ΔE_f. The simulated cyclic voltammogram closely matches the observed as shown in Figure 2. Calculations[4] show that after the waves coalesce, the peak-to-peak separation as read from the oxidation and reduction maxima will decrease as K_c becomes smaller. When $K_c = 4$, ΔE_f for two separate stages is 36 mV, and the peak-to-peak separation observed when the waves corresponding to the two stages are superimposed will be 59 mV. The amplitude will, however, correspond to the flow of 2 electrons rather than 1 electron per molecule. The simulated cyclic voltammogram has a slightly larger value of peak-to-peak separation than the observed, which is likely a result of incomplete resolution in the latter.

After we obtained a value of K_c, the spectrum recorded for a solution nominally containing the [3,2] species was corrected for the contributions by the [2,2] and [3,3] forms in equilibrium with it. The spectrum shown in Figure 1 for the [3,2] species has been obtained in this manner. The prominent features in the spectrum of the [2,2] are the bands in the visible and near-UV region arising from $\pi^* \leftarrow \pi d$ and $\pi^* \leftarrow \pi$ transitions, respectively, while the weak band at ~380 nm is probably a ligand field transition. The Ru(III) species shows the $\pi^* \leftarrow \pi$ transition at higher energy than is the case for the fully reduced, and the weak band observed in the latter is absent. The strong and rather broad band in the near-UV region probably arises from a $\pi d \leftarrow \pi$ transition (perhaps transitions). As expected for a weakly coupled system, the mixed-valence species combines the features of both the [2,2] and [3,3]. Some perturbations are, however, worth noting. The $\pi^* \leftarrow \pi d$ transition is at slightly lower energy than is the case for the [2,2] species, and most of the tailing to lower energies is intrinsic to the band and cannot be accounted for by the intervalence absorption. The oscillator strengths for the transitions are 0.51 and 0.28 ([2,2] and [3,2], respectively). The $\pi^* \leftarrow \pi$ absorption is composite as is expected for a species containing both Ru(II) and Ru(III) and there is a definite shift for each of them to lower energy, possibly suggesting a significant change in the structure of the bridging group as the oxidation states of the metal change.

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Registry No. $[((NH_3)_5Ru)_2\text{-}4,4'\text{-bpy}]^{5+}$, 54065-65-5; $[((NH_3)_5Ru)_2\text{-}4,4'\text{-bpy}](ClO_4)_6$, 69042-75-7; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; $[((NH_3)_5Ru)_2\text{-}4,4'\text{-bpy}]^{4+}$, 36451-88-4.

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Contribution from the Institut für Anorganische und Physikalische Chemie der Universität Bern, CH-3000 Bern 9, Switzerland, and the Institut für Reaktortechnik ETHZ, CH-5303 Würenlingen, Switzerland

Direct Observation of Singlet–Triplet Separation in Dimeric Copper(II) Acetate by Neutron Inelastic Scattering Spectroscopy

HANS U. GÜDEL,* ANTON STEBLER, and ALBERT FURRER

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The singlet–triplet separation in $Cu_2(CD_3COO)_4 \cdot 2D_2O$ has been determined by neutron inelastic scattering spectroscopy. Its value is 298 ± 4 cm^{-1}. Within experimental error there is no temperature dependence of the singlet–triplet separation between 10 and 300 K. Magnetic susceptibility measurements on $Cu_2(CH_3COO)_4 \cdot 2H_2O$ and $Cu_2(CD_3COO)_4 \cdot 2D_2O$ reveal that deuteration has no measurable effect on the exchange coupling.

Introduction

Since the pioneering work of Bleaney and Bowers in 1952[1] a great deal has been written about the electronic structure of copper(II) acetate and related binuclear complexes.[2] There is today no mechanism of coupling of the two paramagnetic copper(II) ions accepted by everyone working in this field. It is not our intention to add one more opinion. Rather, we want to report an experiment which is of some significance to this question.

Inelastic scattering of thermal neutrons is a powerful tool for the study of low-energy excitations in crystalline transition-metal and lanthanide compounds.[3] It offers an alternative to infrared and Raman spectroscopy on the one hand and bulk techniques such as heat capacity and magnetic susceptibility measurements on the other hand. In the case of magnetically

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*To whom correspondence should be addressed at the Institut für Anorganische und Physikalische Chemie der Universität Bern.

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ordered solids, neutron inelastic scattering is particularly informative because of the possibility of magnon scattering. The excitation, in this case, is shared by the ensemble of the magnetic centers in the lattice, as can be shown by dispersion experiments. In a magnetically coupled dimer of paramagnetic ions, on the other hand, localized excitation corresponding to transitions within the split ground-state manifold of the molecule is possible. Taking as a classical example of this family of polynuclear complexes the dinuclear copper(II) acetate complex, the singlet to triplet transition, expected around 300 cm^{-1}, would be of this type. Our question therefore was the following: can this transition be observed by neutron inelastic scattering?

In the following we report the observation of the singlet to triplet transition in fully deuterated copper(II) acetate, $Cu_2(CD_3COO)_4 \cdot 2D_2O$, by means of neutron inelastic scattering for the temperature range 10–300 K. This is the first direct spectroscopic determination of the exchange parameter J_{eff} and its temperature dependence, where J_{eff} is defined by

$$\hat{H}_{ex} = J_{eff}(\hat{S}_a \cdot \hat{S}_b) \qquad (1)$$

Experimental Section

Preparative Procedure. $Cu_2(CD_3COO)_4 \cdot 2D_2O$ was prepared by dissolving freshly prepared $Cu(OH)_2$ in a mixture of 10% CD_3COOD and 90% D_2O. The product was recrystallized from D_2O. The degree of deuteration of the final product was 95.5%.

Commercial $Cu_2(CH_3COO)_4.2H_2O$ was twice recrystallized.

Magnetic Susceptibility. Finely ground powders of $Cu_2(CH_3COO)_4 \cdot 2H_2O$ and $Cu_2(CD_3COO)_4.2D_2O$ were used for the magnetic susceptibility measurements. A moving sample technique, which is described elsewhere,[4] was used. The temperature was measured with a chromel/gold–iron thermocouple. The estimated accuracy of the temperature measurement is ±0.2 K. The magnetic field employed was 10 T. No field dependence was detected. The susceptibility was calibrated with purissimum Ni powder. For the derivation of the exchange parameter J_{eff} literature procedures[5] and a standard least-squares fitting program were used.

Neutron Inelastic Scattering. Because of the large incoherent scattering contribution of H, undeuterated copper(II) acetate is not suited for our experiments. All the measurements were therefore done on a powdered sample of $Cu_2(CD_3COO)_4 \cdot 2D_2O$, sealed into an aluminum cylinder of 1.5 cm diameter and 5 cm length.

In a neutron inelastic scattering experiment the sample is irradiated by a collimated monochromatic neutron beam, and the scattered neutrons are analyzed according to the energy transfer

$$\hbar\omega = (\hbar^2/2m)(k_0^2 - k_1^2) \qquad (2)$$

where m is the neutron mass, and k_0 and k_1 the wavenumbers of incoming and outgoing neutrons, respectively. Besides the energy transfer we have to consider the momentum transfer

$$\hbar\vec{Q} = \hbar(\vec{k}_0 - \vec{k}_1) \qquad (3)$$

where $\vec{Q}$ is the scattering vector, and $\vec{k}_0$ and $\vec{k}_1$ are the wave vectors of incoming and outgoing neutrons, respectively. Assuming that in our dinuclear copper(II) acetate complex both ground singlet and triplet states can be described by wave functions of the type $|S_aS_bSM\rangle$, where $S_a = S_b = {}^1/_2$ and S is the total spin quantum number of the coupled system, we can write down a closed expression for the thermal neutron cross section of a transition $|S\rangle \rightarrow |S'\rangle$.[6]

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{N}{Z}\left(\frac{g\gamma r_0}{2}\right)^2 \frac{k_1}{k_0} F^2(Q) \exp\{-2W\} \times \exp\left\{-\frac{E_S}{k_B T}\right\} \sum_{\alpha,\beta}\left(\delta_{\alpha\beta} - \frac{Q_\alpha Q_\beta}{Q^2}\right) \sum_{i,j} \exp\{i\vec{Q}\cdot(\vec{R}_i - \vec{R}_j)\} \times \sum_{M,M'} \langle SM|\hat{S}_i^\alpha|S'M'\rangle \langle S'M'|\hat{S}_j^\beta|SM\rangle \delta(\hbar\omega + E_S - E_{S'}) \qquad (4)$$

Z is the partition function, $\gamma = 1.913$ the neutron magnetic moment in units of the nuclear magneton, $r_0 = e^2/m_ec^2$ the classical electron radius, $F(Q)$ the magnetic form factor, $\exp\{-2W\}$ the Debye–Waller factor, $\vec{R}_i$ the position vector of the ith Cu ion in the molecule, $|SM\rangle = |(1/2)(1/2)SM\rangle$ and $|S'M'\rangle = |(1/2)(1/2)S'M'\rangle$ the wave functions of the initial and final electronic levels with energies E_S and $E_{S'}$, respectively. α and β stand for x, y, and z. The remaining symbols have their usual meaning. In practice, because of line broadening due to relaxation effects and instrumental resolution, the δ function is replaced by a Gaussian.

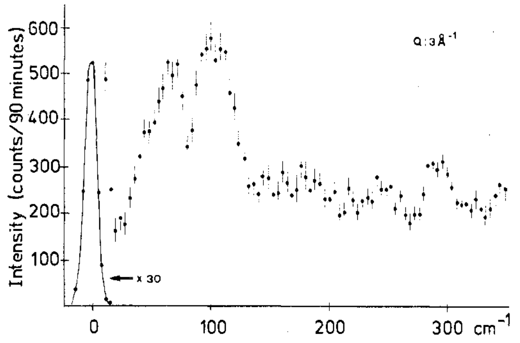

Figure 1. Neutron inelastic scattering survey spectrum of $Cu_2(CD_3COO)_4 \cdot 2D_2O$ in the energy-transfer range 0–350 cm^{-1}. The spectrum was measured on a triple-axis spectrometer. The intense band at zero energy transfer is due to elastic scattering.

All the neutron inelastic scattering measurements were done at the reactor Saphir in Würenlingen by using either a triple-axis or a multiangle reflecting crystal (MARC) spectrometer.[7] The most important difference between the two instruments is that the MARC spectrometer measures the scattered neutrons in a larger solid angle than a triple-axis instrument. In a MARC experiment, in contrast to a conventional experiment with a triple-axis spectrometer, the measurement of an energy spectrum is carried out in a single instrumental configuration, which considerably improves the data collection rate. The MARC spectrometer is very well suited for spectroscopic problems.

The incident neutron energy chosen in our experiments was 67.6 meV. The minimum scattering angle thus obtainable was 10° corresponding to $Q = 2.05$ Å^{-1}. Experiments at higher incident neutron energies, which would enable measurements at smaller Q, were not possible because of the loss of both intensity and resolution.

Results and Discussion

Figure 1 shows a neutron inelastic scattering survey spectrum, measured on a triple-axis spectrometer. The spectrum is characterized by a large number of peaks. The magnetic singlet to triplet transition expected near 300 cm^{-1} is not a dominant feature of the spectrum. The most intense peaks in the low-energy transfer region can be assigned to external vibrations (translations or rotations of individual molecules), internal vibrations occurring at higher energy transfers. The great advantage of neutron inelastic scattering, compared with other spectroscopic techniques lies in the possibility to unambiguously discriminate between transitions of vibrational and magnetic origin. With increasing modulus of the scattering vector $\vec{Q}$ the intensity of vibrational scattering increases approximately as Q^2, whereas, for our system of randomly oriented spin pairs, the Q dependence of a magnetic transition is given by

$$I(Q) \propto F^2(Q)\left(1 - \frac{\sin QR}{QR}\right) \qquad (5)$$

Formula (5) is derived from the general cross section formula (4) by averaging in $\vec{Q}$ space, since the experiments have been performed on a polycrystalline material. $(1 - (\sin QR)/QR))$ is a so-called interference term reflecting the separation R of the two paramagnetic centers.[8] In Figure 2 several MARC spectra taken with different Q are reproduced. Clearly there are bands with different Q dependences in this spectral range, and of these only the prominent band near 300 cm^{-1} behaves like a magnetic transition. This is put on a more quantitative basis in Figure 3, where the intensity of the 300-cm^{-1} band is plotted as a function of Q. Not only does the intensity decrease as expected for $F^2(Q)$ but the modulation due to the interference term is nicely reproduced. This evidence proves

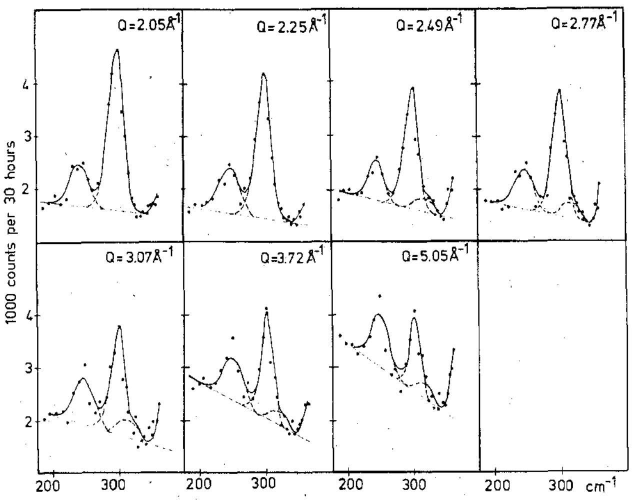

Figure 2. The 10 K MARC spectra between 180 and 360 cm^{-1} for a series of values of Q, where Q is the modulus of the scattering vector $\vec{Q}$. The Q values refer to an energy transfer of 300 cm^{-1}. The full curves represent the least-squares fits to the experimental data assuming a linear background and approximating the peaks by Gaussians (broken lines). For high Q values the analysis becomes more difficult because the assumption of linear background becomes worse.

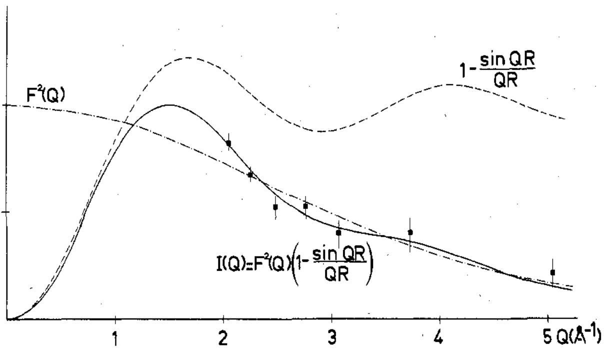

Figure 3. Q dependence of intensity of the neutron inelastic scattering transition near 300 cm^{-1} in $Cu_2(CD_3COO)_4 \cdot 2D_2O$ measured at 10 K. For the plotted functions $F^2(Q)$ and $F^2(Q)(1 - (\sin QR)/QR))$ experimentally determined $F(Q)$ values were used.[9] R, the copper–copper separation, was taken as 2.64 Å.[10]

the magnetic nature of the transition at 298 ± 4 cm^{-1} in $Cu_2(CD_3COO)_4 \cdot 2D_2O$.

The singlet to triplet transition was then measured at various temperatures between 10 K and room temperature in order to determine the temperature dependence of J_{eff}. The results are given in Figure 4. Within experimental error the position of the neutron inelastic scattering transition does not shift within that temperature range. The controversy, much discussed in earlier work on copper(II) acetate, whether J_{eff} is temperature dependent or not, is therefore settled. Our findings are in agreement with the conclusion drawn by Figgis and Martin from their susceptibility measurements on copper(II) acetate.[5] The lack of temperature dependence of the singlet–triplet separation in deuterated copper(II) acetate may have several reasons, and it cannot be used to discriminate between direct and superexchange mechanisms for the coupling between the two copper(II) ions.

The decrease in intensity on increasing temperature of the magnetic transition in Figure 4 is in qualitative agreement with what is expected on the basis of relative Boltzmann populations of the singlet and triplet levels. Estimating the intensity of the magnetic transition at high temperatures is rather difficult because of the underlying tail of a vibrational transition, whose intensity increases very strongly with temperature (see Figure 4). In order to determine the effects of deuteration on the exchange coupling we determined J_{eff} of $Cu_2(CD_3COO)_4 \cdot 2D_2O$ and $Cu_2(CH_3COO)_4 \cdot 2H_2O$ from the temperature dependence of the magnetic susceptibility. The following values were obtained: $Cu_2(CD_3COO)_4 \cdot 2D_2O$, J_{eff} = 291 ± 2 cm^{-1}; $Cu_2(CH_3COO)_4 \cdot 2H_2O$, J_{eff} = 290 ± 2 cm^{-1}. Both values are close to that reported by Gregson et al. for undeuterated copper(II) acetate.[11] Deuteration therefore, has no measurable effect on the exchange parameter. The agreement with the spectroscopically determined value of J_{eff} for $Cu_2(CD_3COO)_4 \cdot 2D_2O$ of 298 ± 4 cm^{-1} (vide supra) is reasonable. The spectroscopic value is, of course, more trustworthy, since it is the result of a direct observation. The magnetochemical procedure, on the other hand, involves the fitting of a theoretical model to a set of bulk data.

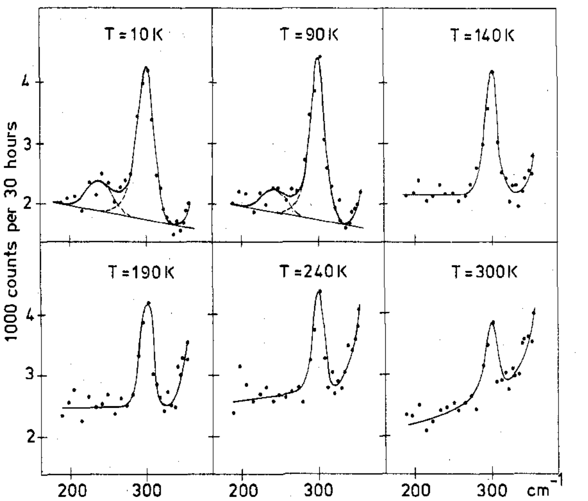

Figure 4. MARC spectra showing the prominent magnetic transition as a function of temperature. In the 10 and 90 K spectra the full curves represent least-squares fits, assuming a linear background and approximating the peaks by Gaussians. The full curves in the higher temperature spectra are only to be considered as a "guide for the eye". Q = 2.25 $Å^{-1}$ for all the spectra.

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Registry No. $Cu_2(CD_3COO)_4 \cdot 2D_2O$, 28978-24-7; $Cu_2(CH_3COO)_4 \cdot 2H_2O$, 15523-07-6.

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