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The Zero-Field-Splitting Parameter *D* in Binuclear Copper(II) Carboxylates Is Negative

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High-field, high-frequency electron paramagnetic resonance measurements performed on two binuclear copper complexes, $[Cu(CH_3COO)_2]_2(H_2O)_2$ (**1**) and $[Cu(CH_3COO)_2]_2$(pyrazine) (**2**), allowed a definitive determination of the sign of the zero-field-splitting parameter *D*. Contrary to literature reports, that parameter is negative in each complex.

Copper acetate monohydrate (**1**) was the first binuclear transition-metal complex ever studied by electron paramagnetic resonance (EPR) in the famous paper by Bleaney and Bowers.[1] The wide group of binuclear complexes in which copper atoms are bridged by four carboxylato bridges in a "paddlewheel" arrangement[2] has played an important role in the history and theory of molecular magnetism. Properties of such systems are governed by the exchange interaction between two paramagnetic Cu^{2+} ions that is represented by a Hamiltonian $\mathbf{H} = J\mathbf{S}_1 \cdot \mathbf{S}_2$ and gives rise to two eigenstates of the coupled spin operator $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$. In copper carboxylates, the singlet ($S = 0$) is the ground state, while the triplet ($S = 1$) lies typically about 300 cm^{-1} higher. The triplet state undergoes a further so-called zero-field splitting (zfs) that is caused by the combined effect of the magnetic dipole−dipole interactions and exchange coupling anisotropy. Triplet-state EPR spectra are interpreted in terms of the spin Hamiltonian

$$\mathbf{H} = \mu_B B \cdot \mathbf{g} \cdot \mathbf{S} + D\{\mathbf{S}_z^{\,2} - S(S+1)/3\} + E(\mathbf{S}_x^{\,2} - \mathbf{S}_y^{\,2}) \quad (1)$$

where *D* and *E* are the zfs parameters, *B* is the magnetic induction, and other symbols have their usual meaning. Although the dipole−dipole and anisotropic exchange contributions cannot be determined separately, the former one can be calculated accurately enough from structures of binuclear systems. In the copper carboxylate dimers, the Cu−Cu and g_z directions are very close to each other, leading to a formula for the dipole−dipole contribution to D^3

$$D_{dip} = -[2g_z^{\,2} + (g_x^{\,2} + g_y^{\,2})/2]\mu_B^{\,2}/2r_{Cu-Cu}^{\,3} \qquad (2)$$

which results in -0.171 cm^{-1} for **1** ($r_{Cu-Cu} = 2.61$ Å)[4] and -0.176 cm^{-1} for **2**($r_{Cu-Cu} = 2.58$ Å),[5] while E_{dip} is close to zero. To extract the anisotropic exchange contribution to zfs, D_{ex}, one has to determine the experimental *D* parameter and subtract the calculated dipole−dipole part. Hence, knowledge of the sign of *D* is crucial for the D_{ex} determination, but it is not available from traditional low-frequency EPR or from other methods, like magnetic susceptibility measurements. The exchange-related component of zfs, D_{ex}, is of primary importance to the theory of metal−metal interactions in polynuclear complexes because it is related to the exchange interactions in excited states of a dimeric molecule:[1,3,5−9]

$$D_{ex} = [J(x^2-y^2,xy)\,\Delta_z^{\,2} - 2J(x^2-y^2,xz)\,\Delta_y^{\,2} - 2J(x^2-y^2,yz)\,\Delta_x^{\,2}]/32 \quad (3)$$

where $\Delta_z = g_z - 2.0023$, etc., and the first term in brackets is expected to be dominant. $J(x^2-y^2,n)$ represents the triplet−singlet separation in excited dimer states in which one of the copper atoms is in its electronic ground state $d_{x^2-y^2}$ while another one is in an excited state *n*. These *J* parameters should be considered as the overall singlet−triplet separations in respective excited states of a dimer rather than as simple two-electron exchange integrals between the orbitals $d_{x^2-y^2}$ and *n*.[9]

After an extensive literature search was done in the course of this work, it was concluded that, contrary to a few scattered reports, the sign of *D* in copper carboxylates has, in fact, never been experimentally determined. Bleaney and Bowers[1] stated that the exchange contribution would be positive (i.e., opposing the dipolar contribution) *if the exchange coupling in excited state were antiferromagnetic*, as it is in the ground state, and because $|D_{ex}|$ was expected to be larger than $|D_{dip}|$, the total *D* would also be positive.

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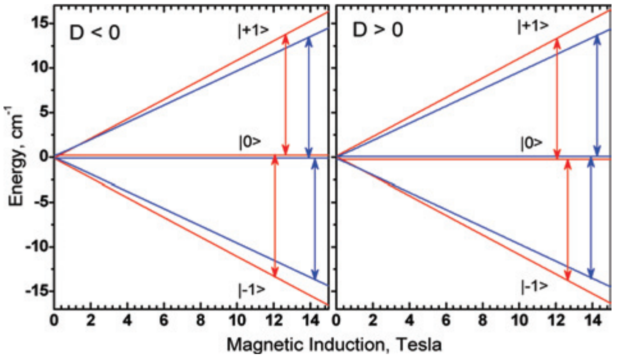

Figure 1. Energy of the triplet-state sublevels calculated with the magnetic field parallel and perpendicular to the z axis (red and blue lines, respectively) by using the EPR parameters of **2** (see Figure 2) with D either negative or positive. The distance between the horizontal red and blue lines is equal to D. The arrows of a length $\nu/c = 13.55$ cm^{-1} show EPR transitions expected at $\nu = 406.4$ GHz. kT at 50 K equals ~35 cm^{-1}.

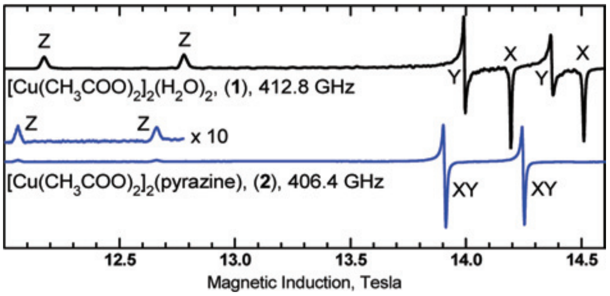

Figure 2. Powder EPR spectra at 80 K of **1**: $g_x = 2.0545(3)$, $g_y = 2.0792(2)$, $g_z = 2.3637(2)$, $D = -0.335(1)$ cm^{-1}, $E = -0.0103(1)$ cm^{-1}. Powder EPR spectra at 80 K of **2**: $g_x = 2.0608(2)$, $g_y = 2.0622(2)$, $g_z = 2.3493(3)$, $D = -0.328(1)$ cm^{-1}, $E = 0.000(1)$ cm^{-1}. Molecular orientations are designed by x, y, and z. The EPR parameters were determined and errors estimated by the global fitting of resonances measured at several microwave frequencies over the range 97−432 GHz.[10,11]

Morosin et al.[5] reported that their Q-band EPR spectra of **2** confirmed a positive sign of D, but that conclusion was not explained. In an extremely sophisticated paper dealing with the same compound, Ross et al.[6] studied polarized absorption and magnetic circular dichroism spectra to gain insight into the energy diagram of its excited states. They determined the $J(x^2-y^2,xy)$ magnitude of 50 cm^{-1} (converted to the notation used in the present paper)[7] from the energy difference between the $^3A_{2g}$ and $^1A_{2g}$ excited dimer states and, based on eqs 2 and 3, concluded that D was positive *in agreement with experiment*, i.e., with ref 5. Other authors have mistakenly considered D of ref 6, including its sign as an experimentally determined quantity.[8]

High-field EPR operating at frequencies of hundreds of gigahertz is now becoming more widely available to researchers.

At very high fields and at low temperatures, the Zeeman interaction is comparable to the thermal energy kT and different intensity patterns in EPR spectra of $S > {}^1/_2$ states are observed depending on the sign of the zfs parameters. As can be seen in Figure 1, at high magnetic fields the triplet sublevel $|-1\rangle$ ($M_s = -1$) has the lowest energy, independently of the sign of D. The EPR transition intensity is proportional to the population difference of the levels involved, and an approximate ratio R of the $|-1\rangle \leftrightarrow |0\rangle$ and $|0\rangle \leftrightarrow |1\rangle$ transition intensities can be derived directly from Figure 1.

$$R = (e^{h\nu/kT} - 1)/(1 - e^{-h\nu/kT}) \qquad (4)$$

At 406.4 GHz, R equals 1.48 at 50 K and 1.28 at 80 K, but it is only 1.01 in 9.5 GHz X-band EPR at 50 K, thus explaining the insensitivity of traditional EPR to the sign of zfs. The intensity ratios shown in Figures 3 and 4 were calculated more rigorously by taking into account the magnitude of D, different magnetic fields for the two transitions, and respective transition probabilities, but the numerical values of R did not differ significantly from those calculated from eq 4. At the z orientation, the resonance field for the more intense $|-1\rangle \leftrightarrow |0\rangle$ transition is $(h\nu + D)/g_z\mu_B$, while the weaker transition $|0\rangle \leftrightarrow |1\rangle$ occurs at $(h\nu - D)/g_z\mu_B$. The intensity information allows the assignment of resonances observed in a spectrum to respective transitions. With D negative (Figure 1) and the magnetic field oriented along the molecular z axis (the Cu−Cu vector), the low-field transition should be more intense than the high-field transition, while the opposite is true if the magnetic field is oriented toward the z axis at an angle Θ greater than 60° (see the Supporting Information). For a positive D, all intensity relations above are inverted. It should be emphasized

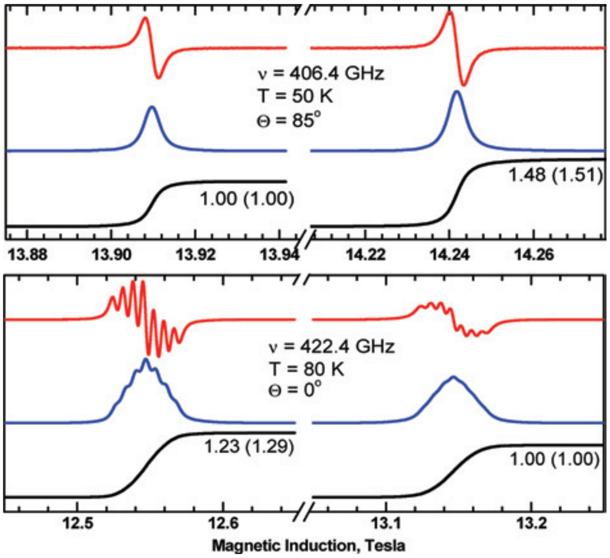

Figure 3. Single-crystal EPR spectra of **2** measured with the frequency, temperature, and molecular orientation as indicated. The red, blue, and black traces are the original EPR spectra and their first and second integrals, respectively. The measured and calculated (in parentheses) relative intensities are shown. Hyperfine splitting due to two copper nuclei is visible when the magnetic field is close to the molecular z axis, $A_{\parallel Cu} = 73.5 \times 10^{-4}$ cm^{-1}.

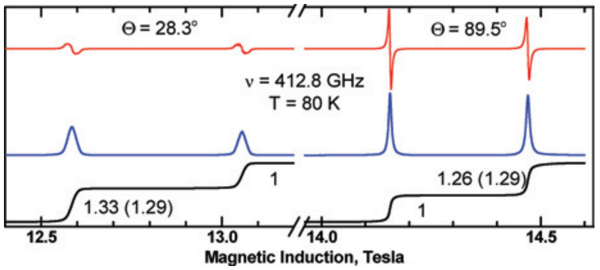

Figure 4. Single-crystal EPR spectrum of **1**. The red, blue, and black traces are the original EPR spectra and their first and second integrals, respectively. The complex crystallizes in a monoclinic system, and signals of two differently oriented binuclear units are observed at a random crystal orientation. The measured and calculated (in parentheses) relative intensities are shown.

that the magnitude of the Zeeman term is of importance here, while that of |*D*| is not. *D* sign determination from powder EPR spectra is possible for mononuclear complexes,[10] as well as for some ferromagnetic polymeric species,[11] because measurements can be taken at temperatures sufficiently low for the effect to be significant, up to the point of completely "freezing out" certain transitions. Copper(II) carboxylates pose an additional problem in that respect because they become diamagnetic and EPR-silent at too low temperatures. Also, the line widths of the two "allowed" EPR transitions are different from each other and, in addition, vary with the molecular orientation. As a result, one cannot judge the transition intensities from powder spectra (Figure 2), even with an *R* factor as large as that calculated above, and these spectra were used here mainly to refine the EPR parameters, which turned out to be significantly different from the literature values for **1**[1,12] (see Figure 2 and the Supporting Information) but much less so for **2**.[5]

To obtain meaningful intensity data, single-crystal EPR spectra of **1** and **2** were measured at frequencies up to 435 GHz, at magnetic fields up to 14.9 T, and at temperatures down to 50 K. Below 50 K, signals were too weak for a reliable intensity determination. The intensity was determined by integrating twice spectra recorded in the usual first-derivative form (Figures 3 and 4). The orientation of molecules whose spectra were observed was easily determined from the **g** and |*D*| values and resonance positions. The measured intensity ratios are qualitatively and quantitatively consistent with negative *D* in each complex (see Figures 3 and 4 and the Supporting Information).

Accordingly, the exchange contribution to zfs is $-0.164\ \mathrm{cm}^{-1}$ in **1** and $-0.152\ \mathrm{cm}^{-1}$ in **2**, and it is comparable to D_{dip} rather than being positive and dominant as previously reported.[5,6,8] The triplet−singlet separation $J(x^2-y^2,xy)$ in eq 3 should thus be on the order of $-40\ \mathrm{cm}^{-1}$, indicating ferromagnetic exchange in the corresponding excited state of a dimer. This magnitude is not surprising because in the highly symmetric molecules of **2** the orbitals $d_{x^2-y^2}$ and d_{xy} of interacting ions are arranged face-to-face and are orthogonal. Ferromagnetic interaction stronger yet has been directly observed in a $\mathrm{Cu^{II}}-\mathrm{V^{IV}}$ heterobinuclear compound with orthogonal arrangement of copper $d_{x^2-y^2}$ and vanadium d_{xy} orbitals.[13]

It may be interesting to explore reasons that led an extremely detailed spectral analysis of **2** to an incorrect conclusion concerning the sign of *D*.[6] The $J(x^2-y^2,xy)$ value was found from the splitting between the $^1A_{2g}$ and $^3A_{2g}$ states. The energy of the former one was clearly found from the low-temperature polarized absorption $^1A_{1g} \rightarrow {}^1A_{2g}$ at 11 900 cm^{-1}. The transition $^3A_{2u} \rightarrow {}^3A_{2g}$ used to determine the $^3A_{2g}$ energy was located in a difficult region of high-temperature magnetic circular dichroism spectra, where it overlapped strongly with the $^3A_{2u} \rightarrow {}^1A_{2g}$ absorption and, in fact, was not observed as a separate band, but rather its position was estimated, resulting in the $^3A_{2g}$ energy of 11 950 cm^{-1}.[6] Moreover, the ground-state exchange integral magnitude (325 cm^{-1}), which may bear an error[14] of ~20 cm^{-1}, played a role in the assignment of the two transitions from the $^3A_{2u}$ state.[6] While no way may exist of handling the problem better than that in ref 6, it seems that small errors are possible and the $^3A_{2g}$ state may lie slightly below $^1A_{2g}$. A very important result of ref 6 confirming the validity of eq 3 was the experimental determination of *D* and **g** for the excited $^3A_{1u}(d_{xy})$ state (from variable-field polarized single-crystal absorption experiments (Figure 7 in ref 6), which were successfully related to the ground-state exchange integral $J(x^2-y^2,x^2-y^2)$ through a formula analogous to eq 3, whose main component is[6,7]

$$D_{\mathrm{ex}}(^3A_{1u}) = J(x^2-y^2,x^2-y^2)\ [g_z(^3A_{1u}) - 2]^2/32$$

This is a remarkable achievement because the excited-state *D* and **g** values cannot be determined from EPR.

The exchange-related contribution to *D* in dihydroxo-bridged copper(II) dimers is much larger[15] than that in copper carboxylates, while the Δ values of eq 3 are smaller, so that the singlet−triplet splittings in excited dimer states should be larger by 1 order of magnitude than those in the carboxylato-bridged dimers.[15] The correctness of eq 3 could be thus assessed more easily in dihydroxo-bridged dimers than in the carboxylates if a study similar to that in ref 6 were performed. Negative *D* for a complex of this kind[15] was determined recently.[16]

The absolute magnitude of *D* varies over a relatively narrow range for most copper carboxylates,[2] while it is larger by 25% in formates[2,17−19] and in halogenated carboxylates.[2,8] Recently, *D* was found to be negative in fluorinated copper carboxylates.[20]

D is thus most likely negative in all binuclear copper carboxylates exhibiting the "paddlewheel" structure, and published reports of positive *D* as well as conclusions inferred from it should be reconsidered.

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Supporting Information Available: Instrumental and preparative details, experimental and simulated powder EPR spectra of **1** and **2**, single-crystal EPR intensities in **1**, and high-field EPR spectra of a copper formate/*N*,*N*-dimethylformamide adduct. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) To be published separately.