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Electron-Spin Delocalization in Antiferromagnetic Dimeric Copper(II) Benzoates

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The copper(II) salts of benzoic acid, *o*-, *m*-, and *p*-methylbenzoic acid, and 2,6-dimethyl- and 3,5-dimethylbenzoic acid exist as dimers with reduced magnetic moments in acetone solution at room temperature. The solution nmr spectra of these compounds, as well as of $[\text{Cu}(\text{formate})_2 \cdot \text{urea}]_2$ and $[\text{Cu}(\text{acetate})_2 \cdot \text{urea}]_2$, exhibit quite large contact shifts of the proton resonances, consistent with a superexchange mechanism for the spin exchange. The pattern of signs of the contact shifts suggests that spin delocalization from the copper ions is into the σ bonding system of the carboxylate groups, although finite spin densities also appear in the π systems of the aromatic rings, possibly *via* hyperconjugation.

Introduction

The anomalously low magnetic moments of many copper(II) alkanoates have generated considerable controversy for many years. Dimeric compounds of the type $[\text{Cu}(\text{RCO}_2)_2 \cdot \text{L}]_2$ (R = alkyl, aryl; L = a neutral or anionic ligand) have been studied most intensively.¹ They have the structure shown in Figure 1, the copper-copper distance being only about 2.64 Å, and are antiferromagnetic with a singlet ground state and a thermally populated triplet excited state.¹

Although Forster and Ballhausen concluded from molecular orbital considerations that the primary antiferromagnetic interaction is a σ bond formed by the copper $3d_{z^2}$ electrons,² opinion in general favors the presence of a δ bond brought about by overlap of the $3d_{x^2-y^2}$ orbitals.^{3,4} A number of modifications to these theoretical approaches have been made and have been summarized by Jotham and Kettle,⁵ who treated the two copper atoms as a two-hole diatomic molecule while including crystalline field and electron-repulsion effects. Generally these procedures assume a direct copper-copper interaction, although indirect coupling or superexchange mechanisms *via* the bridging carboxylate ligands have also been suggested.⁶⁻⁸ Very serious doubt concerning the importance of direct copper-copper bonding has been aroused, however, by magnetic and structural studies on the analogous copper(II) formate and acetate dimers $(\text{Me}_4\text{N})_2[\text{Cu}(\text{RCO}_2)_2 \cdot (\text{NCS})]_2$.⁹ Although the acetate has the shorter copper-copper distance, it is the formate which exhibits the greater degree of spin exchange. Since direct metal-metal bonding should increase with shorter bonding

distances, it seems likely that the carboxylate bridges play a major role in the spin-exchange interaction.

The present investigation was undertaken in order to gain an insight into the nature and extent of electron delocalization into the carboxylate ligands. It is well-known¹⁰ that delocalization of unpaired electron spin density from a paramagnetic transition metal ion into the molecular orbitals of coordinated ligands can cause quite large contact shifts in the proton nmr spectra of the ligands. In some cases, the magnitude and direction of the contact shifts have given useful information concerning the mode of delocalization of electron density into the ligands, and it was expected that a proton nmr study of a series of dimeric substituted copper(II) benzoates could be very informative in this respect.

Although the relatively long electronic relaxation times of monomeric tetragonal copper(II) complexes¹¹ generally cause extreme broadening of the nmr spectra of copper complexes, it was hoped that the electron-spin exchange of the dimeric complexes would provide a sufficiently efficient mechanism for electron-spin relaxation that the proton nmr spectrum could be resolved. Previously, Kawamori¹² and Inoue and Kubo¹³ have reported variable temperature broad line studies on copper(II) acetate hydrate and two modifications of copper(II) formate, respectively. The latter paper is very pertinent to this work. Large contact shifts of the formate protons were detected and electron delocalization mechanisms were discussed.

Experimental Section

Chemicals.—Benzoic acid and the substituted benzoic acids were purchased from K and K, Inc.; copper sulfate and zinc nitrate from Fisher Scientific Co.

Preparations.—The dimeric copper(II) benzoate derivatives were prepared by the method outlined by Lewis, *et al.*¹⁴ A solution of the relevant acid was prepared in water and the pH was

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 (4) E. A. Boudreaux, *Inorg. Chem.*, **3**, 506 (1964).
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 (6) W. E. Hatfield and J. S. Paschal, *J. Amer. Chem. Soc.*, **86**, 3888 (1964).
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 (14) J. Lewis, Y. C. Lin, L. K. Royston, and R. C. Thompson, *J. Chem. Soc.*, 6464 (1965).

TABLE I
ANALYTICAL DATA AND PHYSICAL PROPERTIES

Compound	Mp, °C	Calculated			Found			μ_{eff} , BM
		C	H	Mol wt	C	H	Mol wt (acetone)	
[Cu(benzoate) ₂] ₂	267-268	54.99	3.30	612	55.11	3.51	589	...
[Cu(<i>o</i> -methylbenzoate) ₂] ₂	229-230	57.57	4.23	668	57.38	4.22	650	1.42 ± 0.04
[Cu(<i>m</i> -methylbenzoate) ₂] ₂	233-234	57.57	4.23	668	57.45	4.51	703	1.41 ± 0.04
[Cu(<i>p</i> -methylbenzoate) ₂] ₂	258-259	57.57	4.23	668	57.31	4.12	709	...
[Cu(2,6-dimethylbenzoate) ₂] ₂	257-258	59.74	5.01	724	59.86	6.19	781	1.36 ± 0.04
[Cu(3,5-dimethylbenzoate) ₂] ₂	276-277	59.74	5.01	724	58.94	5.50	762	1.45 ± 0.04

TABLE II
ISOTROPIC SHIFTS FOR THE COPPER COMPLEXES AT 20°, Hz

Complex	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	Methyl
[Cu(benzoate) ₂] ₂	+53 ± 2	-129 ± 2	+266 ± 5	...
[Cu(<i>o</i> -methylbenzoate) ₂] ₂	+123 ± 2	-134 ± 2	+259 ± 5	+1 ± 5
[Cu(<i>m</i> -methylbenzoate) ₂] ₂	+55 ± 2	-136 ± 2	+247 ± 5	+4 ± 2
[Cu(<i>p</i> -methylbenzoate) ₂] ₂	+22 ± 2	-127 ± 2	...	-48 ± 5
[Cu(2,6-dimethylbenzoate) ₂] ₂	...	-135 ± 2	+161 ± 5	-80 ± 5
[Cu(3,5-dimethylbenzoate) ₂] ₂	+46 ± 2	...	+251 ± 5	+6 ± 5

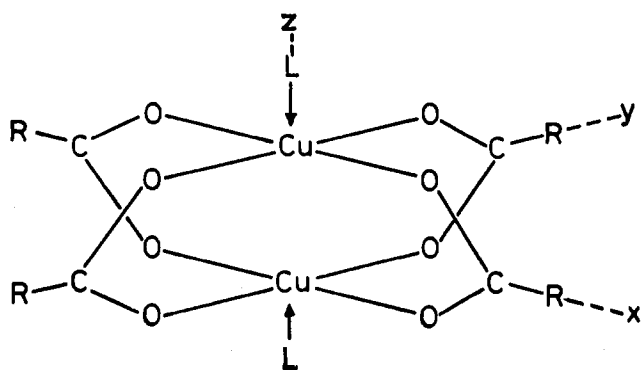


Figure 1.—Structure of copper(II) acetate and formate dimers.

adjusted to approximately 6 by the addition of sodium hydroxide. The addition of a concentrated solution of slightly more copper(II) sulfate than calculated usually resulted in the precipitation of a blue complex. In the case of the *o*-methyl and the 2,6-dimethyl derivatives, standing on a steam bath for several hours was necessary for precipitation of the complex. The products were collected, washed with a dilute solution of the parent acid, and dried *in vacuo* at 100° for 30 hr. After drying, the product was extracted with dry acetone, yielding a blue solution and a large amount of insoluble material. Concentration of the blue acetone solutions at low pressure at room temperature gave crystalline compounds which were recrystallized again from dry acetone and whose infrared spectra showed the complete absence of bands attributable to the free acids at about 3600 cm⁻¹ (ν_{OH}) and at about 1700 cm⁻¹ ($\nu_{\text{C=O}}$). Analytical data are shown in Table I.

The complexes [Cu(acetate)₂·urea]₂¹⁵ and [Cu(formate)₂·urea]₂¹⁶ were prepared by methods described in the literature.

The zinc analogs of the copper benzoates were prepared by adding a concentrated solution of zinc nitrate in methanol to a neutralized solution of the acid in methanol. The solution was boiled down to dryness and the white products were recrystallized from chloroform. The purity of the compounds was indicated by their infrared and nmr spectra.

Physical Measurements.—Infrared spectra were obtained on Nujol and hexachlorobutadiene mulls, nmr spectra on a Bruker HX 60 spectrometer with internal TMS lock at 20°. Molecular weights were determined in dry acetone using a Hewlett-Packard 302B vapor pressure osmometer operating at 37°. Because of the low solubility of the compounds in acetone (5×10^{-3} – 2×10^{-2} M), errors may be as high as ±10%.

Magnetic susceptibilities of the acetone solutions were determined by the method of Evans¹⁶ at a temperature of 20°. Magnetic moments were calculated using the equation

$$\mu_{\text{eff}} = 2.84 [(\chi_m' - N\alpha)T]^{1/2} \quad (1)$$

(15) M. Kishita, M. Inoue, and M. Kubo, *Inorg. Chem.*, **3**, 237 (1964).(16) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

where χ_m' is the molar susceptibility corrected for the diamagnetic susceptibility of the ligands and $N\alpha$ corrects for the temperature-independent paramagnetism of copper(II) (60×10^{-6} cgsu). The low solubilities of the benzoate and *p*-methylbenzoate compounds made it impossible to measure the magnetic susceptibilities of these compounds by this technique. The magnetic moments per copper ion of the other four compounds are listed in Table I.

Results and Discussion

The dimers of copper(II) benzoate and a number of methyl-substituted copper(II) benzoates have been prepared and characterized. Although these compounds are capable of existing in more than one crystalline modification^{14,17} and are easily contaminated with copper oxides and basic salts,^{14,17} the materials described here have been carefully prepared and appear to be as described in Table I. In addition to the completely consistent analytical data, all melting point ranges were equal to or less than 1°. In addition, the magnetic moments in the solutions agree very well with the magnetic moments of these and similar compounds in the crystalline state,¹⁴ although lower moments have been reported¹⁸ for aliphatic alkanoate salts in dioxane. It seems likely that two acetone molecules occupy the axial positions of the dimeric molecules (L = acetone in Figure 1).

The nmr spectra of the complexes were obtained using acetone-*d*₆ solutions. Although the low solubilities in this solvent resulted in very low signal-to-noise ratios, the lines were narrow enough (20–80 Hz) that unambiguous assignments could be made by comparing the spectra of the various complexes. Isotropic shifts were taken as the difference between the chemical shifts of the copper complexes and the chemical shifts of similar diamagnetic complexes,¹⁹ in this case of zinc. In all cases, the isotropic shifts of the para protons were upfield, while those of the meta protons were downfield. The isotropic shifts are listed in Table II.

Before discussing the observed isotropic shifts on the basis of electron delocalization into the molecular orbitals of the ligands, it is necessary to make corrections for any possible through-space dipolar or pseudocontact

(17) C. S. Fountain and W. E. Hatfield, *Inorg. Chem.*, **4**, 1360 (1965).(18) R. L. Martin and A. Whitley, *J. Chem. Soc.*, 1394 (1958).(19) R. E. DeSimone and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 2342 (1970).

shifts.¹⁰ The magnitudes and signs of the dipolar shifts can be calculated from the equation

$$\Delta\nu = -\frac{\nu\beta^2 S(S+1)}{3kT} \left[\frac{3\cos^3\chi - 1}{r^3} \right] \times \left[\frac{(g_{\parallel} - g_{\perp})(3g_{\parallel} + 4g_{\perp})}{15} \right] \quad (2)$$

where $\Delta\nu$ is the dipolar shift, ν is the probe frequency, and χ is the angle between the distance vector from the copper atom to the proton and the tetragonal axis of the complex.²⁰ Values of $g_{\parallel} = 2.345$ and $g_{\perp} = 2.061$ (an average of g_x and g_y) have been reported for polycrystalline dimeric copper(II) benzoate²¹ and were used for each compound here. The dipolar shifts listed in Table III are the average values

TABLE III
AVERAGE DIPOLAR CONTRIBUTIONS AT 20°

Proton	Shift, Hz
<i>o</i> -H	+97
<i>m</i> -H	+34
<i>p</i> -H	+30
<i>o</i> -CH ₃	+108
<i>m</i> -CH ₃	+30
<i>p</i> -CH ₃	+23

for each 15° rotation of the aromatic rings, and it is assumed that each copper atom can be treated as an independent paramagnetic center with $S = 1/2$. The dipolar shifts were then calculated at each position for each of the copper atoms and the overall contributions found by addition of the two terms. The bond distances and angles used were those reported for [Cu(CH₃CO₂)₂·H₂O]₂.²²

Kurland and McGarvey²³ have recently discussed the applicability of eq 2 to the nmr of transition metal complexes. They concluded that it would not apply to complexes with T₁ or T₂ ground states, but could be used to evaluate dipolar shifts for other complexes in which there are no low lying excited states and for systems in which $S > 1/2$, in which the zero-field splitting is small. Equation 2 is thus very suitable for calculations involving the dimeric copper complexes discussed in this paper. The triplet state is very likely ³A_{2u},⁵ with no significantly populated levels at higher energies. Furthermore the zero field splittings are only about 0.33 cm⁻¹.²¹

Although the dipolar shifts were calculated treating the copper ions as completely uncoupled species with $S = 1/2$, the isotropic shifts listed in Table II are for strongly coupled ions with significant populations in the diamagnetic ground states. The fraction in the triplet state for any particular compound is given by the ratio $\chi_m(\text{observed})/\chi_m(\text{theoretical})$, *i.e.*, $\mu_{\text{eff}}^2(\text{observed})/\mu_{\text{eff}}^2(\text{theoretical})$. The theoretical magnetic moments of the hypothetical fully paramagnetic species will be taken here as those of "typical" planar copper complexes containing four oxygen donor atoms such as Cu(acetylacetonate)₂ ($\mu_{\text{eff}} = 1.90 \text{ BM}^{24}$). Experimental

(20) J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967).

(21) F. G. Herring, R. C. Thompson, and C. F. Schwerdtfegen, *Can. J. Chem.*, **47**, 555 (1969).

(22) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **6**, 227 (1953).

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(24) B. N. Figgis and C. M. Harris, *J. Chem. Soc.*, 855 (1959).

values for four of the compounds studied are listed in Table I. The magnetic moments used for the benzoate and the *p*-methylbenzoate compounds were those reported for the solid state.¹⁴

The percentage of each compound in the triplet state is listed in Table IV. Since the observed chemical

TABLE IV
PERCENTAGES OF THE COMPOUNDS IN THE PARAMAGNETIC STATE

[Cu(benzoate) ₂] ₂	54%
[Cu(<i>o</i> -methylbenzoate) ₂] ₂	56%
[Cu(<i>m</i> -methylbenzoate) ₂] ₂	55%
[Cu(<i>p</i> -methylbenzoate) ₂] ₂	54%
[Cu(2,6-dimethylbenzoate) ₂] ₂	51%
[Cu(3,5-dimethylbenzoate) ₂] ₂	58%

shifts are weighted averages of the chemical shifts of the diamagnetic and the hypothetical fully paramagnetic molecules, the isotropic shifts are proportional to the populations of the paramagnetic molecules. Calculated hypothetical isotropic shifts for the fully paramagnetic molecules are listed in Table V.

TABLE V
HYPOTHETICAL ISOTROPIC SHIFTS AT 20°, Hz

	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	Methyl
[Cu(benzoate) ₂] ₂	+99	-241	+497	...
[Cu(<i>o</i> -methylbenzoate) ₂] ₂	+220	-240	+464	+2
[Cu(<i>m</i> -methylbenzoate) ₂] ₂	+100	-247	+449	+7
[Cu(<i>p</i> -methylbenzoate) ₂] ₂	+41	-237	...	-90
[Cu(2,6-dimethylbenzoate) ₂] ₂	...	-263	+314	-156
[Cu(3,5-dimethylbenzoate) ₂] ₂	+79	...	+431	+10

Calculations treating the fully paramagnetic molecules as triplet states rather than essentially as biradicals changes the magnitudes of the isotropic shifts only about 10%. The overall resulting pattern and the conclusions to be drawn do not differ significantly.

The contact shifts corrected for the dipolar contributions are listed in Table VI. Although variable-tem-

TABLE VI
HYPOTHETICAL CONTACT SHIFTS AT 20°, Hz

	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	Methyl
[Cu(benzoate) ₂] ₂	+2	-275	+467	...
[Cu(<i>o</i> -methylbenzoate) ₂] ₂	+123	-274	+434	-106
[Cu(<i>m</i> -methylbenzoate) ₂] ₂	+3	-281	+419	-23
[Cu(<i>p</i> -methylbenzoate) ₂] ₂	-56	-271	...	-113
[Cu(2,6-dimethylbenzoate) ₂] ₂	...	-297	+284	-264
[Cu(3,5-dimethylbenzoate) ₂] ₂	-18	...	+401	-20

perature studies would provide a very appropriate way of checking the above conclusions, the low solubilities of the compounds made satisfactory low-temperature measurements impossible. In addition, high temperatures seem to cause polymerization of at least some of the compounds.

The nmr spectra of [Cu(formate)₂·urea]₂ and [Cu(acetate)₂·urea]₂ were obtained using saturated DMSO-*d*₆ solutions. The former is one of the few known dimeric formate complexes of copper(II),²⁵ while the magnetic moment of the acetate compound¹⁵ suggests that it also has the dimeric structure. Although the formate proton could not be found, the broad (~2000 Hz) acetate resonance was observed at -746 ± 20 Hz relative to the methyl resonance of zinc acetate. Correction for the dipolar shift (+124 Hz) and the population distribution leads to a contact shift

(25) D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, **9**, 1626 (1970).

of -1673 Hz. The effect of the unpaired electrons on T_1 of the methyl protons was quite striking. The methyl resonance was too broad to observe at normal rf power levels, *i.e.*, under conditions where the urea and the residual DMSO protons could be readily observed. Only at very high power levels, where the urea and DMSO protons were saturated, were the acetate protons observable.

The contact shifts listed in Table VI show quite clearly that spin density from the copper ions is delocalized into the molecular orbitals of the bridging ligands. Furthermore, the pattern of the signs of the contact shifts, when considered with the sign of the acetate protons, is consistent only with a predominantly σ delocalization mechanism within the carboxylate groups. In the $^3A_{2u}$ state, both unpaired electrons are in orbitals which are essentially $d_{x^2-y^2}$ in character⁵ and which form σ bonds with the carboxylate ligands. These two electrons, which would be aligned with the magnetic field, mix with the ligand σ orbital system, thus placing positive spin density (up spin) on all atoms with predominantly σ molecular orbital character.¹⁰ The overall effect is then downfield contact shifts, the magnitude of the contact shifts attenuating as the number of bonds between the copper ions and the protons increases. Thus the resonance of the methyl protons of the acetate complex is shifted downfield several hundred Hz, much more than that of the ortho protons of the benzoate derivatives, but much less, presumably, than that of the single hydrogen of the formate complex. We were unable to detect the formate proton resonance of the formate complex, even using deuterated urea, but Inoue and Kubo¹³ have shown, using broad-line techniques, that two polymeric, antiferromagnetic formate complexes with an anti-anti structural arrangement similar to that of the dimeric derivative do exhibit large (~ 30 – 50 ppm) downfield shifts. It is also likely that a π -delocalization mechanism from the copper into the ligands would result in a reversal of sign on going from the formate to the acetate, as has been observed for some acetylacetonates.²⁶

The pattern of contact shifts of the aromatic protons of the benzoate complexes suggests that a π -delocalization mechanism is superimposed on the σ delocalization in the phenyl rings. To be completely consistent with a π mechanism, the ortho proton contact shifts should be about $+400$ Hz, but the small downfield shifts may be rationalized on the basis of the σ mechanism discussed above. The resulting pattern of alternating spin densities is then consistent with π -delocalization into the aromatic rings. Although the meta-methyl contact shifts are anomalous, the change in sign on substituting the ortho and para protons by methyl groups is also consistent with the π mechanism.¹⁰

The mechanism of delocalization of spin density onto the aromatic rings is not known, although it may involve

(26) A. Forman, J. N. Murrell and L. E. Orgel, *J. Chem. Phys.*, **31**, 1129 (1959).

hyperconjugation.²⁷ Fitzgerald and Drago²⁸ have obtained similar results with the complex ion $[\text{Ni}(\text{benzylamine})_6]^{2+}$. Their nmr data indicated that electron spin is delocalized from the nickel ion into the π system of the phenyl groups *via* the methylene σ orbitals.

Possible corroboration of the σ -delocalization hypothesis is indicated in Figure 2. If the positive spin from

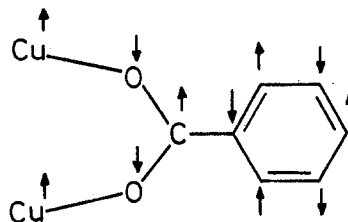


Figure 2.—Mechanism of transmission of spin density into the π system of the bridging benzoate group.

the copper atoms is delocalized throughout the ligand π system, the resulting alternation of the signs of the spin densities would be expected to result in positive spin densities on the ortho and para protons. This is just opposite to what is observed.

In concluding, we note that equations of the form¹³

$$\frac{\Delta H}{H} = -a_i \left(\frac{\gamma_e}{\gamma_N} \right) \frac{\chi - N\alpha}{g\beta N} \quad (3)$$

are not applicable to calculations of electron spin–nuclear spin coupling constants in antiferromagnetic systems such as those discussed here. Temperature dependences of contact shifts for systems which have a diamagnetic ground state and a thermally accessible paramagnetic excited state are given by the equation¹⁰

$$\frac{\Delta H}{H} = \frac{\Delta\nu}{\nu} = -a_i \left(\frac{\gamma_e}{\gamma_N} \right) \frac{g\beta S(S+1)}{3kT[\exp(\Delta G/kT) + 1]} \quad (4)$$

where ΔG is the free energy difference between two states.

Furthermore, since delocalization of spin density from the copper ions is into the σ rather than the π system of the ligands, values of a_i calculated from eq 4 cannot be used to calculate spin densities on the carboxylate carbon atoms of the formate and acetate complexes. The mixing of σ and π delocalization into the aromatic rings of the benzoate complexes would also render suspect any calculations of spin densities on the ring carbon atoms.

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(27) D. A. Levy, *Mol. Phys.*, **10**, 233 (1966).

(28) R. J. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 2879 (1970).