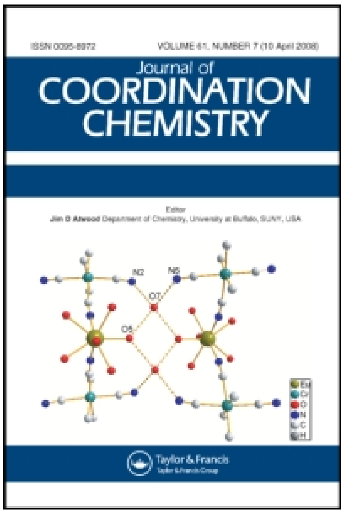

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Mroziński, J. and Heyduk, E.(1984) 'DIMERIC COPPER(II) COMPLEXES WITH BRIDGING UNSATURATED CARBOXYLIC LIGANDS. CORRELATION OF pKa VALUES AND MAGNETIC EXCHANGE PARAMETERS', Journal of Coordination Chemistry, 13: 4, 291 — 298

To link to this Article: DOI: 10.1080/00958978408073881

URL: http://dx.doi.org/10.1080/00958978408073881

J. Coord. Chem., 1984, Vol. 13, p. 291-298
0095-8972/84/1304-0291 $18.50/0

DIMERIC COPPER(II) COMPLEXES WITH BRIDGING UNSATURATED CARBOXYLIC LIGANDS. CORRELATION OF pKa VALUES AND MAGNETIC EXCHANGE PARAMETERS

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(Received January 11, 1984)

The copper(II) salts* of acrylate, crotonate and 3,3′-dimethyl-acrylate anions exist with reduced magnetic moments. Magnetic susceptibility measurements (80–300 K) revealed the strong antiferromagnetic exchange coupling between the copper(II) ions. Singlet-triplet separation values obtained by least-squares fitting to the modified Bleaney-Bowers equation are equal to −302, −305 and −324 cm^{-1}, respectively. Unusual EPR spectra of these compounds, which, besides lines due to dimeric units, also exhibit the lines characteristic for polymeric copper(II) chains ($g \approx 2.10$) are the basis for discussion of the molecular structures of the compounds.

INTRODUCTION

From among copper(II) compounds capable of the formation of dimeric structures, the carboxylates have been investigated for some decades.[1,2] Their structures are in most cases analogous to the structure of copper(II) acetate monohydrate in which two copper ions are coupled by four acetate groups, and the axial positions are occupied by water molecules.[3-8]

Copper(II) carboxylates with this dimeric structure exhibit anomalous paramagnetic properties. Magnetic susceptibilities with increasing temperature pass through a maximum and systematically decrease with further temperature increase. Such magnetic properties are due to the presence of two states: the singlet ground state and the triplet. The singlet-triplet separation determines the magnetic behaviour of these antiferromagnetic molecular systems.[9-22]

Relatively few data have been published on compounds with unsaturated carboxylic acids. This paper is concerned with dimeric copper(II) complexes with the RCO_2^- bridge groups deriving from the α, β -unsaturated carboxylic acids acrylic, crotonic and 3,3′-dimethylacrylic acids.

EXPERIMENTAL

Synthesis

The tetra-μ-carboxylato-dicopper(II) compounds of composition CuX_2 (where X = acrylate, crotonate and 3,3′-dimethyl-acrylate) were prepared by treating copper carbonate with 10-15% more than the stoichiometric ratio of the corresponding free acid in hot methanol solution. Reaction was carried out under reflux with the condenser fitted with a $CaCl_2$ drying tube for 3 h. The hot solution was filtered and left to crystallize. The sapphire-blue crystals formed with about 40% yield. All samples were recrystallized from the hot anhydrous methanol, crushed and stored in a vacuum dessicator over anhydrous $CaCl_2$.

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*Acrylic acid = propenoic acid, crotonic acid = *trans*-2-butenoic acid, 3,3-dimethylacrylic acid = 3-methyl-2-butenoic acid.

Analysis

Tetra-μ-acrylate-dicopper(II) ($C_{12}H_{12}Cu_2O_8$); *Calcd.:* C,35.00; H,2.90; Cu,30.90; *Found:* C,35.32; H,2.95; Cu,31.20%. Tetra-μ-crotonato-dicopper(II) ($C_{16}H_{20}Cu_2O_8$); *Calcd.:* C,41.10; H,4.29; Cu,27.19; *Found:* C,41.05; H,4.31; Cu,27.30%. Tetra-μ-dimethylacrylato-dicopper(II) ($C_{20}H_{28}Cu_2O_8$), *Calcd.:* C,45.80; H,5.35; Cu,24.28; *Found:* C,45.36; H,5.59; Cu,24.41%.

Physical measurements.

Magnetic susceptibility has been measured in the range 77-300 K using a Gouy balance, calibrated with mercury tetrathiocyantocobaltate(II).[29,30] Magnetic susceptibility calculated per copper(II) ion was corrected for diamagnetism using Pascal's constants[31,32] and for temperature independent paramagnetism equal to 60×10^{-6} cm^3 mol^{-1}. The effective magnetic moment was calculated from the equation $\mu_{eff} = 2.83\ (\chi_{Cu}\ T)^{1/2}$ B.M. Exchange parameters, J, and the molar percentage of monomeric forms of the complexes were computed on a Odra 1305 computer.

Electron paramagnetic resonance spectra of complexes were measured at room temperature on a Jeolco JES-ME-3X spectrometer in the X band range. Magnetic fields were calibrated on Mn(II) in MnO ($\Delta H_{3\text{-}4} = 86.9$ G). MJ-110R-Radiopan a nuclear magnetometer was used as a magnetic field marker. Reflectance spectra of undiluted samples have been recorded in the range 250–1000 nm on a Beckman UV 5240 spectrophotometer. Infrared spectra were measured in KBr mulls on a Perkin-Elmer 621 spectrophotometer in the 400–4000 cm^{-1} range.

RESULTS AND DISCUSSION

The correlation of structure parameters and magnetic and spectroscopic properties as well as the influence of the donor-acceptor character of axial and bridging ligands on the magnetic superexchange interaction in the copper(II) carboxylate dimers is the basic problem in studies of these compounds.

The pKa value is usually regarded as the measure of the donor-acceptor ligand effect, although it does not take into account the effect of the metal-ligand bond, or steric effects in axial ligand coordination.

In the present paper we deal with three copper(II) dimers with acrylate, crotonate and 3,3′-dimethylacrylate ligands. In this series of ligands the pKa value varies from 4.25 for acrylic acid to 4.71 and 5.10 for crotonic and 3,3′-dimethylacrylic acids, respectively.[33]

Fresh samples of compounds obtained from methanol solution contain one mol of water per mol of dimer (± 0.2) as confiremd for thermogravimetric and spectroscopic (IR band at *c* 3450 cm^{-1}) methods. The hydrated complex samples, when stored under unhydrous conditions, lose water to yield the anhydrous analogues. The results discussed here concern the anhydrous complexes.

The temperture dependence of magnetic susceptibility for the carboxylates are shown in Fig. 1. Magnetic moments determined at room temperature (Table I) are much lower than the spin-only values for the Cu^{2+} ion and are typical for copper complexes with super-exchange magnetic interactions. In the antiferromagnetics under study, the magnetic interactions are limited to two magnetic centres; the singlet-triplet separation is the measure of this effect, $|2J|$. Determination of this

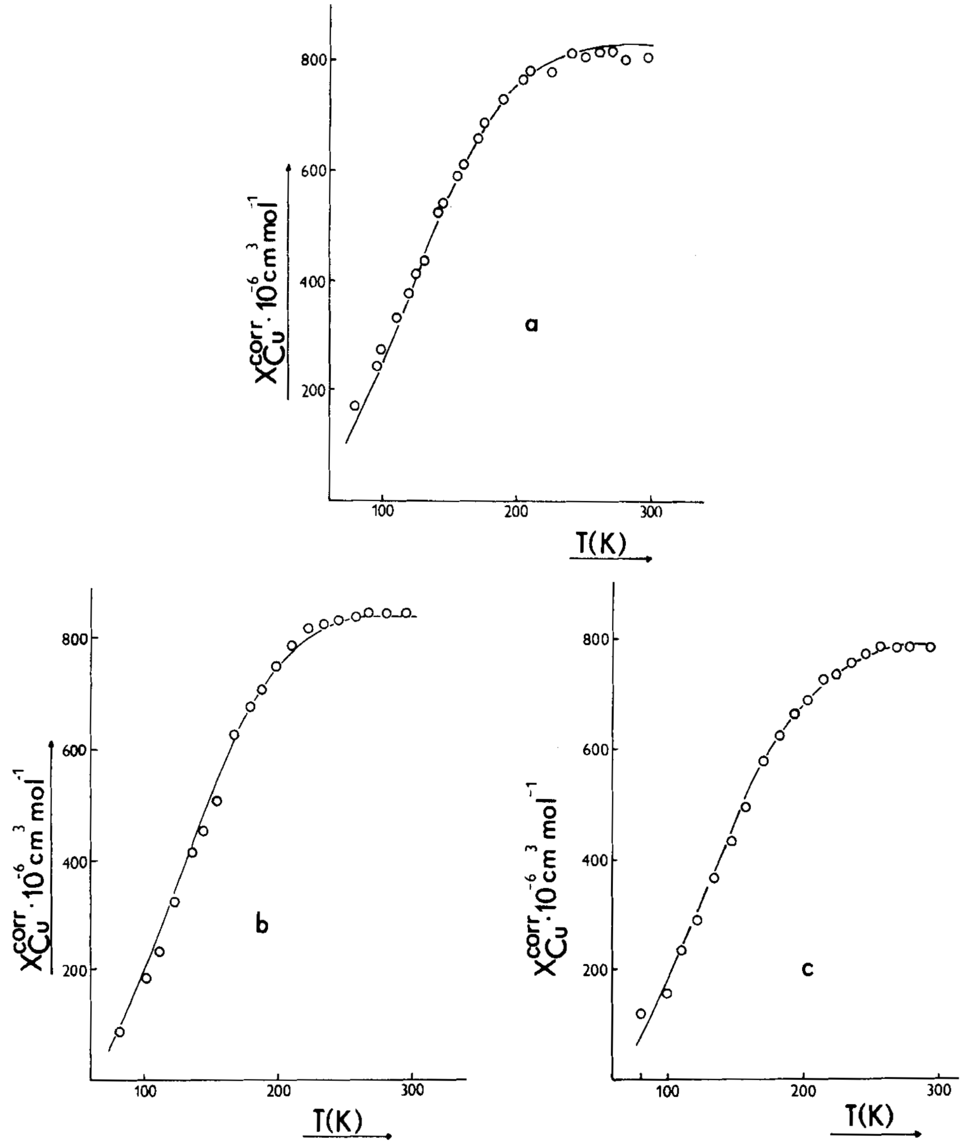

FIGURE 1 Temperature dependence of magnetic susceptibility of the copper(II) carboxylates: acrylate (a), crotonate (b), 3,3'-dimethylacrylate (c). In all figures circles represent the experimental values, and solid lines show calculated susceptibilities.

TABLE I
Magnetic data[a] and EPR parameters.[b]

Compound	μ_{eff} (B.M.)	2J (cm^{-1})	g	g	g_{av}[c]	| D | (cm^{-1})	E(cm^{-1})
$Cu_2[CH_2 = CHCO_2]_4$	1.37	−302	2.40	2.08	2.19	0.350	0.006
$Cu_2[CH_3CH = CHCO_2]_4$	1.42	−305	2.39	2.07	2.18	0.337	0.011
$Cu_2[(CH_3)_2C = CHCO_2]_4$	1.36	−324	2.41	2.08	2.19	0.345	0.011

[a] Magnetic measurement at room temperature. [b] No line of monomeric form complexes were observed. [c] $g_{av}^2 = 1/3(2g_{\perp}^2 + g_{\parallel}^2)$.

parameter was made by fitting the results to the modified Bleaney-Bowers expression[9]

$$\chi_{Cu}^{corr} = \frac{Ng_{av}^2\beta^2}{3kT} \; [1 + 1/3(e^{-2J/kT})]^{-1} \; (1-x) + \left(\frac{Ng_{imp}^2\beta^2}{4kT}\right) x$$

where $\chi_{Cu}{}^{corr}$ is the molar magnetic susceptibility calculated per copper(II) ion, J is the exchange parameter in the Heisenberg-Dirac-Van Vleck Hamiltonian $\mathcal{H} = -2J\ S_1S_2$, x is the percentage of any monomeric form of the complex and other symbols have their usual meaning.

The spectroscopic splitting parameters g_{av} obtained from the EPR spectra (Table I) were used as constants in the fitting of the data. The minimization of the sum of squares of the deviation ERR $= \sum_{i=1}^{n}(\chi_i{}^{calcd} - \chi_i{}^{exptl})^2$ was the criterion used determine the best fit.

The singlet-triplet separation values determined for the series of dimers are equal to −302, −305 and −324 cm^{-1} for copper(II) acrylate, crotonate and 3,3′-dimethyl-acrylate complexes, respectively. In the case of copper(II) acrylate the 2J value is the same as that found for anhydrous copper(II) acetate.[10] Singlet-triplet separation value increase is consistent with decreasing carboxylic acid strength. With a pKa increase, also the electron density on the carboxyl group oxygens increases, and a related electron density change in the magnetic super-exchange paths is directly responsible for the variation of singlet-triplet separation values.

The room temperature EPR spectra of the unsaturated carboxylates exhibit absorption typical for the randomly oriented triplet state (S = 1) of axial symmetry. Such a spectrum is typical also of dimeric systems in which are present the singlet ground state and the thermally accessible triplet excited state. The EPR spectra of the dimers were interpreted using spin Hamiltonian

$$\mathcal{H} = g\beta H\hat{S} + D\hat{S}_z{}^2 + E(\hat{S}_x{}^2 - S_y{}^2) - 2/3\ D$$

where D and E are the zero-field splitting parameters, x, y, z are the main axes of the coordinate system with respect to the Cu-Cu vector. The zero-field splitting parameters $|D|$ of the dimers are within the limits 0.337–0.351 cm^{-1} and exceed the microwave quantum applied. Since $|D| > h\nu$, the EPR spectra show the allowed lines corresponding to the $\Delta M_s = \pm 1$ transitions. No $\Delta M_s \pm 2$ forbidden transition in the downfield area of the spectra was observed. The rhombic zero-field parameter $|E|$ values are lower than the $|D|$ values, and are within the limits 0.006–0.011 cm^{-1}.

The EPR spectra of the acrylate, crotonate and 3,3′-dimethyl-acrylate complexes (Fig. 2.) show a single broad line in the central field area, with the values g = 2.10 ± 0.01, as well as lines typical of the dimeric units (H_{z1}, H_{12}, H_{z2}). At higher temperatures, the spectra of such systems show considerable line broadening and in the extreme case only one broad line.[34-36] An EPR spectrum with one broad line (g = 2.10) is observed, for example, for the linear magnetic $[bipyH_2]\ [Cu_2CL_6]$, which contains limitless chains of dimeric $[Cu_2Cl_6]^{2-}$ units.[37]

These spectra could be interpreted as being the result of exchange interactions in excited triplet states.[34] Due to these interactions, the triplet states undergo delocalization, and the triplet excitons exhibit the ability of migration through the crystal lattice.

The observed spectra of acrylate, crotonate and 3,3′-dimethylacrylate complexes

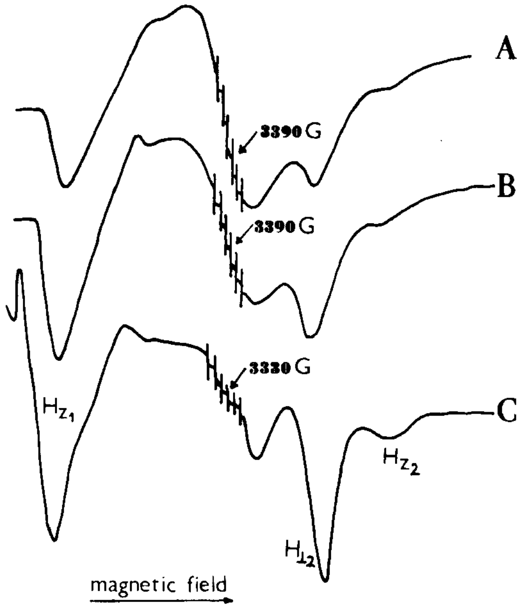

FIGURE 2 X-band (~9.4 GHz) EPR spectra of powdered samples of $Cu_2[CH_2=CHCO_2]_4$ (A), $Cu_2[CH_3CH=CHCO_2]_4$ (B), $Cu_2[(CH_3)_2C=CHCO_2]_4$ (C), at 293 K.

suggest that magnetic centres only partly contribute in the form of a triplet exciton. Interactions between excited triplet states, or more precisely the exchange frequency, is strongly temperature dependent. With sufficient temperature decrease the typical spectrum of the triplet state of the dimeric unit is obtained (Fig. 3).

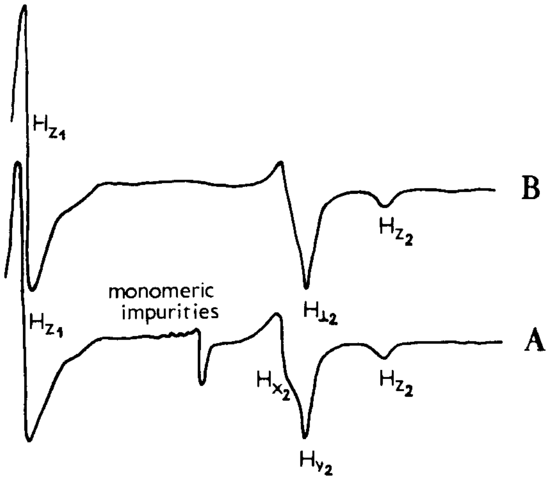

FIGURE 3 X-Band (~9.11 GHZ) EPR spectra of different samples of $Cu_2[CH_2=CHCO_2]_4$ at 133 K; A: sample with a small amount of monomeric impurities, B: sample of a very high purity.

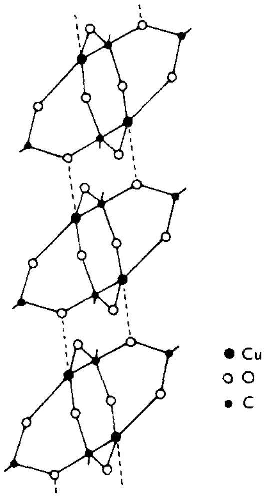

FIGURE 4 The structure of anhydrous copper(II) propionate (reported in ref. 38).

The results of the magnetic investigations as well as the ESR spectra allow the conclusion that in the crystal lattice of the anhydrous acrylate, crotonate and 3,3'-dimethylacrylate complexes there are present chains of dimeric units, linked together by apical Cu-O interaction. A similar structure has been reported for the anhydrous copper(II) propionate complex (Fig. 4).[38,39]

Reflectance spectra of the complexes in the range 250–1000 nm show both the so-called Band I and Band II, characteristic for copper(II) dimers with carboxyl bridges. Band II combined with the (Cu-O-C-O-Cu) bridge system corresponds to the $np_\pi \rightarrow \delta^*(x^2 - y^2)$ transition. This transition has practically constant energies for various carboxylic acids[40] and in the spectrum of the dimers examined appears at 375 nm.

The absorptions of Band I in the reflectance spectra shown by the acrylate, crotonate and 3,3-dimethyl-acrylate dimers are relatively broad and the position of their maxima is at 670 ± 5 nm.

Band I, corresponding to the $(d_{xz}, d_{yz}) \rightarrow (d_x{}^2 - dy^2)$ transition, exhibits a strong dependence on the donor strength of the axial ligands.[41–43] In a case of our dimers without axial ligands, the effect of the influence of bridging ligand donor strength has not been determined.

TABLE II
Carboxylate stretches of the solid complexes.

Compound	Carboxylate stretches[a]		$\Delta\nu = \nu_{asym} - \nu_{sym}$ (cm^{-1})	shift of $\nu_{asym/sym}$
	ν asymmetric (cm^{-1})	ν symmetric (cm^{-1})		
$Cu_2[CH_2 = CHCO_2]_4$	1570 vs (1565 vs)	1435 vs (1430 s)	135 (135)	+ +
$Cu_2[CH_3CH = CHCO_2]_4$	1573 vs (1561 vs)	1417 vs (1416 vs)	156 (145)	+ +
$Cu_2[(CH_3)_2C = CHCO_2]_4$	1570 vs (1525 vs)	1410 vs (1408 vs)	160 (144)	+ +

[a] The bands of the potassium salts of the appropriate carboxylic acids are given in parentheses.

Infrared spectra of the dimers show the characteristic bands in the range 1400–1600 cm^{-1} connected with symmetric and asymmetric stretching vibrations of the carboxyl groups.[44–48] In Table 2 are shown the positions of these bands and others corresponding to the same vibrations for the potassium salt of the appropriate carboxylic acid. The band corresponding to the asymmetric vibrations in the complexes are shifted by 5–18 cm^{-1} to higher frequency compared with the potassium salt of the appropriate acid. Similar effects were observed for the bands corresponding to the symmetric stretching vibrations (shifted by 1–10 cm^{-1}). These results (Table II) indicate symmetrical bridging bidentate coordination of the carboxylate group.[49–54].

ACKNOWLEDGEMENTS

This work was supported by the Polish Academy of Science, Project No. MR-I-9.

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