II. Crystal Data and Data Collection Procedures for $CoCo(CoEDTA)_2{\cdot}2H_2O$

formula	$C_{10}H_{16}Co_2N_2O_{10}$
fw	442.11
space group	*C*2/*c*
a, Å	26.967 (3)
b, Å	9.495 (1)
c, Å	11.154 (1)
β, deg	92.395 (8)
V, Å^3	2854
Z	8
ρ(calcd) (ρ(obsd)), g/mL	2.058 (2.06)
cryst shape; cryst dimens, mm^3	oblique prism; 0.3 × 0.4 × 0.4
radiation	graphite-monochromated Mo Kα; $\lambda(K\alpha_1) = 0.7093$ Å
linear abs coeff, cm^{-1}	23.792
transmission factors	0.65–0.78 (Gaussian integr)
takeoff angle, deg	2.8
scan type	ω
scan speed, deg/min	1.0
scan range, deg	$2.8 < 2\theta(\mathrm{Mo}\ K\alpha_1) < 66.0$
$(\sin\theta)/\lambda$ limits, Å^{-1}	0.0344–0.768
data collected	$\pm h,+k,+l$
p ($1/w = \sigma^2(\mathrm{count}) + (pI)^2$)	0.03
unique data	4379
unique data with $F_0^2 > 3\sigma(F_0^2)$	3319

Electronic Spectra. Liquid paraffin mulls of the solids were used to obtain their transmission spectra in the ranges 300–800 nm and 700–2000 nm. The spectra of $CoCoEDTA{\cdot}2H_2O$ and $CoNiEDTA{\cdot}2H_2O$ were recorded twice, with different spectrophotometers and on different preparations, and were found to be perfectly reproducible, both in the position and relative intensity of their bands. For the obtainment of difference spectra, the [CoNi] hexahydrate spectrum was scaled so that its NiN_2O_4 band matches in intensity that of the [CoNi] dihydrate; then the [CoCo] hexahydrate spectrum was scaled to match the intensity of the band assigned to CoO_6 in the [CoNi] hexahydrate.

Magnetic Measurements. Magnetic susceptibility measurements were performed in the temperature range 4–125 K with a pendulum-type magnetometer and were corrected for diamagnetic contributions. The uncertainty in the data is lower than 0.1 K for temperatures and 2×10^{-5} emu/mol for susceptibilities.

Crystallographic Study of $Co_2EDTA{\cdot}2H_2O$. Precession and Weissenberg photos showed symmetry and systematic absences consistent with space groups *C*2/*c* and *Cc*.

A Picker FACS-I automatic diffractometer was used for data collection. Three standard reflections, measured every 100 reflections, showed no significant change. Crystal mosaicities (peak width at half peak height) as determined by ω scans were typically about 0.15° for intense low-angle reflections, values typical for good-quality crystals on our diffractometer. Lattice parameters were obtained by the centering of 26 reflections in the range $34° < 2\theta < 44°$ with Mo $K\alpha_1$ radiation (λ = 0.7093 Å). Other important features of data collection are summarized in Table II.

The set of programs included in the SDP (Structure Determination Package) of Frenz & Associates and Enraf-Nonius was used in the analysis of the crystal structure.

Patterson maps were initially used to locate the Co atoms, but subsequent difference Fourier analysis based on two different sets of Co coordinates never revealed new atoms that could be successfully refined and incorporated into the model. Direct methods (MULTAN 11/82) were tried with the assumption of both possible space groups, also with poor results. Finally we obtained a satisfactory starting model using RANTAN in space group *Cc* followed by successive Fourier synthesis and refinements. The final *R* value was 0.029. From this point, we continued in

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Table III. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Co1	0.15290 (1)	0.23233 (3)	0.55551 (3)	1.309 (4)	C21	0.13264 (8)	−0.0280 (2)	0.6820 (2)	1.69 (4)
Co2	0.000	0.24557 (4)	0.250	1.528 (7)	C22	0.17190 (8)	−0.0613 (2)	0.5915 (2)	1.74 (4)
Co3	0.250	0.250	1.000	1.452 (7)	C23	0.06411 (9)	0.0517 (3)	0.5507 (2)	2.02 (4)
O1	0.20426 (6)	0.3336 (2)	0.4495 (2)	2.68 (4)	C24	0.06654 (8)	0.1321 (2)	0.4340 (2)	1.65 (4)
O2	0.25306 (6)	0.5857 (2)	0.6262 (2)	2.05 (3)	H(O1)B	0.206 (1)	0.420 (4)	0.426 (3)	6 (1)*
O11	0.0449 (1)	0.6983 (3)	0.4982 (2)	5.39 (5)	H(O1)A	0.223 (2)	0.316 (6)	0.427 (4)	11 (2)*
O12	0.04951 (7)	0.6305 (2)	0.6878 (2)	3.04 (4)	H1A	0.0519 (9)	0.144 (3)	0.767 (2)	2.5 (6)*
O13	0.19656 (6)	0.2600 (2)	0.7148 (2)	2.07 (3)	H1B	0.1094 (9)	0.186 (3)	0.804 (2)	1.9 (5)*
O14	0.20440 (6)	0.3860 (2)	0.8831 (1)	2.04 (3)	H(O2)A	0.269 (1)	0.619 (4)	0.687 (3)	5.5 (9)*
O21	0.18813 (6)	−0.1834 (2)	0.5880 (2)	2.35 (3)	H(O2)B	0.273 (1)	0.529 (4)	0.598 (3)	4.6 (8)*
O22	0.18624 (6)	0.0395 (2)	0.5263 (2)	2.22 (3)	H2A	0.057 (1)	0.388 (3)	0.758 (2)	2.8 (6)*
O23	0.10116 (6)	0.2164 (2)	0.4180 (1)	2.01 (3)	H2B	0.0442 (9)	0.325 (3)	0.631 (2)	1.8 (5)*
O24	0.03226 (6)	0.1058 (2)	0.3571 (2)	2.07 (3)	H11A	0.1230 (8)	0.546 (3)	0.517 (2)	1.7 (5)*
N1	0.11224 (7)	0.4009 (2)	0.6385 (2)	1.59 (3)	H11B	0.0789 (9)	0.454 (3)	0.478 (2)	2.2 (6)*
N2	0.10294 (7)	0.0941 (2)	0.6410 (2)	1.58 (3)	H13B	0.126 (1)	0.503 (3)	0.796 (3)	3.2 (7)*
C1	0.08223 (9)	0.1811 (3)	0.7373 (2)	1.87 (4)	H13A	0.166 (1)	0.545 (3)	0.694 (3)	3.7 (7)*
C2	0.06914 (8)	0.3272 (3)	0.6908 (2)	1.79 (4)	H21A	0.152 (1)	−0.005 (3)	0.754 (2)	2.5 (6)*
C11	0.09605 (9)	0.5049 (2)	0.5462 (2)	1.78 (4)	H21B	0.1154 (8)	−0.103 (3)	0.694 (2)	1.4 (5)*
C12	0.06021 (9)	0.6213 (3)	0.5786 (2)	2.14 (4)	H23A	0.067 (1)	−0.051 (3)	0.534 (2)	3.0 (6)*
C13	0.14554 (9)	0.4649 (3)	0.7320 (2)	1.91 (4)	H23B	0.0311 (9)	0.063 (3)	0.586 (2)	2.1 (6)*
C14	0.18487 (8)	0.3619 (3)	0.7802 (2)	1.76 (4)					

[a] Starred values are for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table IV. Bond Distances (Å)[a]

atom 1	atom 2	dist	atom 1	atom 2	dist
Co1	O1	2.092 (2)	O21	C22	1.241 (2)
Co1	O13	2.107 (1)	O22	C22	1.272 (2)
Co1	O22	2.072 (1)	O23	C24	1.248 (2)
Co1	O23	2.036 (1)	O24	C24	1.259 (2)
Co1	N1	2.169 (2)	N1	C2	1.495 (2)
Co1	N2	2.134 (2)	N1	C11	1.480 (2)
Co2	O12	1.930 (1)	N1	C13	1.478 (2)
Co2	O24	1.965 (1)	N2	C1	1.483 (2)
Co3	O2	2.101 (1)	N2	C21	1.471 (2)
Co3	O14	2.178 (1)	N2	C23	1.478 (2)
Co3	O21	2.070 (1)	C1	C2	1.518 (3)
O11	C12	1.216 (3)	C11	C12	1.521 (3)
O12	C12	1.267 (3)	C13	C14	1.524 (3)
O13	C14	1.259 (2)	C21	C22	1.526 (3)
O14	C14	1.264 (2)	C23	C24	1.512 (3)

[a] X–H bonds are in the range 0.60 (4)–0.87 (4) Å for OH_2 and 0.87 (2)–1.04 (3) for $-CH_2$. Numbers in parentheses are estimated standard deviations.

$C2/c$ since very large correlations were observed among the refined parameters. The four independent Co atoms per asymmetric unit in the noncentrosymmetric case were reduced to three, two of which occupy special positions (2 and $\bar{1}$). Anisotropic refinement of all non-hydrogen atoms yielded final values for R and R_w of 0.030 and 0.034. All hydrogen atoms were found with use of difference Fourier maps, and a final difference Fourier synthesis was essentially featureless (one peak of density, 0.84 e/Å^3, was located between the two methylene carbon atoms, the other peaks had densities smaller than 0.52 e/Å^3). The final data/parameters ratio was 3319/291.

Results and Discussion

Description and Discussion of the Structure. $CoCoEDTA\cdot 2H_2O$ is a crystalline three-dimensional polymer where Co ions are bridged by carboxylate groups from the ligand EDTA. There are three crystallographically independent Co atoms, one of which occupies a general position and is chelated by EDTA and one molecule of water (Co1, distorted-octahedral chromophore CoN_2O_4); the second lies on a twofold axis and is coordinated to two bridging and two nonbridging carboxylate groups from neighboring EDTA molecules (Co2, distorted-tetrahedral chromophore CoO_4). Finally, the third Co sits on a center of inversion and is coordinated to two water molecules and linked by four bridging carboxylate groups to four Co1 atoms (Co3, distorted-octahedral chromophore CoO_6). Figure 1 shows the indicated coordination geometries and includes atom labeling for reference

Table V. Bond Angles (deg)[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	Co1	O13	93.40 (7)	O2	Co3	O14	88.07 (6)	C1	N2	C21	115.5 (2)
O1	Co1	O22	90.88 (7)	O2	Co3	O14	91.93 (6)	C1	N2	C23	111.6 (2)
O1	Co1	O23	93.29 (6)	O2	Co3	O21	85.34 (6)	C21	N2	C23	111.0 (2)
O1	Co1	N1	105.10 (7)	O2	Co3	O21	94.66 (6)	N2	C1	C2	110.5 (2)
O1	Co1	N2	168.61 (7)	O14	Co3	O21	91.08 (6)	N1	C2	C1	112.8 (2)
O13	Co1	O22	90.69 (6)	O14	Co3	O21	88.92 (6)	N1	C11	C12	119.4 (2)
O13	Co1	O23	170.49 (5)	Co2	O12	C12	125.2 (1)	O11	C12	O12	125.7 (2)
O13	Co1	N1	79.79 (5)	Co1	O13	C14	116.1 (1)	O11	C12	C11	117.4 (2)
O13	Co1	N2	92.34 (6)	Co3	O14	C14	129.8 (1)	O12	C12	C11	116.8 (2)
O22	Co1	O23	95.96 (6)	Co3	O21	C22	126.4 (1)	N1	C13	C14	112.2 (2)
O22	Co1	N1	161.75 (6)	Co1	O22	C22	115.5 (1)	O13	C14	O14	124.0 (2)
O22	Co1	N2	79.22 (6)	Co1	O23	C24	115.6 (1)	O13	C14	C13	118.4 (2)
O23	Co1	N1	91.94 (6)	Co2	O24	C24	125.0 (1)	O14	C14	C13	117.5 (2)
O23	Co1	N2	82.27 (6)	Co1	N1	C2	103.7 (1)	N2	C21	C22	110.0 (2)
N1	Co1	N2	85.60 (6)	Co1	N1	C11	109.6 (1)	O21	C22	O22	124.7 (2)
O12	Co2	O12	104.9 (1)	Co1	N1	C13	107.5 (1)	O21	C22	C21	118.0 (2)
O12	Co2	O24	119.25 (6)	C2	N1	C11	111.8 (2)	O22	C22	C21	117.3 (2)
O12	Co2	O24	109.57 (7)	C2	N1	C13	112.1 (2)	N2	C23	C24	113.2 (2)
O12	Co2	O24	109.58 (7)	C11	N1	C13	111.7 (2)	O23	C24	O24	124.2 (2)
O12	Co2	O24	119.25 (6)	Co1	N2	C1	104.2 (1)	O23	C24	C23	120.4 (2)
O24	Co2	O24	95.00 (8)	Co1	N2	C21	106.1 (1)	O24	C24	C23	115.4 (2)
				Co1	N2	C23	107.8 (1)				

[a] Numbers in parentheses are estimated standard deviations.

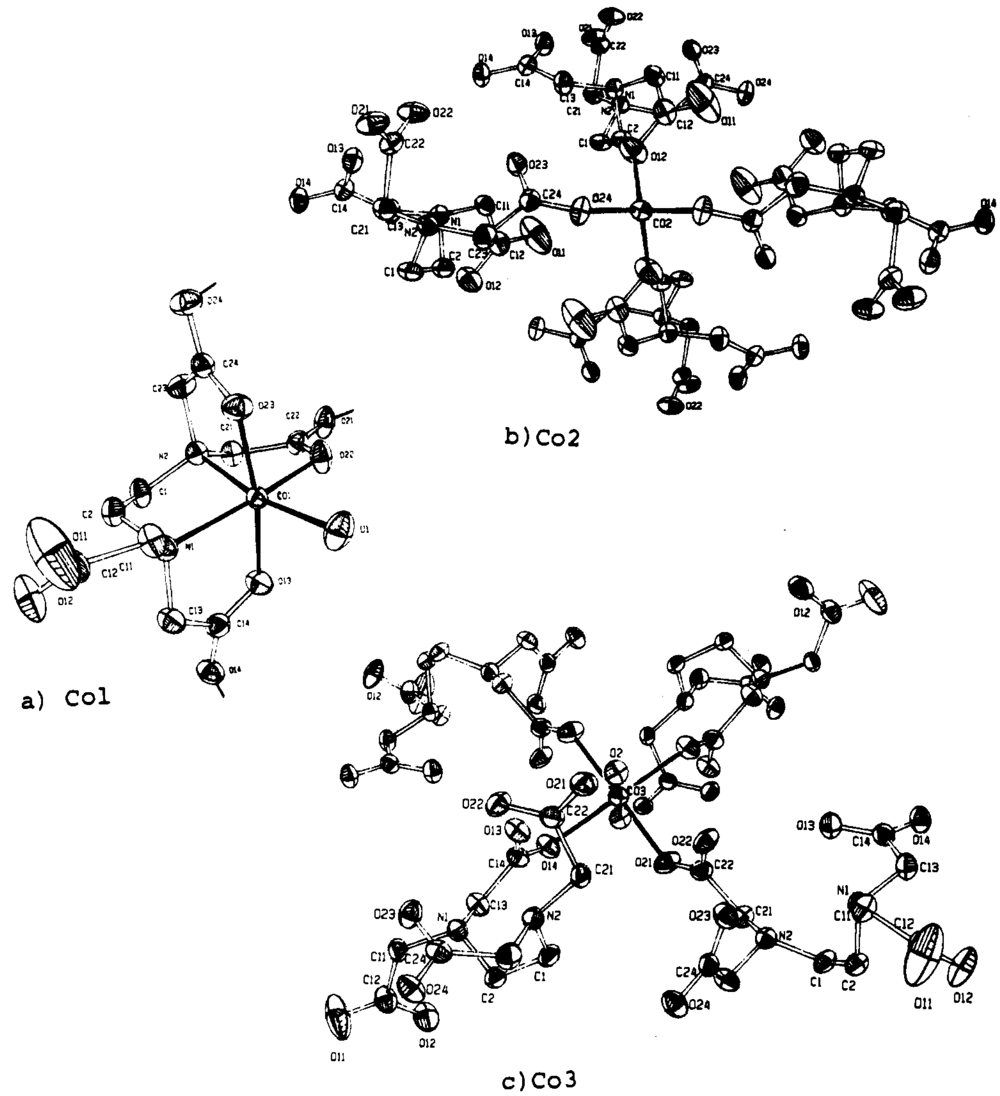

Figure 1. Local coordination for each of the three metal sites in CoCo(CoEDTA)$_2$·4H$_2$O: (a) Co1, occupying a general position and chelated by EDTA; (b) Co2, lying on a twofold axis; (c) Co3 sitting on a center of inversion.

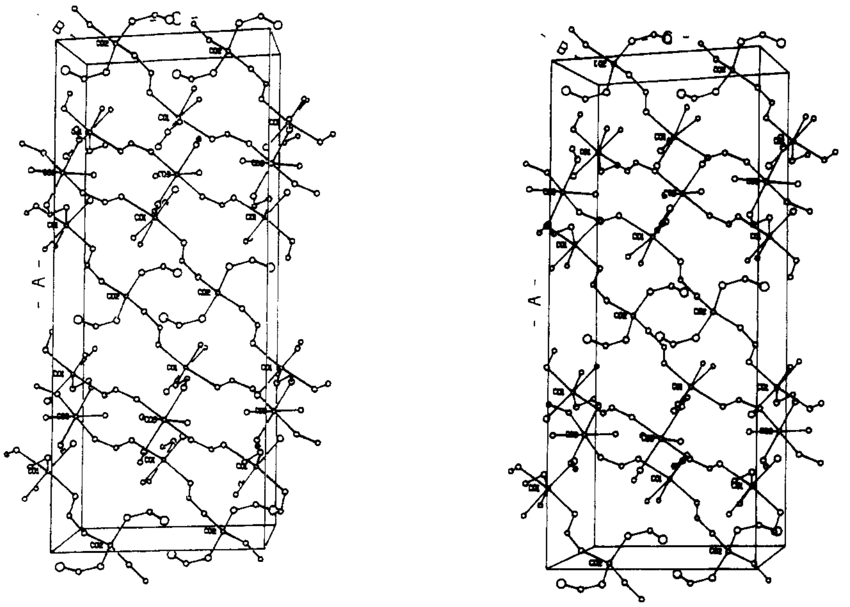

Figure 2. Stereoview of the content of the unit cell. Only metal atoms and their coordination spheres are shown for clarity. The exception is made for carboxylate groups to show the connectivity between metals.

to tables of positional parameters, bond distances, and bond angles (Tables III–V, respectively).

When the structure and different multiplicities are taken into account, the polymeric complex would be better described by the

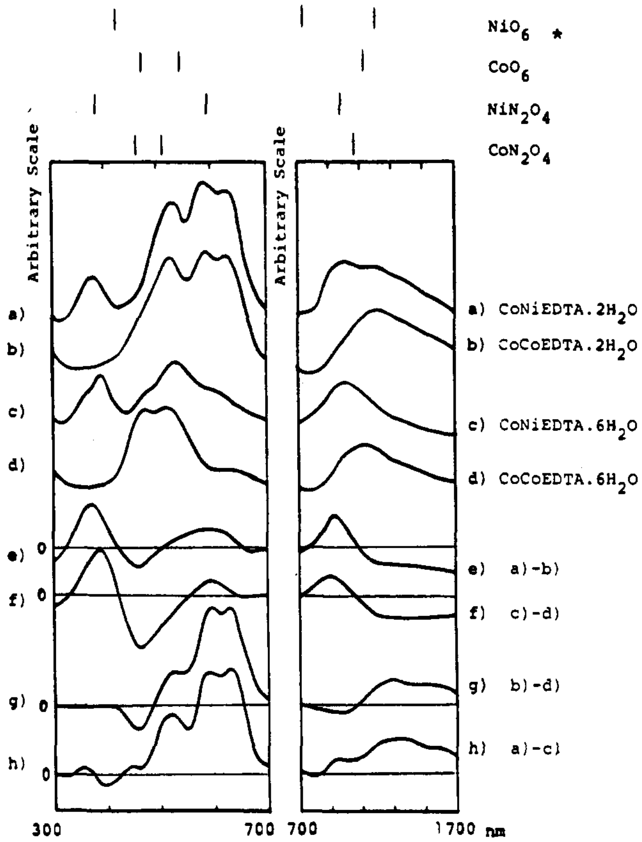

Figure 3. Analysis of the electronic spectra of [CoCo] and [CoNi] complexes. Chromophore assignments are from ref 4.

formula $CoCo(CoEDTA)_2{\cdot}4H_2O$.

No lattice water was found in this efficiently packed polymer; all water molecules are coordinated. This is consistent with the high temperatures required to lose them (TGA) and with the remarkable air stability of these crystals.

The polymeric nature of the crystal is shown in Figure 2: each Co1 is connected with two Co3's and one Co2 (at 5.512 (1)-, 5.324 (1)-, and 5.240 (1)-Å distances, respectively), each tetrahedral Co2 is only bridged to two Co1, and each Co3 to four Co1's, all through syn-anti OCO bridges. Furthermore, all five atoms in each of the two crystallographically independent Co1–O–C–O–Co3 sequences are essentially coplanar, both planes forming dihedral angles very close to 90° around Co1 and Co3.

The polymer can be formally regarded as a succession of layers of tetrahedral CoO_4 groups and of octahedrally coordinated Co atoms, alternating along the *a* axis and connected through bridging carboxylate groups. While the tetrahedral CoO_4 groups are isolated from each other on the corresponding layer, octahedral Co1 and Co3 moieties form a "puckered" two-dimensional network as indicated in Figure 5; each Co1 is bridged to two Co3's and each of these to four Co1's. This approach might be relevant to the interpretation of the magnetic behavior of these compounds.

Electronic Spectroscopy. The three types of chromophores present in the title complexes are known from the crystal structure, and bands from all three should appear in the spectrum of $CoCoEDTA{\cdot}2H_2O$ (Figure 3b). The question arises for $CoNiEDTA{\cdot}2H_2O$ about the occupation of these three sites by two different metals in a molar ratio of 1:1. It would be difficult to answer that question, on the basis of diffraction data, given the very similar electronic densities of Co and Ni. On the other hand, the analysis of the electronic spectra can give some useful information in this respect, particularly when the spectra are compared with those of $Co_xNi_{2-x}EDTA{\cdot}6H_2O$ complexes. In this latter isomorphous series, the metals can occupy only two different octahedral sites: chelated by EDTA (chromophore MN_2O_4) or coordinated to two bridging carboxylate groups and to four molecules of H_2O (chromophore MO_6).[5] In addition, it has been shown unambiguously[4] that Ni occupies only the chelated position in the 1:1 mixed complex. Given the remarkable similarity of chromophores (MN_2O_4, MO_6) between both series of compounds, we will assume that the corresponding bands will appear at approximately the same frequency, with the same extinction coefficient.

First of all, the difference between the $CoCoEDTA{\cdot}2H_2O$ and $CoCoEDTA{\cdot}6H_2O$ spectra (no tetrahedral chromophore in the latter) allows us to assign the two peaks at 590 and 625 nm and probably a shoulder at 520 nm to the tetrahedral chromophore CoO_4. This absorption pattern is indeed typical of tetrahedral Co complexes.[15]

The spectrum of $CoNiEDTA{\cdot}2H_2O$ is rather similar to the former one because it is dominated by the same tetrahedral chromophore pattern. As a matter of fact, the bands appear at exactly the same position, indicating that Co occupies the tetrahedral site in this case too. On the other hand, the isolated band at 370 nm can be assigned to octahedrally coordinated Ni and is also present in the [CoNi] hexahydrate spectrum. We can therefore reject the possibility of total disorder in the occupation of the three sites by Co and Ni.

Nevertheless, there are still two possibilities consistent with the observations discussed so far: an ordered system with chromophores NiN_2O_4, CoO_6 and CoO_4 or one with Ni and Co randomly distributed between the two octahedral sites.

The position of the octahedral Ni band observed for the dihydrate is closer to the transition assigned to NiN_2O_4 in the hexahydrate than to that for NiO_6 (see Figure 3), but this is not a proof of the absence of the last; the band could be the result of both chromophores overlapping, as is in fact the case for $NiNiEDTA{\cdot}6H_2O$. Nevertheless, the difference spectra [$CoNiEDTA{\cdot}2H_2O$ – $CoCoEDTA{\cdot}2H_2O$] and [$CoNiEDTA{\cdot}6H_2O$ – $CoCoEDTA{\cdot}6H_2O$] (Figure 3e,f) are qualitatively identical and show that Ni substitutes Co in the EDTA chelated site in going from the CoCo to the CoNi complex in both families of compounds. Furthermore, the result of subtracting the $CoNiEDTA{\cdot}6H_2O$ spectrum from the $CoNiEDTA{\cdot}2H_2O$ spectrum is the same CoO_4 band structure found in the subtraction of CoCo analogues (Figure 3g,h) and also confirms that, in the isomorphous series $Co_xNi_{2-x}EDTA{\cdot}2H_2O$, the metals are distributed in an ordered way among the sites present, with the Ni preferentially occupying the EDTA chelated position.

This selective occupation of sites observed is consistent with the different stability constants of discrete metal–EDTA complexes in aqueous solutions, where the NiEDTA complex is more stable than the CoEDTA complex.[16]

Magnetic Properties. Parts a and b of Figure 4 show plots of $\chi_m T$ vs. T for $CoCoEDTA{\cdot}2H_2O$ and $CoNiEDTA{\cdot}2H_2O$, respectively. For the [CoCo] system $\chi_m T$ decreases rapidly at low temperature, with a value extrapolated to zero of approximately 2.0 emu mol^{-1} K, significantly smaller than the expected value for isolated Co(II) ions (3.5–4.0 emu mol^{-1} K).[17]

On the other hand, a steady decrease of $\chi_m T$ with T is observed for the [CoNi] system; the value extrapolated to zero is approximately 3.0 emu mol^{-1} K, corresponding roughly to the sum of the $\chi_m T$ values for the isolated magnetic centers (1 Ni1, $^1/_2$ Co2, and $^1/_2$ Co3, as seen before).

The above results suggest the presence of small antiferromagnetic coupling among the Co centers in the [CoCo] complex while no appreciable magnetic interactions can be inferred from the data down to 4 K for the [CoNi] complex. In the latter, the slight increase of $\chi_m T$ with T is most likely due to an orbital contribution from the orbitally degenerate Co3 ion.

A quantitative interpretation of the magnetic properties is difficult, given the complexity of the polymer; there are nevertheless some considerations that could make it easier. As mentioned earlier, these polymers can be regarded as a succession of

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(15) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

(16) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1974; Vol. 1.

(17) See: Hatfield, W. E. In *Theory and Applications of Molecular Paramagnetism*; Boudreaux, E. A., Mulay, L. N., Eds.; Wiley: New York, 1976.

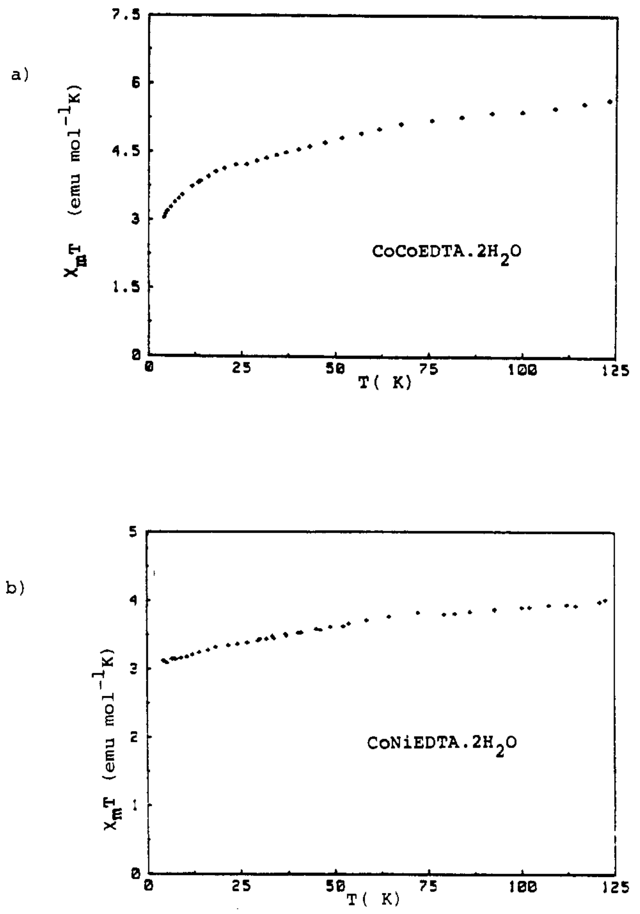

Figure 4. Magnetic behavior of the complexes (a) CoCo(CoEDTA)$_2$·4H$_2$O and (b) CoCo(NiEDTA)$_2$·4H$_2$O.

CoO$_4$ layers intercalated between layers of MN$_2$O$_4$ and CoO$_6$ (M = Co, Ni), forming a two-dimensional puckered network. These exhibit an alternating arrangement of the two octahedral sites and therefore can be viewed as bimetallic ordered layers (Figure 5). According to these structural features novel kinds of magnetic systems formed by alternating magnetic moments arise: two-dimensional ferrimagnets. The magnetic behavior of these is expected to be similar to that observed for 1-D ferrimagnetic systems, exhibiting a minimum of χ_mT and a divergence at lower temperatures.[8,18]

Obviously, magnetic measurements down to very low temperatures, as well as some theoretical developments, are now required to understand the thermodynamics of these new systems.

Final Remarks. As has been shown, the question of preferential occupation of Ni in MN$_2$O$_4$ and Co in MO$_6$ and MO$_4$ sites in the present polymeric structure can be confidently answered. The magnitudes of the several possible intermetallic magnetic interactions have not been found at this point.

The ability of EDTA to wrap around one metal atom while still providing bridging carboxylate groups to a second atom and the configurational freedom of this ligand are the basis for the obtainment of a variety of low-dimensional magnetic systems.

In this way, the series MM′EDTA·6H$_2$O provides an ideal structural support (bimetallic ordered chains) to isolate 1-D ferrimagnetic systems. With a smaller amount of water incorporated into the MM′EDTA structure, a layered phase has now been obtained, which makes possible increasing the dimensionality of the ferrimagnetic system to 2.

For the compounds described here, the connection between layers through tetrahedral Co(II) ions surely increases the interlayer magnetic coupling. The preparation of a compound such as MCo(CoEDTA)$_2$·4H$_2$O, where M would be a diamagnetic dication with strong inclination to form tetrahedral or pseudotetrahedral complexes, would greatly help in the investigation of this last point by making the solid a genuine two-dimensional magnetic structure. This brings about the broader and more interesting point of the potential crystal engineering that can be done on this three-dimensional polymeric structure. By selectively blocking out magnetic interaction pathways with suitable diamagnetic ions, we predict that either magnetic layers or isolated trimers could be created. For example, Mg(II), Zn(II), and Sn(II) could be good candidates to block interlayer interactions: in the complex SnCo(CoEDTA)$_2$·4H$_2$O, tin would most likely occupy the tetrahedral site. On the other hand, in the complex MgCo(CoEDTA)$_2$·4H$_2$O, Mg(II) ions would be likely to occupy the MO$_6$ centers,[4] and in that case, the compound would consist of parallel magnetic trimers of the type CoN$_2$O$_4$–CoO$_4$–CoN$_2$O$_4$.

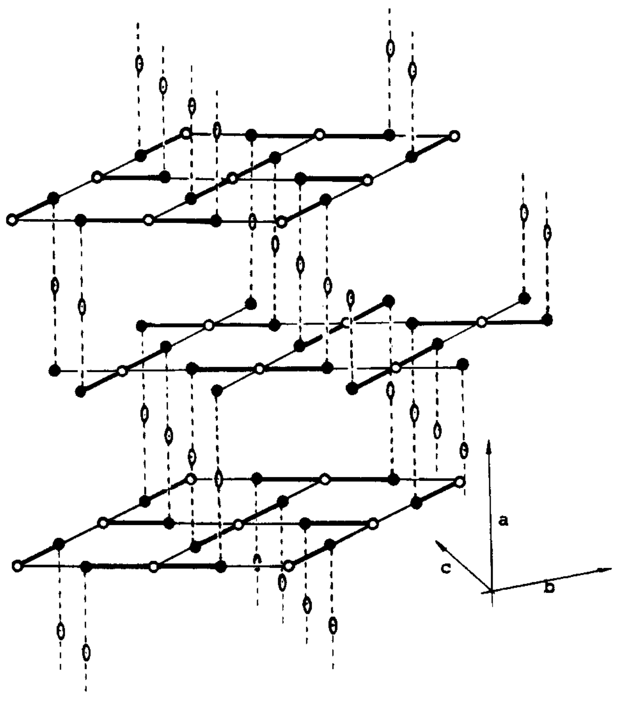

Figure 5. Schematic diagram showing the layers of regularly alternating octahedral sites and their interconnection through tetrahedral centers: (●) M1; (0) M2; (O) M3.

Of course, a limiting condition is that the size and charge of the new metallic ions should be such that the crystal structure is maintained. Mg(II) and Zn(II) meet these requirements, and although Sn(II) is oversized, the crystal structure would probably be maintained since only a change in the *a* axis is required to accommodate this larger ion (see Figure 2).

The variety of sites in the structure, the possibility of "blocking" some of them to constrain magnetic interaction pathways, and the diversity of cations that may be selectively accommodated into the sites, open new possibilities to the design of ordered heterometallic complexes with magnetic interactions of low dimensionality. Furthermore, these complexes would be relevant not only by themselves but also as precursors of easy-to-make mixed oxides (low-temperature preparation) with new compositions and possibly new structures and properties.

Registry No. CoCo(CoEDTA)$_2$·4H$_2$O, 103068-02-6.

Supplementary Material Available: A table of refined anisotropic temperature factors and a stereoview showing a projection along the *a* axis of the two-dimensional puckered network formed by Co1 and Co3 ions (3 pages). Ordering information is given on any current masthead page.

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(18) Drillon, M.; Gianduzzo, J. C.; Georges, R. *Phys. Lett. A* **1983**, *96A*, 413.