mining the total energy change in the molecular mechanics model. This very significant contribution to the total energy of complex formation can be expected to appear as a component of the total energetics of complex formation measured experimentally. However, the attractive term is not part of what is traditionally referred to as the steric property of a ligand. For this reason, it is necessary to employ the results of the molecular mechanics calculations in a different way to extract a quantity that properly reflects the purely steric properties of the ligands. An approach to this goal is described in the following paper in this series.[18]

Acknowledgment. This research was supported by the National Science Foundation through Research Grant NSFCHE89-12273. K.J.L. gratefully acknowledges a University of Illinois Graduate Fellowship (1986–7) and a Department of Education Graduate Fellowship (1989–90). BIOGRAF was made available through an academic grant from Molecular Simulations, Inc. The Stardent Titan computer on which the calculations were carried out was obtained through a University Research Initiative award from the Defense Advanced Research Projects Agency. The crystal structure determination of $Cr(CO)_5PMe_3$ was carried out in the X-ray Diffraction Center of the School of Chemical Sciences by Scott Wilson.

Supplementary Material Available: Tables of crystallographic data, data collection and reduction parameters, information on solution and refinement, atomic positional parameters, and thermal parameters for $Cr(CO)_5PMe_3$, a table of selected bond distances and angles in the energy-minimized structures for the free phosphine ligands, tables of selected bond distances and angles in the energy-minimized structures for $Cr(CO)_5PR_3$ complexes, and figures showing unit cell views for $Cr(CO)_5PMe_3$ (12 pages), a listing of structure factor amplitudes for $Cr(CO)_5PMe_3$ (18 pages).

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Anisotropic Exchange and Dimerization in the Ordered Bimetallic Chains $Co_2(EDTA)\cdot 6H_2O$ and $CoCu(EDTA)\cdot 6H_2O$. Single-Crystal EPR Investigation

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Received May 8, 1991

The bimetallic series $MM'(EDTA)\cdot 6H_2O$ ([MM'] = [MnCo], [MnNi], [MnCu], [CoCo], [CoNi], [CoCu], [NiNi]) comprises zigzag chains built up with alternated "hydrated" and "chelated" sites bridged by carboxylate groups: $...\text{–}M(H_2O)_4O_2\text{---}M'(EDTA)\text{–}M(H_2O)_4O_2\text{---}M'(EDTA)\text{–}...$ The **g** tensors of cobalt(II) on both sublattices are determined from a single-crystal EPR study on Co-doped [ZnZn] samples. On the other hand, a single-crystal EPR study of the bimetallic chain [CoCu] is reported. The angular dependence of the resonance fields are simulated from a triplet spin state with a large zero-field splitting of modulus $|D| \approx 0.3$ cm^{-1}, which is almost parallel to the **g** tensor of cobalt. This result provides some evidence of the presence of cobalt–copper exchange-coupled pairs within the chain, constituting the first spectroscopic proof of dimerization in this chain; furthermore, it emphasizes the anisotropic nature of the exchange, which is in good agreement with the spin anisotropy of cobalt. The factors determining the dimerization of this and other cobalt-containing chains of the EDTA series are discussed.

Introduction

For the past few years much experimental and theoretical effort has been devoted to the properties of one-dimensional (1-D) ferrimagnets, in particular to their static thermodynamic properties (specific heat, magnetic susceptibility, magnetization, etc.).[1–4] In this context, the bimetallic compounds of the EDTA family formulated as $MM'(EDTA)\cdot 6H_2O$ (in short [MM']) provided a remarkable series of magnetic model systems for investigating a great diversity of 1-D ferrimagnets, with many choices in the size and nature (isotropic or anisotropic) of both magnetic moments and exchange interactions.[4–8]

The structure of this series (Figure 1) consists of infinite zigzag chains built up from two alternating octahedral sites bridged by carboxylate groups.[9,10] Further, due to the presence of two different bridging carboxylate topologies, the magnetic centers are also alternating, and so there is alternation not only of the magnetic sites but also of the exchange interactions. Then, the alternating chain may be schematized as

$$...\text{–}M(H_2O)_4O_2\text{---}M'(EDTA)\text{–}M(H_2O)_4O_2\text{---}M'(EDTA)\text{–}...$$

where dashed and full lines refer to the two different exchange pathways, J and J'; $[M(H_2O)_4O_2]$ and $[M'(EDTA)]$ correspond to the hydrated and chelated sites, respectively.

From the analysis of specific heat and susceptibility measurements, significant differences in the degree of exchange alternation have been emphasized, depending on the nature of the interacting ions.[4–7] Thus, while [MnNi] behaves as a uniform chain ($J'/J = 1$), members containing high-spin cobalt(II), as for example [CoCo] and [CoCu], show a drastic alternation, behaving as "quasi"-isolated dimers ($J'/J < 0.01$). This surprising result is difficult to attribute to a structural effect, since intermetallic distances and bridging angles remain almost constant in all the members of the series, so that an orbital effect needs to be invoked. In fact, we suggested that the large alternation of the cobalt-containing chains is likely to be related to the strong anisotropy of this ion. Due to the zigzag structure of chains, the **g** tensor of cobalt on each site would present different orientations with respect to the principal magnetic axes, and two different exchange components are expected, even in the absence of structural alternation.[5,6]

In order to discuss this possibility, the **g** tensors of cobalt on both sublattices are determined from a single-crystal EPR study on a Co-doped [ZnZn] sample. On the other hand, an EPR study of the ordered bimetallic chain [CoCu] is reported. In this system,

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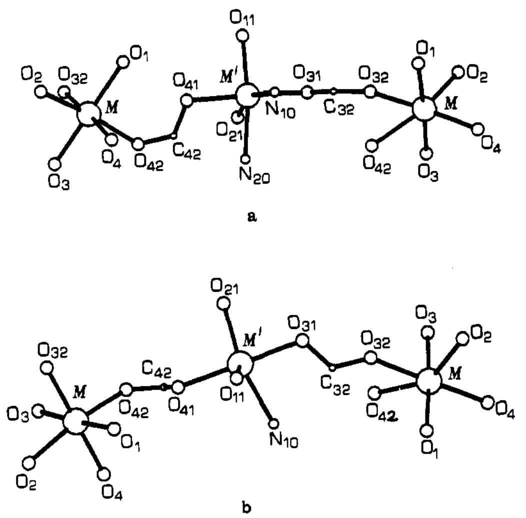

Figure 1. Structure of the series $MM'(EDTA)\cdot 6H_2O$. Views showing the anti–syn (a) and anti–anti (b) configurations of carboxylate bridges alternating along the chain. The numbering of the atoms was taken from ref 10.

EPR provides some information about the anisotropic nature of the exchange as well as about its dimensionality, constituting the first spectroscopic evidence of dimerization in these chains.

Experimental Section

Suitable single crystals for EPR studies were obtained from aqueous solutions containing the tetrasodium salt of the EDTA ligand and the corresponding amounts of the metal nitrates, after addition of acetone until incipient turbidity and slow cooling. The larger ability of EDTA to chelate the Cu^{II} ion with respect to the Co^{II} results in the formation of an ordered bimetallic [CoCu] compound in which Cu^{II} is occupying the chelated site, while Co^{II} is left to occupy the hydrated one.[11] The crystals were oriented with a Nonius CD4 diffractometer. Single-crystal EPR spectra were performed at X-band frequency with a Bruker ER200 spectrometer equipped with an Oxford Instrument ESR9 continuous-flow cryostat.

Results and Discussion

Determination of the g Tensors of Co(II). Taking advantage of the fact that in solution EDTA shows similar abilities for chelating Co^{II} and Zn^{II} ions, we have prepared Co-doped [ZnZn] crystals in which Co^{II} is occupying both sublattices. The powder EPR spectrum at 4.2 K of a sample containing 5% Co is displayed in Figure 2. Comparing this spectrum with that obtained on a Co-doped [MgZn] sample in which Co^{II} selectively occupies the chelated sublattice, it is possible to determine the g components of each sublattice as well as the hyperfine parameters. We obtain $g_\perp = 3.8$ ($A_\perp = 45$ G), and $g_\parallel = 5.79$ ($A_\parallel = 75$ G) for the lowest Kramers doublet of the hydrated cobalt ion, and $g'_3 = 1.23$, $g'_2 = 1.45$, and $g'_1 = 8.0$ ($A_1 = 77$ G), for the chelated one. As expected, the anisotropy of cobalt is larger when it occupies the more distorted chelated position.

A single-crystal of [ZnZn] containing 5% Co has been chosen for the EPR study. This shows well developed 110, $\bar{1}\bar{1}0$, $1\bar{1}0$, and $\bar{1}10$ faces. EPR spectra were recorded rotating the crystal around three orthogonal axes X, Y, and Z, with Z parallel to the crystallographic c axis and X perpendicular to the 110 face. The direction cosines of the laboratory reference frame in the orthorhombic cell are

	a	*b*	*c*
x	0.5567	0.8307	0
y	−0.8307	0.5567	0
z	0	0	1

For an orthorhombic crystal each sublattice gives rise to two magnetically nonequivalent centers in the ab (or XY) plane, becoming equivalent along the a and b axes.[12] When the static magnetic field lies in the XZ and YZ planes, four magnetically nonequivalent centers are expected, two by two equivalent along the X and Y axes. In our case, due to the presence of two magnetic sublattices, the number of nonequivalent magnetic centers duplicates. Despite this complication, the fact that the transition fields of the hydrated cobalt centers show sharp lines, with hyperfine structure, restricted to the central part of the spectra, while those of the chelated sites are observed in a much more extended field range (from 800 to 5500 G), allowing us to follow the angular dependences, shown in Figure 3. We notice that for the chelated sublattice it is straightforward to follow the angular dependence of the signals in the three planes, in particular in the very low- and high-field regions, so that it is possible to obtain a fit of the g tensor using a least-squares procedure. The principal values and directions of the g tensor are reported in Table I.

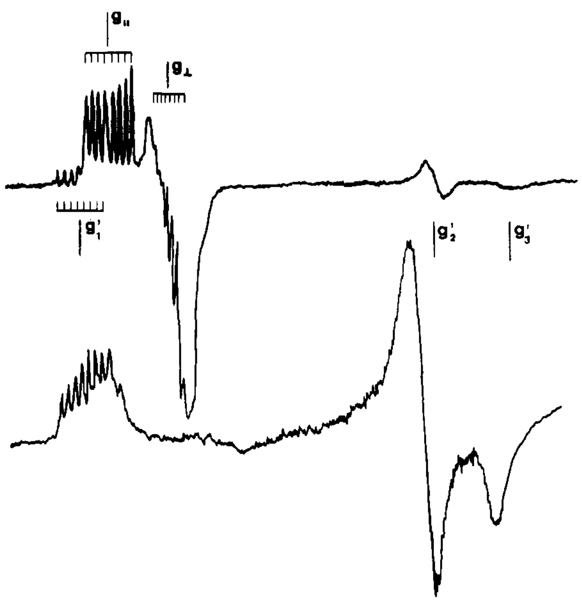

Figure 2. Powder EPR spectra at 4 K in the X-band of Co-doped [Zn-Zn] (top) and [MgZn] (bottom) samples.

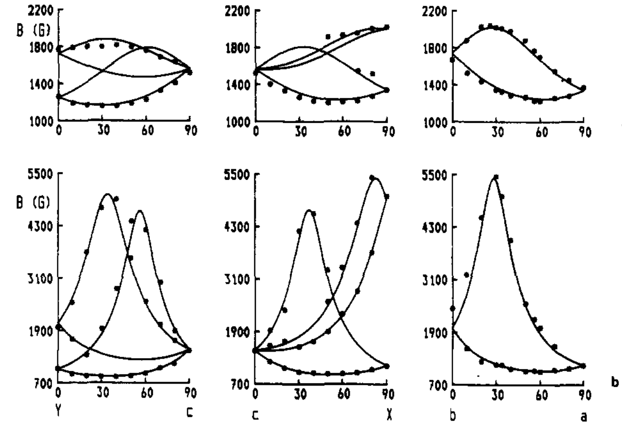

Figure 3. Experimental and calculated angular dependences of the resonance fields of (a) "hydrated" and (b) "chelated" cobalt(II) ions.

In turn, the above procedure is no longer applicable to the hydrated cobalt site since in the intermediate field region the bands of both chromophores largely overlap, making it very difficult to follow the angular dependence of the transition fields in the XZ and YZ planes. In order to fit the experimental data we started from the consideration that in the YZ plane two of the four magnetically non-equivalent sites reach an extreme corresponding to the principal g_3 value of the polycrystalline powder spectrum

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Table I. Calculated Principal *g* Values and Directions for CoCo(EDTA)·6H$_2$O in the Two Sites[a] (See Text)

		Hydrated Site		
g_1	5.80	0.7743	−0.4159	0.4770[b]
g_2	3.76	0.3907	−0.2788	−0.8773
g_3	3.33	0.4978	0.8656	0.4770
		Chelated Site		
g'_1	7.93	−0.0729	0.8273	0.5570
g'_2	1.25	0.0528	−0.5544	0.8305
g'_3	1.14	−0.9960	−0.0906	0.0042

[a] The directions for one of the four magnetically nonequivalent centers of the unit cell are given as the direction consines in the laboratory reference frame *XYZ*. The directions for the other centers are calculated according to the symmetry requirements. [b] The reported values and directions are those used to calculate the curves reported in Figure 3.

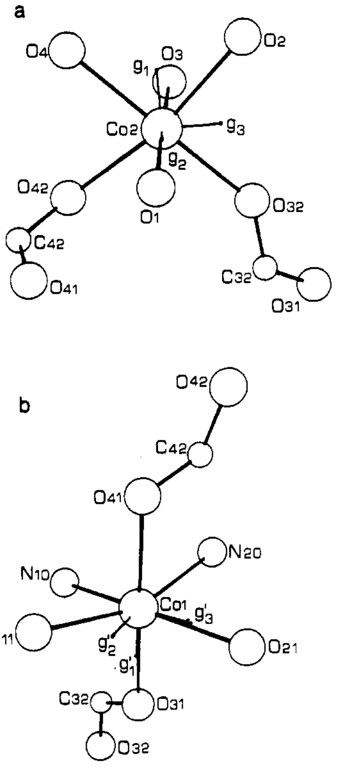

Figure 4. Principal directions of the **g** tensor of (a) "hydrated" and (b) "chelated" cobalt(II) ions in the molecular framework.

at 30 ± 5° and 120 ± 5° from *Y*, respectively. On the other hand in the *XY* (*ab*) plane the principal g_1 values are found at 10 ± 5° and 100 ± 5° from the *X* axis, respectively. These directions nicely correspond with the bisectors of the O$_2$–Co–O$_{32}$ and O$_2$–Co–O$_4$ angles (see Figure 4). The third principal direction of **g**, namely g_2, must be perpendicular to the mean plane Co–O$_2$–O$_4$–O$_{42}$–O$_{32}$ (see Figure 4). The principal directions of the **g** tensors for the other two magnetically nonequivalent centers are calculated according to the symmetry requirements, and the angular dependence of the transition fields is obtained using the **g** tensors of the four sites, which are nondiagonal in the *XYZ* reference frame. The best result is showed as a solid line in Figure 3. The principal values and directions of the **g** tensor are summarized in Table I.

The [CoCu] Compound. In [CoCu] the cobalt(II) ion occupies the hydrated position, and copper(II), the chelated one. The EPR spectra at 4.2 K has been recorded on a single crystal having a morphology similar to that reported in the previous section for the Co-doped [ZnZn] compound. Very broad and featureless bands are observed for all the orientations of the static magnetic field, so that it is extremely difficult to analyze the spectra, and only in the *ab* plane has it been possible to try. In this plane as many as three signals may be distinguished (Figures 5 and 6).

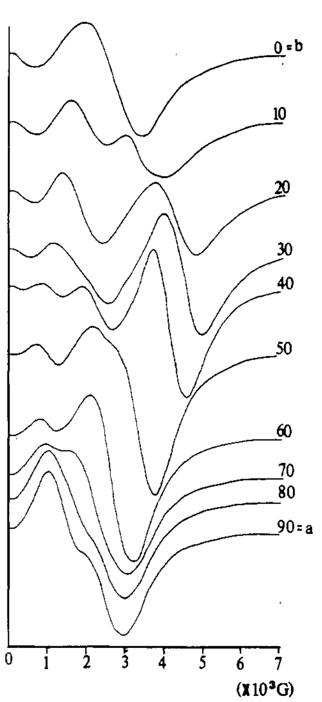

Figure 5. Single-crystal EPR spectra at 4 K in X-band of [CoCu] in the *ab* plane.

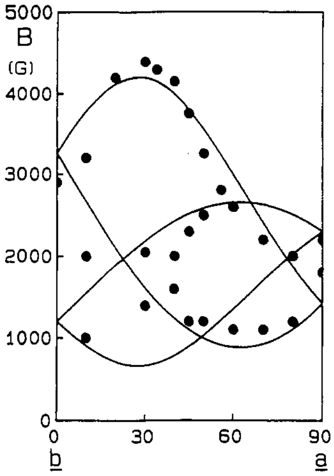

Figure 6. Experimental and calculated angular dependences of the resonance fields of [CoCu] in the *ab* plane.

On the other hand, a broadening of the bands is observed when the temperature is increased, and above 60 K no spectra is observed. This result can be attributed to the relaxation properties of the cobalt(II) and rules out the possibility of having isolated impurities of copper(II).

A possible rationalization of the results in the *ab* plane is to consider the EPR spectra as due to a triplet state characterized by a Landé tensor, $\mathbf{g}_p$, and a zero-field-splitting tensor **D**. Owing to the limited number of experimental data, it has not been possible to obtain a fit of these tensors. Anyway, since such a triplet arises from the coupling between the quasi-isotropic Kramers doublet of copper(II) and the anisotropic lowest Kramers doublet of cobalt(II), one may assume that the directions of $\mathbf{g}_p$ and **D** are mainly determined by the cobalt ion. In agreement with this assumption is the fact that the extreme transition fields around 30° and 60° from *b* (see Figure 5), which are very close to those observed in the hydrated cobalt spectra, are observed. The separation between these two extreme fields is around 3000 G, which suggests a value of $|D|$ of ca. 0.3 cm^{-1}. In fact, a reasonable agreement with the experimental data may be obtained by taking for copper(II) an averaged isotropic *g* value of 2.1 and for cobalt(II) the experimental values reported in Table I (solid lines of Figure 6). A **D**

Table II. Calculated Principal Values and Directions of **g** and **D** for $CoCu(EDTA)\cdot 6H_2O$[a]

g_1	3.95	0.7743	−0.4159	0.4770[b]
g_2	2.79	0.3907	−0.2788	−0.8773
g_3	2.71	0.4978	0.8656	0.4770
D_{xx}	−0.20	0.6947	−0.3611	0.6221
D_{yy}	0.05	0.5192	−0.3468	−0.7811
D_{zz}	0.15	0.4978	0.8656	−0.0534

[a] The principal directions of **g** and **D** tensors are given in the reference frame *XYZ* for one of the four magnetically nonequivalent centers. The **g** tensor of the pair ($\mathbf{g}_p$) has been obtained by assuming that $\mathbf{g}_p = {}^1/_2(g_{Co} + g_{Cu})$. The directions for the other centers are calculated according to the symmetry requirements. [b] The reported values and directions are those used to calculate the curves reported in Figure 6.

tensor almost parallel to $\mathbf{g}_p$ with components $D_{zz} = -0.2$ cm^{-1}, $D_{xx} = 0.05$ cm^{-1}, and $D_{yy} = 0.15$ cm^{-1} results. The principal values and directions of $\mathbf{g}_p$ and **D** are summarized in Table II. Taking into account that $D = {}^3/_2 D_{zz}$ and $E = {}^1/_2(D_{xx} - D_{yy})$, we obtain $|D| = 0.3$ cm^{-1} and $|E| = 0.05$ cm^{-1}. With these values we notice that, in the *XZ* and *YZ* planes, the transition fields are largely indeterminate because of overlapping. That accounts for the large broadening of the bands observed in these planes (with line widths of about 2000 G).

Discussion

The EPR spectra of [CoCu] support the presence of cobalt(II)–copper(II) exchange coupled pairs within the chain. This exchange interaction is actually between the $^4T_1$ state of cobalt(II) and the spin doublet of copper(II). However, the combined effect of spin–orbit coupling and local distortion splits up the $^4T_1$ state of cobalt(II) into six Kramers doublets in such a way that the lowest doublet is separated in energy from the first excited state by at least 100 cm^{-1}. Hence, as long as the exchange interaction is weak compared with this splitting, the exchange pattern of the low-lying levels is determined by the interaction between the effective spin $S = {}^1/_2$ of cobalt(II), which may be strongly anisotropic, and the spin doublet of copper(II). Bulk magnetic properties (susceptibility and specific heat) of [CoCu] have shown[5] that the cobalt–copper pairs are very weakly coupled ($J_\parallel = -3.1$ cm^{-1}), justifying the above assumption.

Most of the works devoted to exchange-coupled pairs of spins $^1/_2$ were restricted to dimers of copper(II)[2,13,14] and to the study of organic biradicals.[15] The zero-field Hamiltonian adequate to describe the interaction within these pairs may be written as

$$\mathcal{H} = -J S_1 \cdot S_2 - S_1 \cdot \mathbf{D} \cdot S_2 \tag{1}$$

where J is a scalar which represents the isotropic part of the exchange interaction, while **D** is a traceless tensor describing the anisotropic contribution. Its effect is to split the triplet state. In this expression the antisymmetric exchange interaction has been neglected. It can be readily shown[16] that when $D_{xx} = D_{yy}$, this Hamiltonian is equivalent to the well-known uniaxially symmetric Hamiltonian used in magnetism

$$\mathcal{H} = -J_\parallel S_{1z} \cdot S_{2z} - J_\perp (S_{1x} \cdot S_{2x} + S_{1y} \cdot S_{2y}) \tag{2}$$

where now the exchange anisotropy is accounted for by considering two effective exchange interactions, $J_\parallel$ and $J_\perp$. Thus, these exchange components can be related to the parameters J and D of (1) through the following expressions:

$$J_\parallel = J + D_{zz} \tag{3}$$

$$J_\perp = J - D_{zz}/2 \tag{4}$$

where an uniaxial **D** tensor ($D_{yy} = D_{xx}$) has been assumed. On the other hand, $J_\parallel$ and $J_\perp$ can be related to the isotropic exchange by:[16]

$$J_{\mathrm{i}} = (g_{\mathrm{i}1}/2)(g_{\mathrm{i}2}/2) \cdot J \qquad \mathrm{i} = \parallel, \perp \tag{5}$$

From this expression one obtains a useful relation between the amount of exchange anisotropy, $J_\perp/J_\parallel$, and the anisotropies in the **g** tensors of the interacting ions:

$$\frac{J_\perp}{J_\parallel} = \frac{g_{\perp 1} g_{\perp 2}}{g_{\parallel 1} g_{\parallel 2}} \tag{6}$$

Notice that (6) has been derived by assuming that the **g** tensors of both sublattices are parallel. If this condition is not fulfilled it can only provide a rough indication about the exchange-anisotropy.

In the copper pairs the interacting ions have no first-order angular momentum, so that the anisotropic part of the exchange remains always considerably smaller than the isotropic part[12] (on the order of 10^{-2} J). In fact, the anisotropic part arises from spin–orbit coupling and may have a magnitude of order $|D| = (\Delta g/g)^2 J$, where Δg describes the orbital contribution to the **g** tensor.[14]

The problem is different in the [CoCu] case since the cobalt(II) ion is orbitally degenerate. Then, the orbital contribution becomes much stronger, and hence the anisotropic exchange term may be of the same order of magnitude as the isotropic one. A value of D_{zz} about -0.2 cm^{-1} has been obtained from the above analysis of the EPR data. From this value, using (3) and (4), we can estimate the amount of exchange anisotropy. Thus, taking $J_\parallel = -3.1$ cm^{-1} (obtained from bulk magnetic properties), we obtain $J_\perp/J_\parallel = 0.7$, which fully agrees with the value estimated from (6). Notice that from the analysis of the magnetic specific heat a value of $J_\perp/J_\parallel = 0.35$ has been calculated.[5] Such a discrepancy between spectroscopic and thermodynamic data may be attributed to the presence of ca. 1% per cent of cobalt in the chelated position. This lack of selectivity is expected to affect the C_p measurements, but not the EPR spectra.

In the case of homometallic [CoCo] the discrepancy between spectroscopic and thermodynamic results is less pronounced; we obtain values of $J_\perp/J_\parallel \approx 0.12$ (from the **g** tensors of Co's) and 0.22 (from C_p data),[5] which, as expected, support a larger amount of exchange anisotropy in that case.

The last point deserving a discussion concerns the dimerization in this family of bimetallic chains. The magnetic and thermal properties have indicated[5–7] that the degree of J alternation varies in the order [NiNi] ≈ [MnNi] < [MnCu] < [MnCo] ≪ [CoNi] < [CoCu] ≈ [CoCo]. Then, while [NiNi] and [MnNi] behave as uniform chains, [CoNi], [CoCu], and [CoCo] show a large dimerization, behaving as quasi-isolated dimers. In view of the structural features of the chains a source of J alternation may come from the presence of anti–anti and anti–syn carboxylate configurations, alternating along the chain (Figure 1). In this respect, it has been suggested[17] that the anti–anti configuration is more favorable for the transmission of the exchange interaction than the anti–syn one. However, in the EDTA family the exchange interaction always remains weak, so that the influence of this structural factor is difficult to evaluate. In fact, bimetallic dimers of the EDTA family are known in which the exchange values are close to, or even larger than, those reported in the bimetallic chains, despite the fact that the coordination of the carboxylate bridge is in between anti–anti and anti–syn.[18] Other factors are then required in order to understand the drastic alternation of cobalt-containing chains.

When both interacting ions are appreciably anisotropic, as for example in [CoCo], the different relative orientation of two adjacent **g** tensors could participate in the J-alternation effect. Thus, in [CoCo] the chelated Ising-type cobalt ion establishes a pref-

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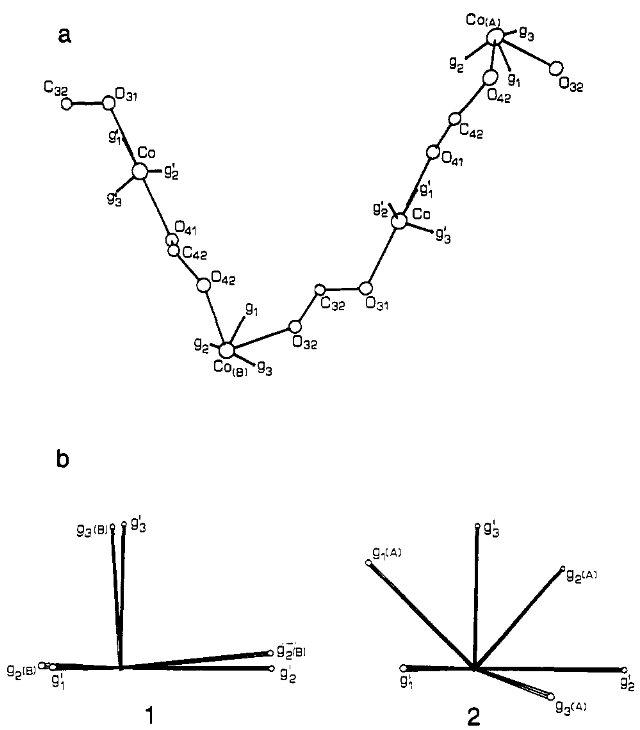

Figure 7. (a) Relative orientation of the g tensors of the cobalt(II) ions along the zigzag chain. (b) Comparison between the g tensor of the chelated cobalt(II) with those associated to the two hydrated neighbors: (a) Co_A and (2) Co_B (see Figure 4).

erence for the moments to align along the z axis (i.e. along the g'_3 direction). As far as the tensors of two consecutive hydrated cobalt ions (namely Co_A and Co_B in Figure 7a) have different orientations with respect to the tensor of the chelated cobalt, the two effective couplings along this direction (namely $J_\parallel$ and $J'_\parallel$) are expected to be different. In this respect, we observe that the g tensor of Co_A is, within experimental error, parallel to the g tensor of the chelated site, while the g tensor of Co_B is fully misaligned, with g_{3B} almost orthogonal to g'_{3B} (see Figure 7b). A simple estimate of the ratio $J'_\parallel/J_\parallel$ may be obtained examining the relative orientation of the moments associated to Co_A and Co_B, which are along the g_3 directions, with respect to g'_3. We obtain

$$\frac{J'_\parallel}{J_\parallel} = \frac{\cos\theta_B}{\cos\theta_A} \qquad (7)$$

where θ_A (θ_B) refers to the angle between g'_3 and g_{3A} (g_{3B}). From Table I we calculate $\theta_A = 5°$ and $\theta_B = 82°$, and finally $J'_\parallel/J_\parallel \approx 0.1$. Notice that the structural factor pointed out above may reinforce this alternation since the largest exchange pathway ($J_\parallel$) involves at the same time the anti–anti configuration (see Figure 7a).

The strong dimerization observed in [CoCu] is more difficult to understand from the above arguments since copper(II) shows a small spin anisotropy. Anyway, an orbital reason may be still invoked in that case owing to the large orbital anisotropy of both ions. A detailed orbital study including the bridging carboxylate configurations should be now required in order to conclude this point.

Acknowledgment. This work was supported by the Comisiôn Interministerial de Ciencia y Tecnologia (Grant MAT89-177), and by the Italo-Spanish Integrated Action Number 41 and 27A. J.J.B.-A. thanks the Ministero de Educaciôn y Ciencia for a fellowship. The financial support of the Italian Ministry of Public Education and the CNR are gratefully acknowledged.

Registry No. $Co_2(EDTA)\cdot 6H_2O$, 84222-22-0; $CoCu(EDTA)\cdot 6H_2O$, 84222-24-2.

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Temperature- and Axial-Ligand-Dependent EPR Spectra of Cobalt Porphyrin Cation Radicals: Effects of Mixing of the A_{1u} and A_{2u} States and a Locally Excited Triplet State

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Received October 10, 1990

The ground electronic states of cobalt tetraphenylporphyrin and octaethylporphyrin cation radicals ($Co^{III}TPP^{\bullet+}$, $Co^{III}OEP^{\bullet+}$) were reexamined by EPR spectroscopy. They are not purely an A_{1u} or A_{2u} state (nomenclature in D_{4h} symmetry), but they contain A_{1u} and A_{2u} components, respectively. The contribution of the A_{2u} state increases with increasing axial-ligand field. Equilibria were found between species having different axial-ligand interactions in solution. At low temperatures, the species having weaker axial-ligand interactions and having less A_{2u} character are dominant. The marked line width broadening observed for the EPR spectra of $Co^{III}OEP^{\bullet+}$ complexes ligated by Br^-, Cl^-, and CN^- was explained by the effect of mixing of a locally excited triplet state. Such mixing is less important for $Co^{III}TPP^{\bullet+}$ complexes having an A_{2u} dominant ground state.

Introduction

There have been extensive studies on the oxidation states of metalloporphyrins from biological and biochemical standpoints, as well as a physicochemical one in porphyrin chemistry. The oxidation of metalloporphyrins occurs at either the central metal or the porphyrin ring, or at the both locations. It is well-known that there are two types of ground states, A_{1u} and A_{2u}, in porphyrin cations. The cation radicals of cobalt tetraphenylporphyrin (($Co^{III}TPP^{\bullet+}$)(X^-)$_2$, X^- = axial ligands) have been assigned the A_{2u} ground state,[1] and no contradictory assignment has been reported. However, for the electronic state of the cobalt octaethylporphyrin cation radicals (($Co^{III}OEP^{\bullet+}$)(X^-)$_2$) assignments different from those originally given have been reported.

According to the UV–visible spectral criterion, ($Co^{III}OEP^{\bullet+}$)(ClO_4^-)$_2$ was initially assigned the A_{2u} state, while when the counteranion ClO_4^- in ($Co^{III}OEP^{\bullet+}$)(ClO_4^-)$_2$ was re-

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0020-1669/92/1331-0298$03.00/0 © 1992 American Chemical Society