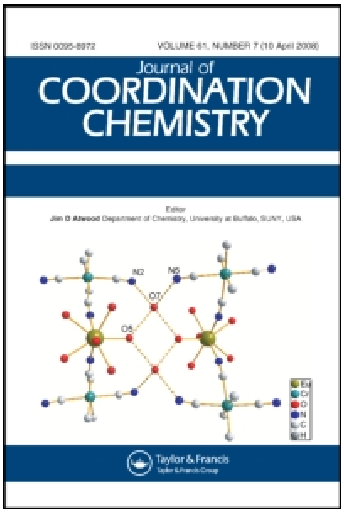

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LINEAR CHAIN FATTY DIACIDS: COPPER(II) COMPOUNDS

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LINEAR CHAIN FATTY DIACIDS: COPPER(II) COMPOUNDS

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Copper(II) complexes of linear chain fatty diacids have been obtained in the solid state with diacids containing up to thirteen carbon atoms. The green compounds were studied by spectroscopic and magnetic methods. The results conform to an antiferromagnetically coupled dimer model which can be influenced by distortions in the carboxylate bridge structure. Thus the magnetic exchange parameter is at a maximum of 360 cm^{-1} in copper(II) adipate and decreases, as the chain length increases, to a value of 280 cm^{-1} in copper(II) brassylate. The hydrophobic methylene chains influence the inter-chain packing interactions at the polar carboxylate functions.

INTRODUCTION

Linear chain fatty diacids are simple molecules of biological importance. In the series succinic, adipic, sebacic acids, *etc.*, the two carboxylic acid functional groups are separated by a hydrocarbon chain of increasing length. These acids form polymeric copper(II) complexes[1] where the metal ions bridge two carboxylate groups forming infinite chains as illustrated in Figure 1. Furthermore the copper(II) complexes have the familiar dimer structure found for many monocarboxylic acids.[2] In contrast to other carboxylates, copper(II) complexes of dicarboxylic acids have been scarcely studied.[3] One expects these compounds to be interesting with respect to their magnetic properties. As the hydrophobic chain length increases in this series, some of the more subtle effects influencing the antiferromagnetic properties of such compounds should be revealed. We wish to present the findings of our magnetic and spectroscopic investigations on the new copper(II) complexes obtained as the chain length increases up to thirteen carbon atoms in brassylic acid.

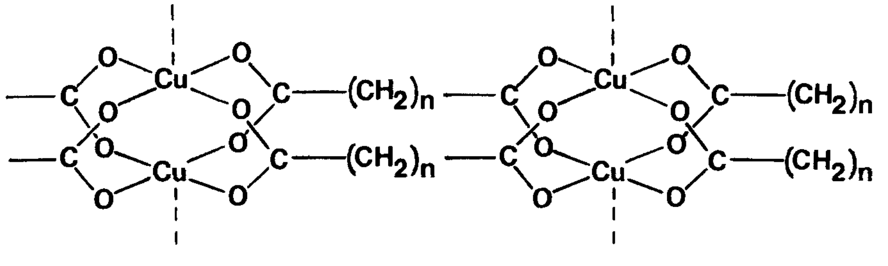

FIGURE 1 Schematic outline of the structure of copper(II) complexes of saturated dicarboxylic acids.

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EXPERIMENTAL

Synthesis

The longer-chain fatty diacids are not sufficiently soluble in water even as their sodium salts to use the normal aqueous preparation route. Two methods of synthesis were used. In the first, stoichiometric amounts of copper(II) sulphate and dicarboxylic acid were dissolved in water containing enough alcohol to dissolve more than half the fatty diacid. An excess of urea was then added and the solutions thermostatted for several days at 60°. The green complexes which slowly precipitated were filtered and washed with water, then ethanol and air-dried. The yield of complex was close to 80%. In the second, a solution containing copper(II) sulphate in water was connected to a solution of disodium dicarboxylate in alcohol *via* a U-tube filled with water through a stopcock, the two solutions were allowed to diffuse for several days and then the asembly was opened to collect the green precipitate which was treated as in the first method. The yields were near 50% in this case. The copper(II) complexes were obtained in good analytical purity.

Physical measurements

The EPR spectra were recorded with a Varian E-9 spectrometer operating at

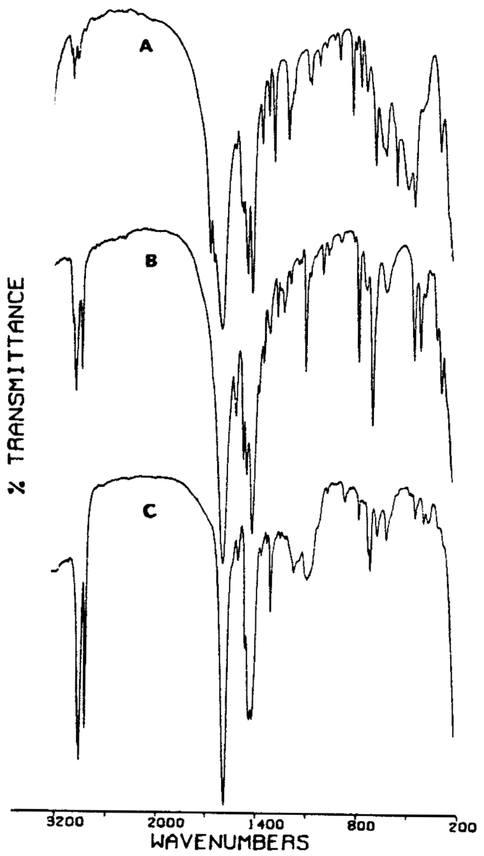

FIGURE 2 IR spectra of copper(II) glutarate (A), copper(II) pimelate (B) and copper(II) brassylate (C).

X-band frequencies as described previously.[1] Magnetic susceptibilities were measured by the Faraday method as described elsewhere.[7] Visible spectra were recorded on a Cary 14 spectrometer. The samples were mulled in nujol. KBr pellets were used for the infrared spectra which were recorded on a Nicolet MX-1 spectrometer.

RESULTS AND DISCUSSION

The green copper(II) complexes of longer-chain, fatty acids are solids insoluble in the common solvents due to their polymeric structure. Adding cupric ions directly to the disodium dicarboxylates or *vice versa* causes the immediate precipitation of complexes with many impurities. Our synthetic methods, selected for their slow rate of complex formation, yielded products of good analytical purity. Selected infrared spectra are presented in Figure 2. The copper(II) complexes show typical symmetric and antisymmetric COO stretching vibrations at $\simeq$ 1410 cm^{-1} and $\simeq$ 1585 cm^{-1}, respectively. As the organic chain length increases, the CH_2 carbon-hydrogen stretching absorptions become progressively more intense, as do the CH_2 wagging absorptions near 1400 cm^{-1}, thus partly masking the symmetric COO stretching vibrations. The other peaks have not been assigned but belong to the CH_2 twisting, scissoring and rocking modes and to COO bending modes.

The EPR spectra show triplet state paramagnetic absorptions with additional absorptions of varying intensity near $g_{\perp} \sim 2.16$ characteristic of mononuclear impurities in a doublet state. The spin Hamiltonian parameters solved in the usual way[8] are reported in Table I together with data obtained from the visible absorption spectra.

The 77 K EPR spectra show resolved H_{z2}, H_{x2} and H_{y2} absorptions as shown in Fig. 3. The dicopper hyperfine structure is not resolved in any of the presently reported complexes except in the case of copper(II) glutarate where the H_{z1} absorptions shows a few shoulders corresponding to the excepted seven line pattern. All the compounds show fairly well resolved $S = ½$ signals with $A_{\parallel}$ splitting. The brassylate is somewhat unusual in that this signal is superimposed on a broad absorption also centred near $g = 2$, as shown in Figure 3. Copper(II) adipate also shows interesting behaviour in terms of the temperature dependence of the EPR spectra. Figure 4 shows the broad absorption occuring at room temperature which scans the range 0 to 4500 gauss (X-band). As the temperature is lowered the triplet state features emerge and one strong broad band occurs near $g = 4$. This absorption is no longer observed when the temperature is below 150 K, and at 77 K, a classical spectrum is obtained.

TABLE I
EPR† data and electronic spectra for the copper(II) dicarboxylates.

Compound	$g_{\perp}$	$g_{\parallel}$	g_{av}	$\lvert D \rvert$ (cm^{-1})	$\nu_{max}(\mu m^{-1})$	
Cu succinate	2.065	2.341	2.157	0.332	1.47	2.7 sh
Cu succinate.2 H_2O	2.077	2.350	2.168	0.320	1.40	2.7 sh
Cu glutarate	2.095	2.380	2.190	0.338	1.35	2.7 sh
Cu adipate	2.066	2.351	2.161	0.340	1.50	2.7 sh
Cu pimelate	2.068	2.354	2.163	0.332	1.46	2.7 sh
Cu suberate	2.070	2.352	2.168	0.336	1.48	2.7 sh
Cu azelate	2.069	2.349	2.166	0.338	1.47	2.7 sh
Cu sebacate	2.061	2.342	2.154	0.335	1.47	2.7 sh
Cu undecandedioate	2.071	2.354	2.169	0.339	1.43	2.7 sh
Cu brassylate	2.069	2.345	2.165	0.340	1.44	2.7 sh

†g (± 0.002)

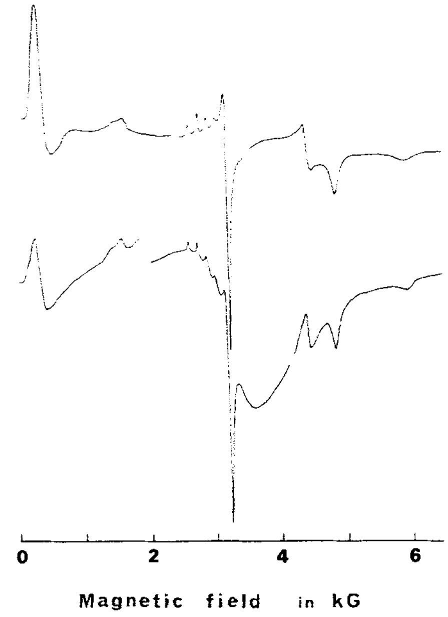

FIGURE 3 EPR spectra at 77 K and 9.1 GHz of copper(II) azelate (top) and copper(II) brassylate (lower spectrum).

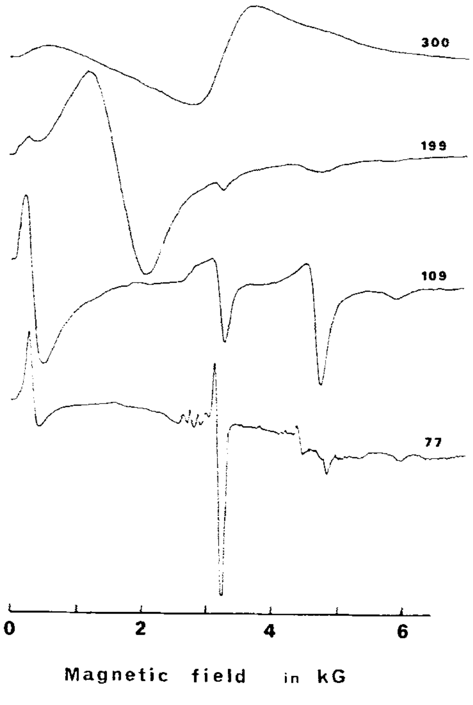

FIGURE 4 EPR spectra of copper(II) adipate as a function of temperature (X-band).

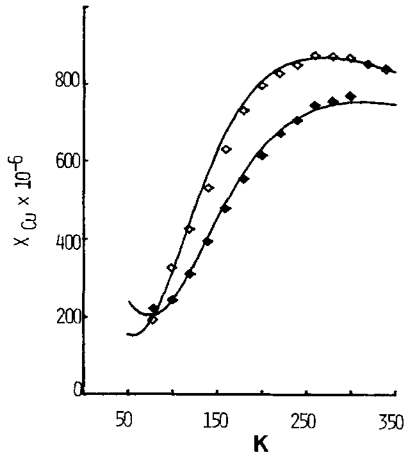

FIGURE 5 The plot of the experimental corrected magnetic susceptibility data (x_M^{CORR}) *vs* T, for copper(II) pimelate (open symbols) and copper(II) adipate (closed symbols). The curves represent the best fit to the data obtained with eq. (*1*).

The magnetic susceptibilities, corrected for diamagnetic contributions, show a low room temperature paramagnetic moment. The behaviour of the magnetic susceptibilities as a function of temperature show the complexes are antiferromagnetically coupled with a maximum close to room temperature. The data was fitted to a theoretical curve calculated with a computer programme and which included an adjustable paramagnetic component described by the usual Van Vleck equation, yielding (*1*)

$$\chi_M^{corr} - N_\alpha = \left(\frac{g^2N\beta^2}{3KT}\left(1 + \frac{1}{3}\left(e^{-2J/kT}\right)\right)^{-1}\right)(1-x) + x\left(\frac{g^2N\beta^2}{4KT}\right) \qquad (1)$$

where x is the fraction of mononuclear species. The g values were fixed at the g-average values obtained by EPR. Two examples of the temperature dependent magnetism and the fitted curves are presented in Figure 5, and the data is gathered together in Table II.

TABLE II

Molar magnetic susceptibility $\chi_M^{corr} \times 10^{-6}$ data for Cu adipate (1), Cu pimelate (2), Cu suberate (3), Cu azelate (4), Cu sebacate (5), Cu undecanedioate (6) and Cu brassylate (7).

T(K)	1	2	3	4	5	6	7
340		844	827	771	851	900	
320		856	827	794	859	903	942
300	771	872	825	797	867	903	947
280	756	875	822	804	867	918	963
260	746	877	822	805	865	920	964
240	706	853	829	798	851	918	954
220	670	830	792	777	810	916	932
200	614	798	751	733	777	889	888
180	554	732	711	673	704	884	820
160	478	631	615	618	647	780	757
140	395	532	515	485	524	724	660
119	310	427	397	392	459	664	507
99	243	326	361	280	393	565	371
79	226	223	317	192	279	543	291
M.I. (%)[1]	2	1	2.5	1	1.5	6	1.5
$\Delta \times 10^{-6}$ c.g.s.[2]	128	139	150	161	172	183	208

[1]M.I. = mononuclear impurity; [2]Δ = diamagnetic correction.

Green copper(II) complexes of dicarboxylic acids can be prepared near pH $\simeq$ 5.5. As is usual for copper(II) carboxylates, the complexes are sensitive to pH changes and blue-green compounds result at higher pH, similar to the hydrosuccinate copper(II) case reported previously.[9] We have also isolated some blue paramagnetic copper(II) complexes with the diacids as well as blue alkali metal salts, analogous to those previously reported in the case of succinic acid.[10] The homologous series of complexes herein reported were all prepared in a similar way. Although the succinate crystallizes readily, only powders were obtained for the higher homologues which are all anhydrous compounds. On the basis of the similarity in the physical data pertaining to these complexes, we can propose similar structures for all the members of the present series, based on the structure known for copper(II) succinate,[11] schematically presented in Fig. 1.

The infrared spectra do not allow us to confirm that the compounds are isostructural, contrary to the case of copper(II) and chromium(II) succinates.[12] This is because the parent diacids have different spectra, and the more flexible longer chains may adopt a greater number of possible conformations. Indeed, the CH_2 twisting and wagging modes reveal complicated patterns. The antisymmetric and symmetric CH stretching bands appear systematically at 2915 and 2840 cm^{-1} and increase regularly in intensity as the chain length increases, as expected for species with higher CH_2 contents.

The EPR and magnetic data are conveniently explained by the usual spin-paired model accounting for the properties of dimeric copper(II) carboxylates. The $g_\perp$ values fall in the range 2.061 to 2.095 and the $g_{\parallel}$ values in the range 2.342 to 2.380, which yield normal values for the Landé factors. The zero-field parameters $|D|$ range from 0.320 to 0.340 cm^{-1}, close to the values reported for binuclear copper(II) carboxylates.[12] The rhombic distortion in the copper(II) coordination geometry is apparent at liquid nitrogen temperatures only as shown in Figs 3 or 4. The E values are 120 gauss and are the same within experimental error for the whole series of compounds presented. It remains unclear why copper(II) adipate shows a strong and unexpected absorption near $g = 4$ at intermediate temperatures. However, we note that the half-field position of this absorption is an indication that it may be a forbidden or $\Delta m_s = 2$ transition. Copper(II) adipate may have a particular packing arrangement promoting intra- or inter-dimer interactions. This same compound is precisely the one that yields the largest magnetic exchange parameter in the series, as discussed below. The spectral features are in good agreement with previous observations on other members of the series.[1]

The exchange parameters, $-2J$, listed in Table III range from 360 to 280 cm^{-1}. They are of the same order of magnitude as found in other copper(II) carboxylates and conform to previous observations. Table III shows the malonate to be an exceptional case, with $-2J$ much smaller than is found with the other diacids. The oxalate is strongly influenced by water content, reflecting the dependence of the super-exchange interactions on small variations in structure and exchange pathways.

Upon comparing the metal-metal distances or the pKa values of the acids in dimer complexes of carboxylic acids, no clear and definitive trend has been found in the magnetic parameters, indicating the interaction is of the super-exchange type and depends on the stereo-electronic properties of the bridging ligands. The Cu-Cu, Cu-O and Cu-basal plane distances, 2.610, 1.975 and 0.197 Å, respectively, in copper(II) succinate dihydrate are well comparable to those of copper(II) acetate monohydrate, 2.616, 1.969 and 0.19 Å, respectively. Yet, $-2J$ is $\approx$330 cm^{-1} for the dicarboxylate, almost 50 cm^{-1} more than the corresponding value of 284 cm^{-1} found in the acetate complex. The exchange coupling seems to be sensitive not just to the Cu-O-C-O-Cu bridge distance but mostly to the bond

TABLE III
Review of the magnetic parameters of the copper(II) dicarboxylates.

Compound	μ eff(B.M.), (T)	g_{av}	$-2J$ (cm^{-1})	ref.
Cu oxalate	1.20 (288)	2.20[1]		5
			330.6	6
Cu oxalate.0.3 H_2O	1.22 (297)		379.5	4
Cu oxalate.0.5 H_2O	1.25 (295)			5
Cu malonate	1.78 (300)		60.6	4
	1.86 (300)			3
	1.76 (286)			5
Cu malonate.2.5 H_2O	1.79 (319)		8.3	4
Cu malonate.3 H_2O	1.95 (296)			5
Cu succinate	1.40 (299)			5
	1.40 (300)	2.12[1]	332	3
	1.37 (328)	2.12[1]	324	4
	1.39 (298)			9
Cu succinate.2 H_2O	1.40 (298)			5
	1.40 (321)	2.22[1]	331	4
	1.40 (300)	2.20[1]	329	3
Cu glutarate	1.45 (300)			5
	1.34 (292)	2.17[1]	320	4
	1.40 (300)	2.16[1]	325	3
Cu adipate	1.33 (289)			5
	1.25 (314)	2.04[1]	348	4
	1.36 (300)	2.161[2]	360	This work
Cu pimelate	1.41 (291)			5
	1.40 (300)	2.163[2]	305	This work
Cu suberate	1.44 (288)			5
	1.45 (300)	2.16[1]	322	3
	1.40 (300)	2.168[2]	325	This work
Cu azelate	1.41 (290)			5
	1.38 (300)	2.166[2]	320	This work
Cu sebacate	1.44 (288)			5
	1.44 (300)	2.154[2]	310	This work
Cu undecanedioate	1.47 (300)	2.169[2]	300	This work
Cu brassylate	1.51 (300)	2.165[2]	280	This work

[1]From magnetic data; [2]EPR value.

angles in the bridge. This is as expected considering other work which shows that orbital overlap is indeed sensitive to small changes in orientation of the orbitals of bridging atoms.[13]

In the case of copper(II) carboxylates, it is known that the anhydrous complexes are subject to inter-dimer interactions leading to broadening of the room temperature EPR spectra.[14] The axial positions in anhydrous copper(II) propionate[15] or butyrate[16] are occupied by oxygen atoms from carboxylate groups of neighboring molecules. A similar effect may be proposed for the dicarboxylates presented here. Distortions of varying magnitude may then account for the small variations encountered in the $-2J$ values. Copper(II) adipate has the largest $-2J$ value of 360 cm^{-1}, corresponding to the more favourable geoemtry of the bridging carboxylate groups for increased super-exchange interaction. Clearly the other members of the series can differ only slightly in the basic structure. The longer chains prefer hydrophobic contact interactions between the methylene chains to the expense of the packing interactions occuring in the vicinity of the polar groups. This leads to a regular decrease in the $-2J$ values from 360 cm^{-1}, for the adipate, to 280 cm^{-1} for the brassylate. Such an influence, presumably due to inter-dimer interactions, causes variations of the order of 30% in the super-exchange parameter.

Despite the magnitude of interdimer effects on $-2J$, we believe our data show that small distortions in bond angles in the bridging ligands are sufficient to explain the observed trend.

On the basis of our findings we draw several conclusions. Linear chain fatty diacids form dimer copper(II) carboxylate units linked into infinite polymer chain arrangements. Magnetic results show the copper(II) ions are antiferromagnetically spin-coupled by a super-exchange mechanism *via* the π-bond system of the carboxylate groups. Even though there are no magnetic exchange or dipolar interactions between the dimer units along the methylene chains, a significant decrease in $-2J$ occurs from the adipate to the brassylate. We interpret this as evidence that the super-exchange pathway is sensitive to small variaitons in bond angles within the bridging carboxylate groups. Thus interdimer interactions can alter the magnetic properties of copper(II) carboxylates in the solid state by distorting the symmetry required for optimum orbital overlap in the carboxylate bridges.

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