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Electron Paramagnetic Resonance Spectra of Polycrystalline Dimeric Complexes. Copper Propionate Monohydrate and Zinc-Doped Copper Propionate Monohydrate

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Electron paramagnetic resonance spectra have been observed in the polycrystalline form of copper propionate monohydrate and zinc-doped copper propionate monohydrate. The studies were carried out at liquid nitrogen temperature and at both X-band and K-band frequencies. The K-band $S = 1$ spectrum arises from $\Delta M = 1$ and $\Delta M = 2$ transitions. Copper nuclear-hyperfine structure was observed in the parallel spectra at X-band and K-band frequencies as well as in the $\Delta M = 2$ spectral region at K band. The magnetic parameters for the exchange-coupled copper–copper pairs are $g_{||} = 2.348$, $g_{\perp} = 2.060$, $A_{||} = 0.0073\ \text{cm}^{-1}$, $A_{\perp} < 0.001\ \text{cm}^{-1}$, $D = 0.327\ \text{cm}^{-1}$, and $E < 0.001\ \text{cm}^{-1}$. For the $S = {}^1/_2$ spectra associated with the copper–zinc pairs, the magnetic parameters are $g_{||} = 2.348$, $g_{\perp} = 2.064$, $A_{||} = 0.0152\ \text{cm}^{-1}$, and $A_{\perp} < 0.001\ \text{cm}^{-1}$. A consistent interpretation of the data is presented on the basis of a weak metal–metal interaction. A simple model is used to estimate covalency parameters for the metal–ligand bonds. Order of magnitude estimates for the exchange integrals and the supertransferred hyperfine interaction are also derived from the data.

Introduction

There has been considerable interest in the magnetic and optical properties of exchange-coupled pairs of transition metal ions.[2–10] These studies have been carried out on suitable diamagnetic host lattices by incorporating large percentages of a paramagnetic species or on pure dimeric cluster complexes.[11–15] In a review of copper-containing cluster complexes in 1964, Kato, Jonassen, and Fanning[16] listed over 100 compounds which were believed to be dimeric. Many of these materials have been extensively studied by susceptibility methods, but there have been relatively few studies with electron paramagnetic resonance (epr) spectroscopy. The reasons for the emphasis on the older of the two magnetic techniques are manifold, the possibility of accurately determining the exchange integral, J, by measurements on polycrystalline samples being only one. The susceptibility data are usually fitted to the Bleaney–Bowers equation[14]

$$\chi = \frac{Ng^2\beta^2}{3kT}\left[1 + \frac{1}{3}\exp(J/k)\right]^{-1} + N\alpha$$

The J value can be obtained from either epr or susceptibility studies, but the latter method is generally more reliable.[17] On the other hand, the g values obtained from susceptibility studies can sometimes be subject to greater uncertainty than those derived from epr measurements.

Most of the epr work on cluster compounds has been carried out with single crystals.[2] The disadvantages associated with single-crystal investigations include difficulties in growing and mounting the crystals and sometimes problems in analyzing the data. However, such studies have the decided advantage that the magnetic parameters can be related to the crystalline axes and, generally, to the molecular axes in an unambiguous fashion. Furthermore, it may sometimes occur that the principal axes for various magnetic tensors do not coincide.[13] This noncoincidence can be more readily ascertained from single-crystal investigations. Once one or more model complexes have been studied with single crystals, however, closely related complexes can be examined in the polycrystalline form. Such studies often yield the magnitudes of the various components of the magnetic tensors since it is usually possible to make reasonable assumptions regarding the orientations of the principal magnetic axes with respect to the molecular geometry. There have been numerous epr studies of polycrystalline and glassy samples of $S = {}^1/_2$ species in both inorganic and organic compounds.[18] Relatively few studies have been carried out on $S = 1$ species, and these have been almost entirely confined to organic materials where the g-factor anisotropy is usually small.[19,20]

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An important class of compounds, the dimeric cupric alkanoates, contain a number of features which make them suitable candidates for study in the polycrystalline form. The model complex in this case is copper acetate monohydrate.[14] This complex contains two cupric ions joined together by four bridging acetate groups.[21] Each ion resides in a crystalline (ligand) field which has a distorted octahedral configuration. The four alkanoate oxygens define the xy plane about each copper(II) ion. The oxygen from the water molecule and the other cupric ion lie on the z axis. The two unpaired electrons associated with the two copper ions are coupled by an isotropic exchange Hamiltonian of the form

$$\mathcal{H}_{\text{ex}} = J\vec{S}_1 \cdot \vec{S}_2$$

The magnitude[14,22] of J is about 300 cm^{-1}. An anisotropic spin–spin interaction also obtains and is three orders of magnitude smaller than the isotropic part. The principal axes of this tensor coincide with those of the g tensor. It is reasonable to assume that a similar situation occurs in the other dimeric cupric alkanoates.

The purpose of this paper is to demonstrate the feasibility of determining magnetic parameters of dimeric cupric alkanoate complexes in polycrystalline samples. The specific examples selected are copper propionate monohydrate [Cu(Pro)_2] and zinc-doped Cu(Pro)_2. The latter material was studied since previous investigations have shown that a relationship exists between the epr data obtained from the copper(II)–copper(II) dimers and the copper(II) "monomers" which are present when a small amount of zinc is incorporated substitutionally into the host lattice.[23,24]

Experimental Section

Copper propionate monohydrate can be prepared by heating copper carbonate and propionic anhydride in a small amount of water.[25] The dark blue-green color, characteristic of the copper complex, appears after a few minutes. The zinc analog was prepared in a similar fashion. Solutions which contain only the copper complex (solution a) and an equimolar mixture of the copper complex and zinc complex (solution b) were allowed to evaporate slowly in a constant-temperature environment, which produced small but identifiable single crystals. All the crystals obtained from solution a were dark blue-green as were the crystals initially formed from solution b. Chemical anaylsis of a sample of the dark blue-green crystals was carried out by the Microchemical Analysis Section of the NBS. *Anal.* Calcd for $\text{C}_6\text{H}_{12}\text{O}_5\text{Cu}$: C, 31.65; H, 5.13; H_2O, 7.9. Found: C, 31.5; H, 5.3; H_2O, 7.4. Crystals from the latter solution were gathered at regular intervals and after a few days some transparent or nearly transparent crystals appeared. These could be visually separated from the dark green crystals.

Epr spectra were obtained from three polycrystalline samples which were prepared by grinding the dark blue-green crystals of solution a (sample 1), the dark blue-green crystals of solution b (sample 2), and the nearly transparent crystals from solution b (sample 3). These samples were examined at 77°K with an X-band spectrometer and the epr spectra of samples 1 and 2 were also obtained at K band.

Results

The X-Band Spectrum.—All three samples gave $S = {}^1/_2$ spectra and identical $S = 1$ spectra were obtained from samples 1 and 2. The $S = {}^1/_2$ spectra will be considered first. Extensive discussions of line-shape analyses of polycrystalline $S = {}^1/_2$ spectra have been given by many authors[18] and therefore a detailed exposition will not be given here. The doubly integrated intensities from samples 1, 2, and 3 were roughly in the ratio 0.1:150:1. In sample 1, the signal appears to be caused by a small amount of $S = {}^1/_2$, monomeric copper(II) species. This result is in accord with other observations of small concentrations of monomers in the predominantly dimeric copper compounds.[17] The relatively low intensity of this signal introduces no problem in the interpretation of the spectra from samples 2 and 3.

In sample 2 the largest signal was observed; comparison with calibrated samples indicates that the number of spins which give rise to this signal is roughly equal to the number of zinc ions in the sample. Therefore, it was assumed that the spectrum observed in sample 2 was not due to monomeric copper(II) ions but rather to copper(II)–zinc(II) pairs where a small number of zinc(II) ions enter the Cu(Pro)_2 lattice substitutionally. This assumption is consistent with the results of previous investigations.[23,24] The $S = {}^1/_2$ spectrum from sample 3, however, was rather different from those obtained from the other two samples. No unambiguous assignment for this spectrum was made. It appears reasonable that it is associated with small numbers of monomeric copper(II) species in a predominantly zinc propionate lattice.

For the $S = 1$ species, only the high-field spectra were clearly resolved, owing to the large value of the anisotropic spin–spin coupling (see below). The parallel portions of these spectra showed hyperfine structure which consisted of a seven-line pattern as is shown in Figure 1. The separation between these lines is about 70 G. For purposes of comparison, a polycrystalline sample of the model complex, copper acetate monohydrate, was also obtained and the appearance of the "parallel" spectrum was nearly identical with that observed in Cu(Pro)_2.

The K-Band Spectrum.—Spectra from samples 1 and 2 were obtained at K band. The spectrum associated with the $S = 1$ species was identical in both samples. The $S = {}^1/_2$ spectrum observed in sample 2, and attributed to the copper–zinc pairs, is shown in Figure 2. Since the line widths of the individual components which make up the polycrystalline line shape are essentially independent of magnetic field for the range of fields employed in these experiments, a more precise determination of the value of $g_\perp$ and a more reasonable upper limit for $A_\perp$ is obtained at this frequency. The very simple line shape also affords

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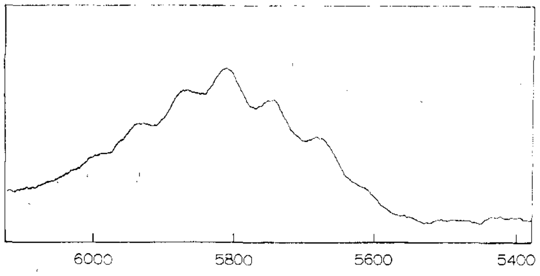

Figure 1.—The high-field parallel components of the $S = 1$ spectrum at X band. The abscissa gives the magnetic flux density in gauss (10^4 G = 1 Tesla).

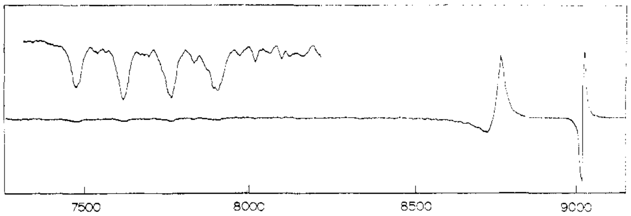

Figure 2.—The complete $S = {}^1/_2$ spectrum at K band. The parallel components in the upper left-hand portion of the figure were obtained at a gain of about 20 times that of the rest of the figure. The signal at the far right is DPPH. The abscissa gives the magnetic flux density in gauss (10^4 G = 1 Tesla).

the opportunity of setting upper limits on the anisotropy of the g tensor in the xy plane. The magnetic parameters for the $S = {}^1/_2$ species are shown in Table I.

TABLE I

MAGNETIC PARAMETERS[a] FOR $Cu(Pro)_2$ AND $Cu[Zn](Pro)_2$

	$Cu(Pro)_2$	$Cu[Zn](Pro)_2$
$g_{\|}$	2.348 ± 0.004	2.348 ± 0.003
$g_{\perp}$	2.060 ± 0.005	2.064 ± 0.005
$A_{\|}$, cm^{-1}	0.0073 ± 0.0004	0.0152 ± 0.0005
$A_{\perp}$, cm^{-1}	<0.001	<0.001
D, cm^{-1}	0.327 ± 0.004	*b*
E, cm^{-1}	<0.001	*b*

[a] The uncertainties represent the maximum spread of the data at both frequencies. [b] D and E do not appear in an $S = {}^1/_2$ spin Hamiltonian.

The $S = 1$ spectrum can be divided into three major regions. These are the high-field parallel and perpendicular components, the low-field parallel and perpendicular components, and the $\Delta M = 2$ transitions. The latter are sometimes referred to as the "zero-field transitions" and are discussed at length in a number of papers.[19,20] The high-field perpendicular component is shown in Figure 3 and the $\Delta M = 2$ spectral region is shown in Figure 4.

The data were interpreted with the usual $S = 1$ spin Hamiltonian[14]

$$\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2) + \beta(g_zH_zS_z + g_xH_xS_x + g_yH_yS_y)$$

The energy levels in the z direction[14] are

$$\begin{aligned} E_1 &= D + (E^2 + g_z^2\beta^2H^2)^{1/2} \\ E_2 &= D - (E^2 + g_z^2\beta^2H^2)^{1/2} \qquad (1) \\ E_3 &= 0 \end{aligned}$$

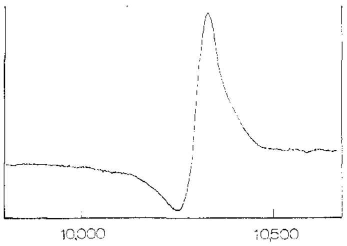

Figure 3.—The high-field perpendicular component of the $S = 1$ spectrum at K band. The abscissa gives the magnetic flux density in gauss (10^4 G = 1 Tesla).

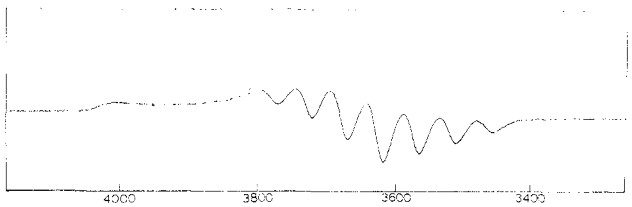

Figure 4.—The $\Delta M = 2$ spectral region. The perpendicular component is on the left, and the seven-line "minimum field" spectrum is on the right. The abscissa gives the magnetic flux density in gauss (10^4 G = 1 Tesla).

while in the x direction the energy levels are given by similar expressions with g_z, D, and E, in eq 1 replaced by g_x, $(3E - D)/2$, and $-(D + E)/2$, respectively. In the y direction, g_z, D, and E are replaced by g_y, $-(3E + D)/2$, and $(D - E)/2$.

The positions of the two perpendicular components can be used to derive values for $g_{\perp}$ ($\approx g_y \approx g_x$) and D. In addition, upper limits can be assigned to the value of E and the maximum anisotropy of the components of the g tensor in the xy plane on the basis of the observed line widths.

Because of the relatively large amount of experimental data, the value of D can be obtained by several independent methods. From the perpendicular $\Delta M = 1$ K-band spectrum, values of $g_{\perp} = 2.060$ and $D = 0.331$ cm^{-1} are calculated. The two parallel components give values for $g_{\|} = 2.347$ and $D = 0.327$ cm^{-1}. With these values for $g_{\|}$ and $g_{\perp}$, the high-field X-band data were used to derive two additional values of D of 0.323 and 0.329 cm^{-1}. Finally, the perpendicular component of the $\Delta M = 2$ spectrum which appears at about 4000 G (Figure 4) can also be used to obtain D. The resonance condition for this absorption is given by the equation

$$h\nu = 2[(D/2)^2 + g_{\perp}^2\beta^2H^2]^{1/2}$$

With $g_{\perp} = 2.060$, the value for D is 0.325 cm^{-1}. The average of all of these values is 0.327 ± 0.003 cm^{-1} where the uncertainty is the mean deviation from the mean. The over-all consistency of these calculations as reflected by the small mean deviation supports the assumption in our analysis of a small value for E.

The seven-line hyperfine pattern in the $\Delta M = 2$ spectral region shown in Figure 4 deserves additional comment. This absorption corresponds to the minimum field at which resonance occurs. This threshold absorption need not arise from crystallites which have a principal axis parallel to the external magnetic field.[19] A comparison of the hyperfine separation with those obtained in the $\Delta M = 1$ spectral region indicates that this resonance is due to crystallites oriented such that their z axis lies on a cone which makes an angle θ, different from zero, with respect to the magnetic field. The value for θ may be derived by iteration from the two equations which give the angular variation of A and g

$$g^2A^2 = g_{\|}^2A_{\|}^2 \cos^2\theta + g_{\perp}^2A_{\perp}^2 \sin^2\theta$$

$$g^2 = g_{\|}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta$$

With the experimental values of A, $A_{\|}$, $g_{\|}$, and $g_{\perp}$ and with the assumption that $A_{\perp} = 0$ (see Table I), a value of $\theta \approx 30°$ is readily obtained. Kottis and Lefebvre[19] have discussed the $\Delta M = 2$ spectral region for an isotropic g factor in great detail. By a simple extension of their treatment to the case of $E = 0$, it is possible to derive a closed-form expression which relates the angle θ to D and $h\nu$, the microwave energy. This equation is

$$\cos^2\theta = \frac{18(h\nu)^2 - 16D^2}{27(h\nu)^2 - 36D^2}$$

from which a value of $\theta = 34°$ is calculated. In view of the experimental uncertainties and the assumptions inherent in our use of this formula, the agreement between the two values of θ is quite satisfactory.

Abe[26] has studied single crystals of copper propionate monohydrate and has found evidence for three chemically nonequivalent types of dimers. The values of the magnetic parameters which he derived from his data are somewhat different from those obtained here. It seems likely that different crystalline modifications of $Cu(Pro)_2$ are the source of the minor discrepancies.

Discussion

There have been a number of models proposed which have attempted to account for the magnetic and optical behavior of dimeric copper(II) alkanoate complexes.[22,27,28] Because of the relatively complicated nature of these systems, the theoretical calculations of the exchange mechanisms necessarily involve a number of simplifying assumptions. The models which have proven most successful assume a weak metal–metal bond with the interaction proceeding largely through the bridging acetate groups.[22-28] There is a σ pathway through the oxygen–carbon–oxygen atoms as well as a number of π pathways.

Some insight into the nature of the exchange mechanisms in these systems may be provided by an analysis of the covalent character of the metal–ligand bonds. Two recent review papers[29,30] have discussed the calculation of covalency parameters obtained from magnetic and optical data of transition metal ions. The most reliable calculations have usually centered around relatively simple systems such as nickel(II) in $KMgF_3$. A number of more approximate theoretical procedures have been used for copper(II) complexes.[31-35] In order to obtain a rough estimate for the covalency parameters associated with a single copper(II) ion in copper propionate monohydrate, we will use the simplest type of treatment.

It will be assumed that the following wave functions describe the system

$$\psi_{x^2-y^2} = \alpha d_{x^2-y^2} - \alpha'|\phi_{x^2-y^2}\rangle$$

$$\psi_{xy} = \beta d_{xy} - \beta'|\phi_{xy}\rangle$$

$$\psi_{xz,yz} = \beta_1 d_{xz,yz} - \beta_1'|\phi_{xz,yz}\rangle$$

The kets in the second portion of these expressions represent the wave functions of atoms close to the copper(II) ion which can be admixed into the primarily 3d orbitals centered on the copper ion. It is expected that the admixed ligand wave functions will be made up largely of the 2s or 2p orbitals on the alkanoate oxygens. The d_{xz} and d_{yz} orbitals have been assumed to be degenerate.

The Abragam and Pryce theory[36] as modified by many workers[31-35] is used to derive the following expressions which relate the experimental epr data to the covalency parameters α, β, and β_1

$$g_{\|} = 2.0023 + \frac{8\lambda}{\Delta_{xy}}\alpha^2\beta^2$$

$$g_{\perp} = 2.0023 + \frac{2\lambda}{\Delta_{xz,yz}}\alpha^2\beta_1^2$$

$$A_{\|} = P\left\{-\frac{4}{7}\alpha^2 - K + (g_{\|} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023)\right\}$$

$$A_{\perp} = P\left\{\frac{2}{7}\alpha^2 - K + \frac{11}{14}(g_{\perp} - 2.0023)\right\}$$

The derived parameters based on this simplified approach may differ from those calculated by a more exact theory by perhaps 10%.

With the assumptions $P = 0.042$ cm^{-1} [34] and $A_{\perp} = 0.000$ cm^{-1}, the values of α^2 and K, the Fermi contact term, may be calculated from the two hyperfine equations. From the $S = {}^1/_2$ spectral data, $\alpha^2 = 0.80$ and $K = 0.28$ are obtained. Optical studies on a variety of copper(II) alkanoate complexes[4,27,37] yield values of $\Delta_{xy} \approx 11{,}000$ cm^{-1} and $\Delta_{xz,yz} \approx 14{,}000$ cm^{-1}. These numbers will be used here as will a value of 828 cm^{-1} for λ, the free-ion spin–orbit coupling constant.[32] With these data, $\beta^2 = 0.72$ and $\beta_1^2 = 0.66$ are calculated

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from the two g-factor equations. These results suggest moderately covalent σ and in-plane π bonds between the copper(II) ion and the oxygen ligands. The lower value of β_1^2 indicates a greater degree of covalent character for the out-of-plane π bonds.

The σ-bonding parameter, α^2, can be used to obtain an estimate of the exchange integral, J, based on a configuration interaction model.[38] The value obtained here for α^2 implies about an 80% electronic density on the metal ion and a 5% unpaired electronic density on each of the four in-plane ligands. Thus, in the copper propionate complex, there is a probability of $(\alpha^2)(\alpha^2) = 0.64$ for the structure which may be schematically represented by Cu^{2+}–$CH_3CH_2COO^-$–Cu^{2+}. If we assume that the exchange interaction occurs entirely through a configuration in which both electrons are simultaneously transferred from a single bridging group to the two metal ions, the exchange integral, J, can be calculated by the method of Griffiths, Owen, Park, and Partridge.[38] This configuration can be represented by Cu^+–$CH_3CH_2COO^+$–Cu^+ and has a probability of

$$4\left[\frac{1-\alpha^2}{4}\right]^2 = 0.01$$

where the four possible exchange pathways have been taken into account. The value of J is then given by the expression

$$J = 4\left[\frac{1-\alpha^2}{4}\right]^2 J'$$

where J' is the singlet–triplet separation for the propionate ion. For most organic species these transitions occur in the ultraviolet spectral region.[39] With a value for J' between 10,000 and 100,000 cm^{-1}, J lies between 100 and 1000 cm^{-1}, compared to the experimental value of about 300 cm^{-1}.[16] This order of magnitude agreement lends support to the interpretation of the experimental data on the basis of a weakly bonded model.

As a further test of this model, the magnetic parameters associated with copper–zinc and copper–copper pairs can be compared. To within experimental uncertainty, the g values for these two complexes are identical. This result is in accord with an extension of the Slichter theory to the case of anisotropic g and A tensors.[40] Implicit in this theory is the assumption that the g tensor is not perturbed by the introduction of an exchange interaction.[28] Within the framework of the weakly coupled model, however, differences in the $S = 1$ and $S = {}^1/_2$ g tensors may arise as a result of a variation in the exchange parameters from the ground state to appropriate singly excited states. An upper limit can be assigned to this variation, δJ, on the basis of the uncertainties in the experimental g values. If these uncertainties are taken as upper limits to possible differences between corresponding components of the g tensors, the value of δJ may be obtained from the equation

$$\frac{(g_\perp - 2.0023)_{S={}^1/_2}}{(g_\perp - 2.0023)_{S=1}} = 1 + \frac{\delta J}{\Delta_{xz,\,yz}}$$

The maximum value of δJ obtained from the data is less than 100 cm^{-1}. This result is in general agreement with the theoretical results of Hansen and Ballhausen[28] for the singly excited levels.

An estimate for the exchange integrals in the excited states may also be made through the use of the anisotropic spin–spin coupling parameter, D. This spin–spin interaction[41] arises from direct-dipolar coupling as well as from a pseudo-dipolar interaction of the form

$$D_{\text{pd}} = \frac{1}{32}\left|[J_1(g_\parallel - 2.0023)^2 - 4J_2(g_\perp - 2.0023)^2]\right|$$

The direct-dipolar contribution is about 0.2 cm^{-1} and is believed to be of opposite sign to the pseudo-dipolar term.[41] With this assumption for the relative signs and the further assumption that $J_1 = J_2$, the value of J_1 is determined to be about 160 cm^{-1}. Some caution must be exercised in placing too much significance in this calculated value of J_1, since the assumption $J_1 = J_2$ is not necessarily justified.[27]

Another test of the validity of the weakly bonded model can be made from a consideration of the experimental data for the hyperfine splittings. The Slichter theory[40] predicts that the quantity

$$\Delta A_i = |A_{S={}^1/_2} - 2A_{S=1}|_i$$

for corresponding components of the hyperfine tensors should be zero. In this study, the value of ΔA can be as large as 0.001 cm^{-1}. One possible contribution to this discrepancy is the dipolar interaction of an unpaired electron in an orbital of one magnetic ion with the nucleus of the other ion. This interaction can produce a contribution of approximately 0.0001 cm^{-1} to ΔA. An experimental value of ΔA different from zero can also arise from a transfer of an unpaired electron centered on one magnetic ion into the orbitals of the other magnetic ion in the dimer.[42] In this case, the resultant hyperfine field at the nucleus of a magnetic ion would be composed of the usual hyperfine contribution plus a supertransferred hyperfine field (STHF).[42] It will be assumed that the STHF in $Cu(Pro)_2$ arises from the partial transfer of an electron in the 3d orbital of one copper(II) ion to the 4s orbital of the other. If the unpaired electrons were completely in a 4s orbital, the interaction energy would be[35] 0.0975 cm^{-1}. A comparison of this value with the upper limit for ΔA obtained here suggests that the maximum fractional unpaired electronic density in this orbital is about 0.01. In view of the uncertainties associated with the data and the possibility that other orbital transfer mech-

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anisms may also contribute to the STHF, this value should be regarded as giving only a rough upper limit for such a direct metal–metal interaction.

Conclusions

This work has demonstrated the feasibility of determining magnetic parameters in dimeric copper(II) alkanoates from epr studies of polycrystalline samples. It appears likely that the techniques discussed here can be generalized to other dimeric or even polymeric cluster complexes. For these systems, the magnetic parameters may be derived by several different methods depending upon the relative magnitudes of the anisotropic spin–spin coupling parameter, D, and the microwave energies employed. If the two energies are comparable, a measurement of the high-field spectrum at two different microwave frequencies should suffice. If the spectrometer frequency corresponds to an energy sufficiently greater than D, unambiguous high- and low-field spectra as well as a zero-field spectrum obtain. For such a case, a study at a single microwave frequency would serve to determine, and possibly overdetermine, the magnetic parameters. Studies at higher microwave frequencies have the additional advantage in providing more accurate data owing to the smaller fractional line widths.

Our studies of copper propionate monohydrate are in accord with previous single-crystal epr investigations of copper(II) alkanoate systems in that the g values for the copper–copper pairs agree with those of the copper–zinc pairs. For these systems, only a single-frequency X-band study of the $S = {}^1/_2$ and the high-field $S = 1$ spectra is required for the specification of all of the magnetic parameters. Furthermore, a comparison of the hyperfine splitting for the $S = 1$ and $S = {}^1/_2$ species may provide information regarding the supertransferred hyperfine field. Extension of this doping technique to other cluster complexes must await appropriate single-crystal studies on model complexes.

The weakly coupled model has been found to give a satisfactory account of the experimental data for $Cu(Pro)_2$ as well as for other copper(II) alkanoates. In this connection, it is of interest to consider the relationship between the metal–metal distance and the nature of the bonding. In the model complex copper acetate monohydrate, the internuclear distance is 2.64 Å. A recent calculation by Schleuter, Jacobsen, and Rundle[43] has shown that, at this distance, the overlap between corresponding copper(II) 3d orbitals is quite small. Although the internuclear distance in the copper(II) alkanoates is only about 0.1 Å larger than that found in copper metal, a somewhat more meaningful comparison may be made by considering the bond length in the Cu_2 molecule. For this molecule, Hare, Sleight, Cooper, and Clarke[44] have estimated that the highest filled σ molecular orbital contains only about 7% $3d_{z^2}$ character and that this value occurs at an internuclear separation of 2.19 Å. Thus, the much larger distance found in the copper(II) alkanoates would seem to rule out the existence of a strong direct metal–metal interaction.

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The Preparation and Properties of Methyl(germyl)silanes and Some Related Compounds[1]

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Methyl(germyl)silanes, $(CH_3)_nSi(GeH_3)_{4-n}$ in which $n = 0, 1, 2,$ or 3, have been synthesized by the reaction of sodium germyl with the appropriate methylchlorosilane. The related compounds 1,1,1-trimethyldigermane, digermane, and germylsilane have been prepared by the reaction of sodium germyl with trimethylfluorogermane, bromogermane, and bromosilane, respectively. The new compounds, except tetragermylsilane, have been characterized by elemental analysis and measurement of their molecular weights, vapor pressures, and melting and boiling points. Proton nmr spectra of the neat liquids have been recorded and the results are interpreted in terms of inductive and anisotropic effects. Infrared spectra in the range 4000–650 cm^{-1} have been measured on samples in the gas phase and frequency assignments have been made.

Introduction

The use of alkali metal derivatives of germane, $M^+GeH_3^-$, in which M is the alkali metal, for the preparation of compounds containing the GeH_3 group has not yet been fully explored. Alkylgermanes, $C_nH_{2n+1}GeH_3$, in which $n = 1, 2,$ or 3, have been synthesized by the reaction of sodium germyl with alkyl halides in liquid ammonia as solvent.[3]

More recently, Van Dyke and coworkers have demonstrated the advantages of hexamethylphosphor-

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