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Random-Exchange-Coupled Chain in the Amorphous Complex $Co_2(EDTA)\cdot 6H_2O$: Comparison with the Crystallized Complex

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Received December 8, 1983

The compound $Co_2(EDTA)\cdot 6H_2O$ was isolated and characterized in crystallized and amorphous states. In the former, the system may be viewed as regular chains with alternating "hydrated" and "chelated" Co(II) sites. As shown by large-angle X-ray scattering investigation, the only noteworthy difference in the amorphous state is the random distribution of bond angles between nearest neighbors within the chains. EPR measurements on polycrystalline samples led to $g_a = 4.5$ and $g_b = 4.23$ for the "hydrated" and "chelated" Co(II) sites, respectively. The magnetic behaviors, recorded in the range 2–100 K, confirm the structural assignments. The crystallized complex is shown to be well described, below $T = 20$ K, by a $S = {}^1/_2$ chain model with an exchange coupling ranging from $J = -3.7$ K (Heisenberg) to $J = -5.6$ K (Ising). The behavior of the amorphous complex somewhat differs, since it follows the law $\chi = AT^{-\alpha}$, which is typical of random-exchange Heisenberg antiferromagnetic chains. Such a variation agrees with a classical spin 1D system involving a J distribution.

Introduction

In the last few years, numerous works have been devoted to the thermodynamic behavior of disordered systems. Among these, the random-exchange magnetic chains[1] (1-D systems characterized by a random distribution of the exchange coupling) have been shown to provide the most significant features when the correlations between properties and the amount of structural disorder are studied. The systems reported so far concern highly conducting charge-transfer complexes generally based on the TCNQ molecule as acceptor[2] or polymetal phosphinate complexes.[3]

This paper deals with the synthesis and magnetic behavior of a novel random-exchange chain isolated in the amorphous $Co_2(EDTA)\cdot 6H_2O$ complex (abbreviated as [CoCo]). The properties will be compared to those of the crystallized complex, equally synthesized, making this study of particular interest. These materials belong to a series formulated as $MM'(EDTA)\cdot 6H_2O$ (with M, M′ = Mg, Mn, Co, Ni, Cu, Zn), previously characterized as the first example of a one-dimensional ferrimagnetic system.[4–6]

In the crystallized state, the structural organization determined by McCandlish et al.[7] consists of infinite zigzag chains with an alternation between two distinct octahedral positions for the Co(II) ions: one, denoted as "hydrated" (Figure 1a), where the Co(II) ion is surrounded by four water molecules and two oxygen atoms belonging to carboxylate functions of the EDTA ligand, and another, denoted as "chelated" (Figure 1b), exhibiting hexacoordination through the EDTA.

Owing to these distinct environments, the [CoCo] complex can be described as isolated regular chains with alternating g_a and g_b Landé factors:

$$-\underset{g_a}{Co(H_2O)_4}-\underset{g_b}{Co'(EDTA)}-\underset{g_a}{Co(H_2O)_4}-$$

The local structure of the amorphous material, investigated by large-angle X-ray scattering (LAXS),[8] is nearly the same with both coordination schemes of the transition ions and chain groups conserved. The only significant feature is the existence of a ∠MM′M angle distribution within chains. So, the amorphous complex can be viewed as made of flexible chains in contrast with the crystallized complex. The aim of the present paper will be to show how this slight structural alteration brings about a divergence of the magnetic behaviors.

Experimental Section

Synthesis. I. Crystallized Samples. These were prepared by a previously described procedure.[9] Anal. Calcd for $Co_2(N_2O_8C_{10}H_{12})(H_2O)_6$: Co, 22.93; N, 5.45; C, 23.36; H, 4.70. Found: Co, 22.4; N, 5.3; C, 23.6; H, 4.6.

II. Amorphous Samples. A 1.45-g (4.98-mmol) amount of $(NO_3)_2Co\cdot 6H_2O$ and 0.94 g (2.45 mmol) of $(EDTA)Na_4$ were dissolved separately in the minimum quantity of water. Both solutions were then mixed and filtered. The amorphous phase is isolated by adding to the solution an excess of acetone or ethanol. In the presence of acetone, a slimy solid is obtained (A), while ethanol gives a copious precipitate (B). Solid A separated by decantation and dried in air appears in the form of red flakes. Solid B separated by filtration and dried in air is metastable, leading to solid A in the presence of moisture. Anal. Found for $Co_2(N_2O_8C_{10}H_{12})(H_2O)_6$: Co, 21.1; N, 5.5; C, 22.2; H, 4.3.

The above method constitutes a general synthetic procedure for $MM'(EDTA)\cdot 6H_2O$ complexes in the amorphous state.

Physical Measurements. EPR measurements were recorded on a Bruker ER 200D X-band spectrometer.

Magnetic measurements were performed in the temperature range 2–100 K with a pendulum-type magnetometer. The susceptibilities were corrected for the diamagnetism of the constituent atoms (estimated to be 173×10^{-6} emu·mol^{-1}). The data are given with an uncertainty of 0.1 K for temperatures and 2×10^{-5} emu·mol^{-1} for susceptibilities.

Results

In the bimetallic complexes, the dominant factor that controls the selectivity of occupation in the two environments is the tendency to form, in solution, the $[MY]^{2-}$ complex anion (where Y^{4-} is the EDTA anion). These materials correspond to ordered bimetallic chains when the constants of formation of $[MY]^{2-}$ are very different for the two metal ions M and M′.[4,9,10] So, we show that, in the [MgCo] complex, the Co(II) ion occupies the chelated position, whereas in [CoNi], it occupies the hydrated one. Assuming an insignificant variation of the local environment in all complexes, we are thus able

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(1) See, for instance: (a) J. Bernasconi and T. Schneider, Eds., *Springer Ser. Solid-State Sci.*, **23** (1981) (Part VI); (b) Z. G. Soos and S. R. Bondeson, in "Extended Linear Chain Compounds", Vol. 3, J. S. Miller, Ed., Plenum Press, New York and London, 1983.

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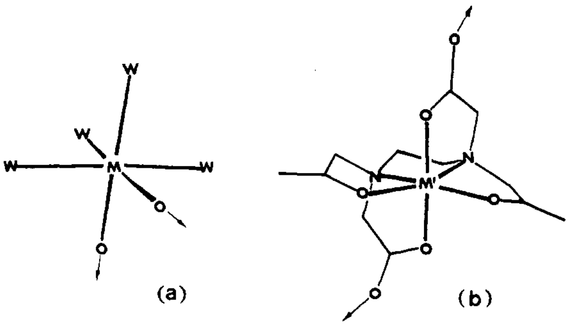

Figure 1. Metal ion environments in the crystallized MM'-(EDTA)·$6H_2O$ complexes: (a) "hydrated" site; (b) "chelated" site.

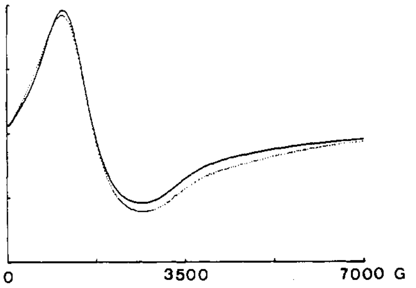

Figure 2. EPR spectra of [CoCo] (dashed line) and [CoNi] (solid line) amorphous complexes.

to determine Landé factors of the Co(II) ion on each site.

In describing the magnetic properties, we have to bear in mind that the high-spin Co(II) ion in an octahedral field behaves, at very low temperatures, as an effective spin $S = {}^1/_2$ system (instead of $S = {}^3/_2$ as given by the three unpaired electrons). This results from the combination of crystal field distortion and spin–orbit coupling effects, which split the $^4T_{1g}$ ground term into six Kramers doublets, causing the ground state to be described as a spin doublet.[11] Using the data of UV–visible spectra, we show that the first excited levels are located around 310 ± 20 cm^{-1}, so that they are not thermally accessible below ca. 20–25 K. Then, the Landé factor determined in the ground doublet is expected to be $g \simeq 4.30$–4.50.[12]

From these results, we assume in the following that at low enough temperatures ($T < 20$ K), the system is well described by an effective spin $S = {}^1/_2$.

1. EPR Measurements. EPR spectra were recorded at liquid-helium temperature on polycrystalline [MgCo] and [CoNi] samples. The former exhibits an axial spectrum with $g_\parallel = 9.85$ and $g_\perp = 1.42$ ($g_b = 4.23$), as currently observed in distorted-octahedral systems.[13] An estimate of g components is not so easy in the [CoNi] complex because of the presence of paramagnetic Ni(II) ions, which interact antiferromagnetically with Co(II) neighbors. Owing to the magnitude of this interaction, which is less than 5 K,[14] we can assume nearly independent g values for both ions. A rough estimate of g is then deduced for Co(II) in the hydrated position ($g_a \simeq 4.5$).

These results are consistent with the expected g values in an octahedral environment and indicate a large distortion of the "chelated" site in agreement with structural findings. The influence of the distortion on g components was recently reported by Banci et al.[13] From this calculation a large and positive D parameter and a non-zero E value corresponding to a slight rhombic distortion are brought out but subsequent studies on single crystals are yet required for a quantitative estimate.

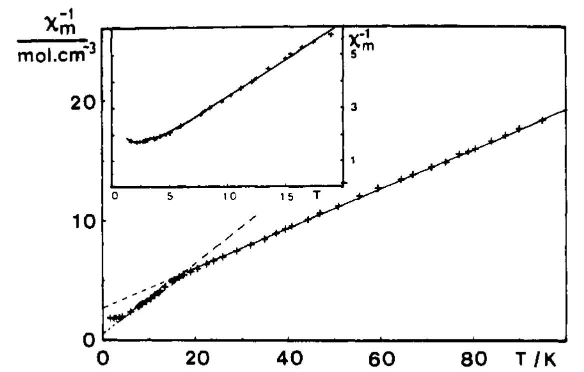

Figure 3. Plot of the magnetic behavior of the [CoCo] crystallized complex showing the change of slope of $\chi_m^{-1} = f(T)$ around 20 K.

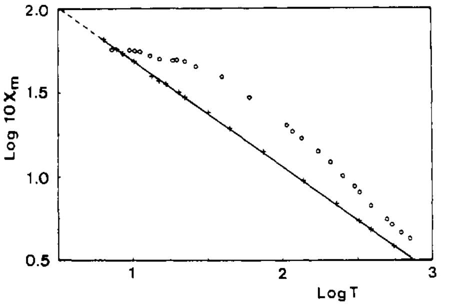

Figure 4. Low-temperature behaviors ($T < 20$ K) of crystallized (○) and amorphous (+) [CoCo] complexes. The observed variation for the latter is typical of a REHAC system.

Let us now compare EPR spectra recorded on amorphous [CoCo] and [CoNi] samples (Figure 2). The main features are (i) their great similarity although one of them contains two distinct paramagnetic ions and (ii) the broadening of the signal, in contrast with crystallized complexes, which prevents an accurate g-value determination. The reasons to be invoked are a shorter relaxation time, a random distortion of the sites, and the effect of a distribution of magnetic interactions. This will be discussed later on.

2. Magnetic Susceptibility. The magnetic susceptibility of the crystallized [CoCo] complex is reported in the range 2–100 K as $\chi_m^{-1} = f(T)$ (Figure 3).

Curie–Weiss behavior is observed above $T = 20$ K corresponding to $C = 3.02$ and $\theta = -16$ K. Below this temperature, a change of slope arises ($C = 1.7$, $\theta = -2$ K), which results from the splitting of the $^4T_{1g}$ ground term as pointed out above; the low-lying Kramers doublet being the single populated level, the system may be described, according to the structure, in terms of a $S = {}^1/_2$ linear chain below $T = 20$ K. Obviously, such a procedure becomes irrelevant at higher temperatures since, due to the thermal occupation of the upper levels, we can no longer ignore the orbital contributions. Then, the exchange coupling is shown to involve both orbital and spin components,[15–18] making the problem intractable in the whole temperature range. The rounded minimum of $\chi_m^{-1} = f(T)$ located around 2.5 K (see the inset to Figure 3) confirms the presence of weak antiferromagnetic interactions in a 1-D system just as was found for the corresponding Ni(II) complex.[4]

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Table I. Magnetic Results

compd	g	J, K	J_c,[a] K	λ, K	λ_c,[a] K	R[b]	model
[CoCo] crystallized	4.40	−3.70	−1.33			1.5×10^{-4}	quantum (Heisenberg)
	4.37	−5.56	−2.00			1.8×10^{-4}	quantum (Ising)
	4.54	−5.27	−1.89	$<10^{-4}$		1.9×10^{-3}	classical
[CoCo] amorphous	4.28, 4.76	−10.47	−3.77	17.70	6.37	0.9×10^{-4}	classical

[a] J_c and λ_c are the corrected exchange and disorder parameters (from the effective J and λ parameters: $J_c\ (\lambda_c) = {}^9/_{25}J\ (\lambda)$). [b] R is the agreement criterion defined as the sum of the squares of the relative deviations.

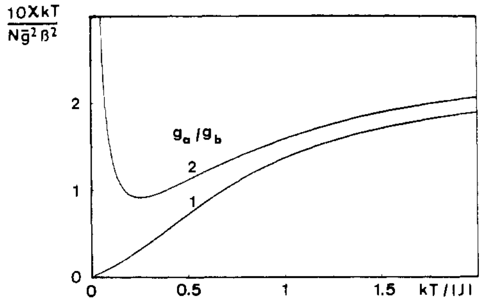

Figure 5. Influence of a g_a/g_b alternation in the $S = {}^1/_2$ Heisenberg chain. $\bar{g}$ is defined in the text.

A somewhat different behavior is obtained with the amorphous material. In particular, the low-temperature variation reported in Figure 4 agrees with the law $\chi = AT^{-\alpha}$ (with $A = 1.03$ emu·mol^{-1} and $\alpha = 0.64$), which characterizes random-exchange Heisenberg antiferromagnetic chains (REHAC).[19] Notice that, in all random systems, the exponent α is usually found to vary in the range 0.6–0.9. The behavior of the crystallized complex, drawn on the same graph for comparison, cannot be described in the same way by a power law. This result clearly indicates that disorder effects play a special role at low temperatures and, consequently, they cannot be neglected in theoretical analysis.

Analysis and Discussion

1. The Crystallized Complex. According to the previous remarks, we assumed, in a first step, a $S = {}^1/_2$ Heisenberg chain made of two g sublattices, namely g_a and g_b. Considering a finite closed chain of $2N$ spins, the Hamiltonian to be solved is given by

$$\mathcal{H} = -J\sum_{i=1}^{2N}\vec{S}_i\vec{S}_{i+1} + \left(g_a\sum_{i=1}^{N}\vec{S}_{2i-1} + g_b\sum_{i=1}^{N}\vec{S}_{2i}\right)\beta\vec{H} \quad (1)$$

where a negative J value refers to an antiferromagnetic coupling and cyclic boundary conditions impose $\vec{S}_{2N+1} = \vec{S}_1$. As previously shown in similar treatments, a very significant reduction of the computational work is obtained by taking into account the geometrical and spin space symmetries of the $2N$-site closed chain.[20,21] The computations, performed on finite rings of increasing size, were limited to $N = 6$ because of the size of the matrices to be diagonalized (the largest being 52 × 52) and the required computing times. The results of the extrapolation to $N \to \infty$, reported in Figure 5 (for $g_a/g_b = 1, 2$), were obtained from the expression

$$\chi_\infty T = \chi_N T + a/N^\alpha \quad (2)$$

where a and α are coefficients depending on kT/J.

When $g_a = g_b$, the curve corresponds to a $S = {}^1/_2$ uniform chain, first solved by Bonner and Fisher;[20] χT (in reduced units) decreases regularly as the temperature is lowered. The g alternation results in a drastic variation of the χT product, which shows a minimum and, then, diverges as $T \to 0$ K. This behavior is to be attributed to second-order Zeeman contributions which arise from mixing between Bloch states characterized by the same S^z whereas the S's differ by unity. This effect is all the more pronounced as the g_a/g_b ratio is increased. It may be noticed that the variation is totally similar to that of alternating spin chains $(S_a - S_b)_N$ previously investigated by the same procedure.[21]

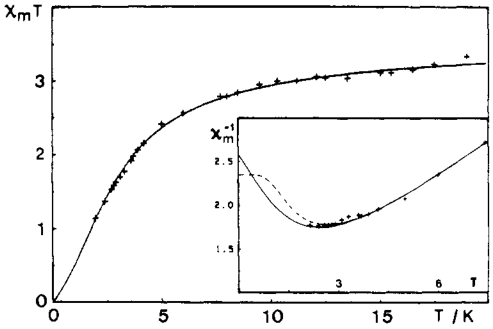

Figure 6. $\chi_m T = f(T)$ curve for the crystallized [CoCo] complex. The solid line is the result of the fit from the $S = {}^1/_2$ Heisenberg chain model. The comparison with the Ising model (dashed line) is reported in the inset as $\chi_m^{-1} = f(T)$.

In the system under consideration, the g_a/g_b ratio determined by EPR is close to unity ($\simeq 1.06$) so that the above result fails in the temperature range of interest. Then, the atomic susceptibility of the chain may to a good degree of approximation be expressed as[22]

$$\chi = \frac{3\bar{g}^2}{8kT}\,\frac{0.25 + 0.14995x + 0.30094x^2}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3} \quad (3)$$

where $x = |J|/2kT$, $\bar{g}^2$ stands for ${}^1/_2(g_a{}^2 + g_b{}^2)$, and J is the exchange constant.

With use of this expression, a good agreement with experiment is obtained in the range 2–20 K for an exchange constant $J = -3.70$ K and a mean Landé factor $\bar{g} = 4.40$ (see Figure 6 and Table I).

From EPR results, indicative of a high anisotropy of the "chelated" site ($g_\parallel = 9.85$ and $g_\perp = 1.42$), it may be emphasized that the Co(II) ion is a better candidate for an Ising model. Recently, we have solved the 1-D Ising system with alternating g_a and g_b factors by means of a transfer matrix method.[23] However, the results being only available for an applied field parallel to the Ising axis, we have used in the present case the exact solutions of the uniform chain as expanded by Fisher[24] and Katsura,[25] namely

$$\begin{aligned}\chi_\parallel &= \frac{N\bar{g}^2\beta^2}{4kT}\exp(2x)\\ \chi_\perp &= \frac{N\bar{g}^2\beta^2}{8kT}(|x|^{-1}\tanh|x| + \operatorname{sech}^2 x)\end{aligned} \quad (4)$$

with $x = J/4kT$. In the studied temperature range, this model

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[19] See W. C. Clark, ref 1a, p 289; J. E. Hirsch and J. V. Jose, ref 1a, p 302.

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leads equally to a satisfying description of the magnetic behavior (Figure 6), yielding the values of the parameters listed in Table I.

Notice that, down to 2 K, the Heisenberg and Ising models give the same agreement with experiment so that further investigations at lower temperatures are required to conclude. Examination of the parameters reveals that $\bar{g}$ factors deduced from both models agree with the findings of EPR and UV–visible spectra.

2. The Amorphous Complex. The power law variation of the amorphous [CoCo] is usually recognized as being the signature of a REHAC system.[19] According to the structure investigated by the LAXS technique, the problem can be solved by assuming a random exchange coupling between nearest neighbors within flexible chains of infinite length. Nevertheless, Bondeson and Soos[26] have recently proved that the same variation is obtained from weakly interacting random segments involving only two energies, J and ϵJ, namely the intra- and intersegment exchange constants.

We discuss now these two models.

Random Exchange Model. Consider, at first, a random exchange interaction within infinite chains. Several theoretical works have appeared using renormalization schemes, but they are not always available for real systems. The most significant result to be pointed out is that REHAC systems show a quasi-universal thermodynamic behavior independent of the nature of the J distribution.[27,28] In the system under consideration, both randomly occurring interactions and g_a/g_b alternation play a special role at low temperatures. Consequently, a classical spin treatment appears to be convenient though it is generally carried out for large spin systems.[6] This severe approximation will be discussed in the concluding remarks.

Assuming a square distribution of the exchange interactions centered at J and of width 2λ, we show that the magnetic susceptibility per Co(II) pair can be written

$$\chi = \frac{N\beta^2}{2kT}\left[{g_+}^2 \frac{1 + F_0}{1 - F_0} + {g_-}^2 \frac{1 - F_0}{1 + F_0} \right] \qquad (5)$$

where

$$F_0 = \frac{kT}{2\lambda} \log \frac{(J - \lambda) \sinh [\tfrac{3}{4}(J + \lambda)/kT]}{(J + \lambda) \sinh [\tfrac{3}{4}(J - \lambda)/kT]}$$

$$g_+ = \tfrac{1}{2}(g_a + g_b)$$

$$g_- = \tfrac{1}{2}(g_a - g_b)$$

We neglect in this treatment the distribution of g factors which could be expected from the slight variations of octahedral field as deduced from EPR spectra.

A least-squares refinement of the experimental data led to the best values of g_a, g_b, J, and λ. The result, listed in Table I, provides a very good description of the experiment (Figure 7). Notice that J and λ must be renormalized by the factor $^{25}/_9$, which results from the treatment of Co(II) as an effective spin $S = 1/2$ system.[11]

For comparison, we have drawn equally on Figure 7 the power law variation $\chi T = 1.03T^{0.36}$. Clearly, this function vanishes as $T \rightarrow 0$ K while eq 5 gives a non-zero intercept when the absolute temperature is approached. This divergence is due to the fact that, for $\lambda > |J|$, the proposed $P(J)$ distribution involves some zero exchange couplings, thus giving rise to noninteracting segments.

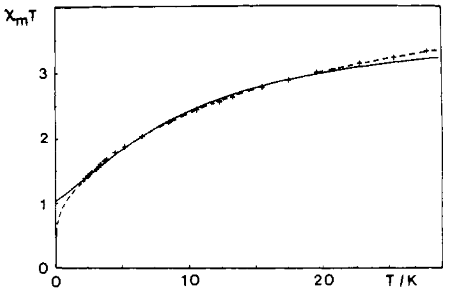

Figure 7. $\chi_m T = f(T)$ curve for the amorphous [CoCo] complex. The result of the fit by a random exchange model is displayed in the solid line. The power law $\chi_m T = 1.03T^{0.36}$ is shown by the dashed line.

Connected Finite Fragment Model. The low-temperature behavior may apparently reflect a distribution of rather short chain lengths, giving a REHAC in the trivial sense, that is to say, randomly distributed zero couplings along a chain. The finite chain problem, solved by Fisher in the classical limit ($S \rightarrow \infty$),[29] does not allow us to predict a power law variation. Recently, Bondeson and Soos have reinvestigated this problem by assuming just two distinct exchange interactions whose ratio is defined by ϵ.[26] The random occurrence of these interactions is sufficient to explain the power law, as long as $kT/|J| < \epsilon$. At higher temperatures, the consecutive fragments are thermally decoupled so that the finite-chain model becomes relevant.

In the present system, the absolute value of J is expected to be less than 5 K. Owing to the topology of the EDTA ligand, the exchange between two consecutive segments cannot exceed 20–30% of J. Thus, the upper limit for observing the power law behavior would be 1–2 K while, actually, it is followed up to 20 K.

Therefore, the low-temperature variation does not seem to originate from connected finite fragments involving two interactions only.

Further clarity arises from the magnetic study of the crystallized complex $Co_{1-\gamma}Mg_\gamma Co(EDTA)\cdot 6H_2O$ ($\gamma < 0.05$), where the $S = {}^1/_2$ chains are cut by diamagnetic Mg(II) ions. All the examined materials do not show the features of REHAC down to 2 K, thus confirming that spin segments are, when they are induced by doping, fairly well isolated.

Concluding Remarks

Several remarks can be drawn from the above results.

(i) A source of criticism is the use of a classical formalism for describing a $S = {}^1/_2$ spin chain randomly coupled, thus neglecting significant quantum effects at low temperatures. In previous studies on similar systems, such an approximation was justified by a good prediction of REHAC characteristics. Here, it is shown to be convenient, since a compact closed expression of the susceptibility can be deduced and compared to the experimental data.

An estimate of the approximation can be made from the results of both quantum and classical decriptions of the crystallized complex [CoCo] (Table I). Then, it appears that the classical model leads to a 40% overestimated J parameter. However, this disagreement does not affect the conclusions of this study. On the other hand, the other two parameters, g and λ, fully agree with the expected values; for instance, the width of the J distribution, $\lambda < 10^{-4}$ K, is consistent with the regular chain packing within crystallized material.

(ii) It can be noticed, from eq 5, that the low-temperature behavior of a REHAC is particularly sensitive to the $\lambda/|J|$ ratio. Experimentally, the extrapolated $\chi_m T$ product as $T \rightarrow 0$ K implies a ratio greater than unity, i.e. the presence of a broad J distribution with both ferro- and antiferromagnetic

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exchange couplings. Owing to the chosen box-type distribution, it is clear that the results can only be qualitative. Notice that more sophisticated distributions, such as $P(J) = \lambda^{\alpha-1}|J|^{-\alpha}$ with $0 < |J| < \lambda$, provide the same divergence, $\chi = AT^{-\alpha}$, as $T \rightarrow 0$ K.[19] Further investigations, such as low-temperature specific heat studies, are now required for a better understanding of the critical parameter α.

Finally, whatever the kind of distribution, the $\lambda/|J|$ ratio must play a special role when the "degrees of disorder" in the EDTA amorphous complex series are compared. On account of their very close local structure[8] such a comparison should lead to a better knowledge of the correlations structure–exchange mechanisms in the amorphous state. Our groups are working in this way.

Acknowledgment. We thank Dr. C. Schwab and B. Meyer from the Laboratoire de Spectroscopie et d'Optique du Corps Solide (Strasbourg) for their assistance with EPR measurements.

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

Contribution from the Dipartimento di Chimica Generale and Istituto di Cristallografia,
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Studies on Copper(II) Complexes of *o*-Quinone Monooximes. Adducts of Bis(4-chloro-1-benzoquinone 2-oximato)copper(II) with Some Heterocyclic Bases. Structure of the 2,2′-Bipyridine Adduct[1]

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Received December 27, 1983

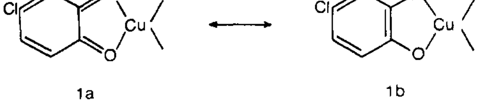
Stable 1:1 adducts of bis(4-chloro-1-benzoquinone 2-oximato)copper(II), $Cu(qo)_2$, with 2,2′-bipyridine, 1,10-phenanthroline, imidazole, and pyrazole, have been isolated. The crystal structure of bis(4-chloro-1-benzoquinone 2-oximato)(2,2′-bipyridine)copper(II), $C_{22}H_{14}Cl_2CuN_4O_4$, has been determined. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 15.499$ (14) Å, $b = 14.260$ (13) Å, $c = 11.097$ (15) Å, $\alpha = 71.26$ (8)°, $\beta = 75.25$ (4)°, $\gamma = 81.07$ (5)°, $V = 2238.8$ (4) Å^3, $Z = 4$, and d(calcd) = 1.581 g cm^{-3}. The structure converged to a weighted R factor of 3.37% for 6228 observations and 596 parameters. The copper ion attains coordinative saturation through cis,cis-octahedral geometry tetragonally distorted. The formation constants for $Cu(qo)_2(bpy)$ and $Cu(qo)_2(phen)$ are reported. A corresponding series of adducts containing benzene in the crystal lattice has been isolated.

Introduction

It is well-known that bis-chelated complexes of copper(II) behave as Lewis acids and react with donor ligands, thus increasing their coordination number.[3] The more usual product of the reaction with bases is the square-pyramidal 1:1 type of adduct; six-coordination is attained only when the electron-withdrawing nature of the chelating ligands increases the residual positive charge on the metal ion; for instance, this is the case for bis(hexafluoroacetylacetonato)copper(II), which forms octahedral isolable adducts with pyridine and bipyridine, whereas bis(acetylacetonato)copper(II) forms only an unstable 1:1 pyridine adduct, which loses the base on exposure to air.[4] Extensive research on this subject has been carried out on Cu(II) complexes derived from β-diketones and from salicylaldimine type ligands,[5] but very little information is reported about the Lewis acidity of Cu(II) bis-chelated derivatives of *o*-quinone monooximes. Moreover these compounds are presently the focus of attention of many researchers because of their peculiar reactivity. In fact, they react easily with many potentially basic compounds (i.e., dimethyl acetylenedicarboxylate,[6] amines,[7] triphenylphosphine,[8] benzaldehyde,[9] methanol[10]) to give a wide variety of organic products. The mechanism of these reactions (which do not occur if the *o*-quinone monooximes are not complexed with the metal) has been explained by assuming, as a preliminary step, the formation of adducts between the basic reagent and the copper ion;[6,7] therefore, in order to understand the reactivity of copper(II) complexes derived from *o*-quinone monooximes, it is advisable to know more about their Lewis acid behavior and the molecular structure of their adducts.

The number of adducts that have been isolated so far is very meager; as regards Cu(II) complexes of *o*-benzoquinone monooximes, only the 1:1 square-pyramidal adduct with pyridine has been characterized;[11] it is reported that other strong donors such as triethylamine, dimethyl sulfoxide, and acetonitrile fail to react,[12] and the existence of a water adduct is very doubtful.[10] Only if the chelated ligand is a naphthoquinone monooximate can a square-pyramidal monohydrate be obtained[13a] and a weak octahedral acetone adduct can be isolated.[13b]

In order to obtain more information on this subject, we investigated the reaction of bis(4-chloro-1-benzoquinone 2-oximato)copper(II) [**1a** ↔ **1b**, referred to as $Cu(qo)_2$] with



1a 1b

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[1] Presented at the XVI National Congress of Inorganic Chemistry, Ferrara, Italy, Sept 12–16, 1983.

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