MAGNETIC CIRCULAR DICHROISM STUDY OF THE EXCHANGE-COUPLED COBALT(II) DIMER

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Abstract

MCD spectrum of the exchange coupled $[Co_2(\mu\text{-}H_2O)(\mu\text{-}OAc)_2(OAc)_2(tmen)_2]$ complex was analyzed. The analysis is based on the assumption that weak exchange interaction does not change the optical properties of the interacting ions and affects the saturation magnetization behavior only. The feature of MCD behavior, namely, the disappearance of some lines with increasing magnetic field and appearance again with the opposite sign, was explained by the overlap of the electronic transitions at different but near wavelengths.

1. Introduction

MCD spectroscopy [1] is a very powerful method to characterize high-spin Co(II) monomers as well as oligomers. This technique is popular in biochemistry due to the possibility of determination of the intrinsic geometry and the electronic structure of the active centers in metalloenzymes. Cobalt ion being in the active center is a valuable probe to study enzymatic activity [2-5].

Cobalt complexes are interesting not only from the biochemical point of view. Cobalt can show very high anisotropy because of a not completely frozen orbital moment. This is important for the design of new devices for use in information storage. Due to their high anisotropy, polynuclear Co complexes are good candidates for single molecule magnets [6-8].

From a theoretical point of view, the case of the interaction of two (or more) Co(II) ions in octahedral surroundings is very interesting but complicated since the $^4T_{1g}$ ground state is orbitally degenerate. This orbital degeneracy leads to highly anisotropic interactions, and the effective Hamiltonian contains not only spin operators but also orbital ones [9].

In the previous study, the title compound $[Co_2(\mu\text{-}H_2O)(\mu\text{-}OAc)_2(OAc)_2(tmen)_2]$ was fully characterized by a combination of different experimental techniques [10]. Magnetic properties were investigated by susceptibility vs. temperature and magnetization vs. field measurements accompanied by the magnetic circular dichroism (MCD) studies. The key parameters of the complex that govern the magnetic behavior were obtained. The observed features of MCD behavior, namely, the disappearance of some lines with increasing magnetic field and appearance again with the opposite sign, were successfully explained by the overlap of the different electronic transitions. However, the theoretical analysis of the MCD saturation behavior was based on some assumptions. At low temperatures, each Co(II) ion can be treated as a pseudo-spin-1/2 system. Exchange interaction couples these pseudo-spins to the states with the total angular momentum $J = 0$ and 1. Since the applied magnetic field strongly affects the $J = 1$ triplet, it was assumed that the MCD C-term of the regarded complex is mainly due to this $J = 1$ triplet and the contribution of $J = 0$ singlet was neglected. In this paper, a different analysis of the MCD

behavior of the title compound is presented. The MCD spectrum is analyzed as a superposition of spectra that belong to each of the interacting cobalt ions. Like in the previous study, the unusual MCD saturation behavior is explained by the overlap of the electronic transitions at different but near wavelengths. However, the found polarizations of the corresponding optical transitions refer to the local coordinate systems and reflect the local symmetry of the interacting ions.

2. Model

A general formula for the analysis of MCD spectra requires the calculation of the difference between molar extinction coefficients for the left and right circularly polarized light, i.e., $\Delta\varepsilon = \varepsilon_L - \varepsilon_R$. The MCD saturation behavior of the signal from the randomly oriented mononuclear complexes with the orbitally degenerate ground state can be simulated as [11]

$$\Delta\varepsilon \propto M_{xy}\left\langle \bar{L}_z \right\rangle_T + M_{yz}\left\langle \bar{L}_x \right\rangle_T + M_{zx}\left\langle \bar{L}_y \right\rangle_T, \tag{1}$$

where M_{ij} is a combination of matrix elements of *i*-th and *j*-th components of electric dipole operator and $\left\langle \bar{L}_k \right\rangle_T$ is the thermally and orientationally averaged *k*-th component of the orbital angular momentum within ground state:

$$\left\langle \bar{L}_k \right\rangle_T = \frac{1}{4\pi}\int\int \sum_a \left\langle a\left|L_k\right|a\right\rangle \frac{\exp\left(-E_a / k_B T\right)}{Z} A_{zk} \sin\vartheta \, d\vartheta d\varphi . \tag{2}$$

In Eq.(2) $A_{zx} = \sin\vartheta\cos\varphi$, $A_{zy} = \sin\vartheta\sin\varphi$, $A_{zz} = \cos\vartheta$ and angles ϑ and φ describe the orientation of the magnetic field with respect to the molecule-fixed coordinate system.

The exchange interaction in the studied dimeric complex was found to be -1.2 cm^{-1} [10]. It is assumed that this weak exchange does not change the optical properties of the interacting ions. This assumption means that the positions of optical lines and the polarizations of the corresponding transitions are the same as without exchange interaction. As a result, the entire MCD spectrum represents a superposition of MCD spectra of the interacting ions and its temperature and magnetic field behavior can be simulated as

$$\Delta\varepsilon \propto \sum_{n=1,2} M_{xy}(n)\left\langle \bar{L}_z(n) \right\rangle_T + M_{yz}(n)\left\langle \bar{L}_x(n) \right\rangle_T + M_{zx}(n)\left\langle \bar{L}_y(n) \right\rangle_T , \tag{3}$$

where $M_{ij}(n)$-values are equal to that ones for non interacting *n*-th center and $\left\langle \bar{L}_k(n) \right\rangle_T$ is the thermally and orientationally averaged *k*-th component of the orbital angular momentum of *n*-th Co-ion within ground state of the entire exchanged-coupled complex.

To obtain the energy levels of the exchange coupled Co dimer, the following Hamiltonian is used:

$$\hat{\mathbf{H}} = \sum_{n=1,2}\left(-\frac{3}{2}\kappa_n \lambda \mathbf{S}_n \mathbf{L}_n + \mathbf{L}_n \mathbf{\Delta}_n \mathbf{L}_n + \mu_B\left[g_0 \mathbf{S}_n - \frac{3}{2}\kappa_n \mathbf{L}_n \right]\mathbf{H} \right) - 2J_{ex}\mathbf{S}_1\mathbf{S}_2 , \tag{4}$$

where the first term is the spin-orbit coupling within the $^4T_{1g}$ triplet of each Co ion and the second part is the low symmetry (non cubic) crystal field. Assuming that distortion from the octahedral surrounding is axial, in the main axes of $\boldsymbol{\Delta}$ tensor, the low-symmetry field term can be written as

$$\boldsymbol{\Delta}_n^{loc} = \Delta_n\left(\mathbf{L}_z^2 - L[L+1]/3\right) \tag{5}$$

with the positive Δ_n parameter corresponding to the axial elongation and the negative one for the axial compression [12]. To obtain the $\boldsymbol{\Delta}_n$ tensor in the arbitrary coordinate system, the unitary transformation should be performed:

$$\boldsymbol{\Delta}_n = \nu_n^{-1}\boldsymbol{\Delta}_n^{loc}\nu_n, \tag{6}$$

where ν_n are orthogonal transformation matrices.

The third term in eq.(4) is the Zeeman perturbation that consists of both spin and orbital contributions. The last part of the Hamiltonian represents the exchange interaction between Co(II) ions. Using the approach of Lines [13], this magnetic exchange is assumed to be isotropic and operate with the real spins of the interacting cobalt ions. In eq.(4) S = 3/2 is the spin of Co ion and L = 1 is the fictitious orbital angular momentum, λ = -170 cm^{-1} and κ are the spin-orbit coupling parameter and the orbital reduction factor, respectively, μ_B means the Bohr magneton and J_{ex} is the exchange coupling parameter.

Eq.(4) allows one to fully describe the magnetic behavior of the exchange coupled Co dimer in the entire temperature range. The ground state magnetic properties of the entire complex strongly depend on the value of the exchange coupling parameter and this is reflected in the MCD spectra via the temperature and magnetic field dependence of $\left\langle \overline{L}_k(n)\right\rangle_T$-values. It should be noted that $\left\langle \overline{L}_k\right\rangle_T$-values for the real orbital angular momentum of an isolated cobalt ion are negative. It is a consequence of the fact that the electron charge is negative and its orbital angular momentum is pointed opposite to the direction of the magnetic moment of the electron. The external magnetic field tries to orient the magnetic moment of a cobalt ion parallel to this field direction and, as a result, the orbital angular moment is antiparallel to the field direction. Since equation (3) is defined up to a constant factor, in the following consideration all calculations are performed for the fictitious orbital momentum L = 1. For this fictitious orbital angular momentum $\left\langle \overline{L}_k(n)\right\rangle_T$-values calculated for non-interacting cobalt ions are positive. To obtain the corresponding values for the real orbital momentum one needs to multiply all calculated matrix elements by the factor (-3/2).

3. Discussion

Magnetic properties of the investigated compound were fully analyzed in [10]. The key parameters of the complex that govern the magnetic behavior were obtained. It was found that each of the interacting ions is axially compressed with Δ_n = -870 cm^{-1} and the angle between the local axes being α = 120º. The obtained value of the orbital reduction factors κ_n = 0.858 lies between the limits for the weak and strong crystal fields. The exchange interaction was found to be weak (J_{ex} = -1.2 cm^{-1}) that is typical for the cobalt(II) complexes, where a magnetic exchange

takes place through the bridging water and carboxylate groups [12, 14]. It is assumed that this weak exchange does not change the optical properties of the interacting ions and the behavior of the MCD spectrum of the dimer can be simulated with the use of Eq.(3). Since the investigated compound is a homonuclear symmetrical dimer, the condition $M_{ij}(1) = M_{ij}(2)$ holds.

We start the analysis of the MCD magnetization saturation behavior of the studied dimer from the theoretical simulation of the magnetic field and temperature behavior of $\left\langle \overline{L}_k(1) \right\rangle_T$ -values in the local coordinate system of ion 1. In these simulations the values of the best fit parameters obtained in [10] were used. The result is shown in Fig. 1. The $\left\langle \overline{L}_k(2) \right\rangle_T$ values in the local coordinate system of ion 2 demonstrate the same behavior. The axial compression results in a partial quenching of the components of the orbital angular momentum perpendicular to the compression axis. However, these components are not completely quenched and, in general, optical transitions of all polarization could participate to the MCD spectrum. The exchange interaction leads to the different magnetic field and temperature behavior of $\left\langle \overline{L}_x(1) \right\rangle_T$ and $\left\langle \overline{L}_y(1) \right\rangle_T$ values, the most interesting being the behavior of the $\left\langle \overline{L}_x(1) \right\rangle_T$ value. With increasing magnetic field the $\left\langle \overline{L}_x(1) \right\rangle_T$ value starts to increase, passes through the maximum, decreases and appears again with the opposite sign. With the temperature increase the change in sign occurs at lower magnetic field. According to eq.(3), similar behavior should be demonstrated by the MCD signal with yz-polarization of the optical transitions (in the present study, all polarizations of the optical transitions refer to the local coordinate systems).

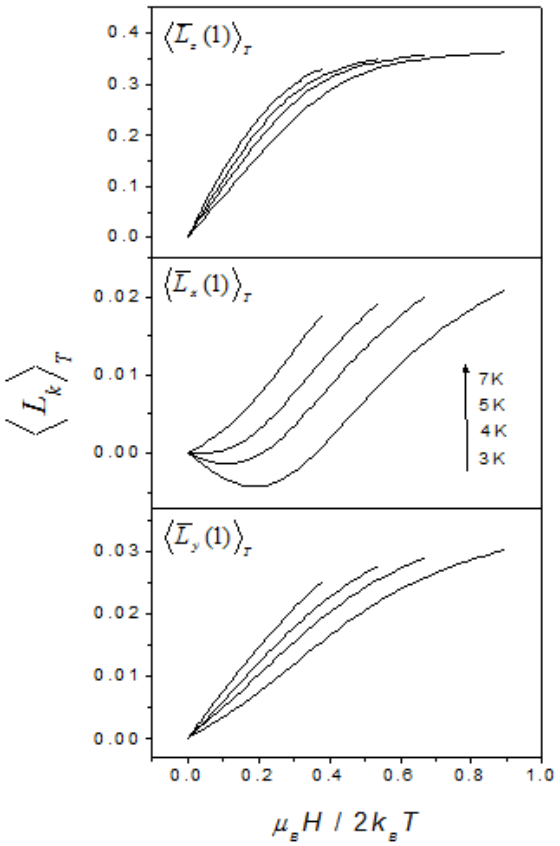

Fig. 1. Simulated behavior of $\left\langle \overline{L}_k(1) \right\rangle_T$ -values in the local coordinate system of ion 1 calculated at $\kappa_1 = \kappa_2 = 0.858$, $\Delta_1 = \Delta_2 = -870$ cm^{-1}, $J_{ex} = -1.2$ cm^{-1} and $\alpha = 120°$.

One finds that the disappearance of the MCD signal with increasing magnetic field and the appearance again with the opposite sign can be demonstrated by an individual MCD line. However, all attempts to explain the observed MCD saturation behavior of the investigated dimer by single line behavior failed. Moreover, the Gaussian decomposition presented in [10] demonstrates that there is a strong overlap of neighboring lines and it should be included into consideration. The signal behavior at different wavelength was analyzed as a sum of the corresponding contributions at the assumption of different polarization of optical transitions. It was found that the best agreement with the experimental data is obtained at the assumption that the optical transitions with positive intensity are yz-polarized and the transitions with negative intensity are xy-polarized. The result of the theoretical simulation of the MCD saturation behavior at three selected wavelengths is shown in Fig. 2 as solid lines. One sees a very good agreement between the theoretical curves and the experimental points. Although the obtained results differ quantitatively from the results presented in [10], they are qualitatively the same. The behavior of the MCD signal depends on two contributions of different signs. At low values of the external magnetic field, the negative contribution is larger and the resulting signal is negative. Since the field and temperature behavior of these two contributions is different, with increasing magnetic field, the positive term becomes larger and the corresponding MCD signal disappears and appears again with the positive sign.

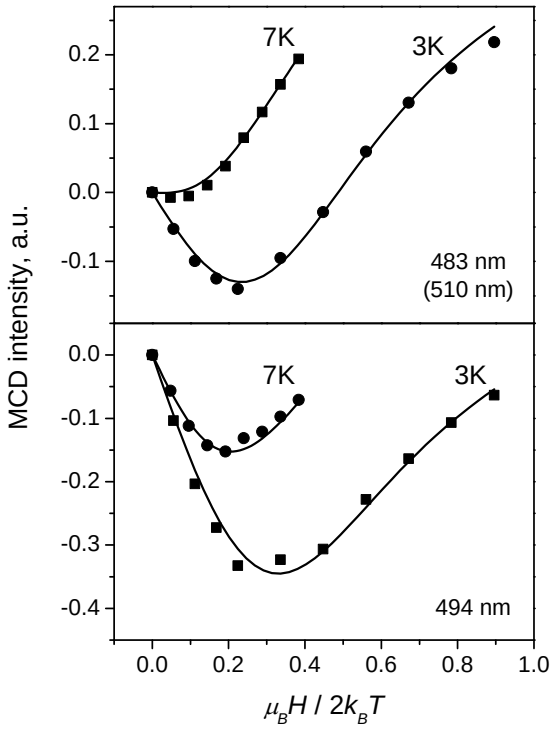

Fig. 2. Magnetization curves recorded at 483 and 510 nm (top, M_{yz} / M_{xy} = -52.36, M_{zx} = 0) and 494 nm (bottom, M_{yz} / M_{xy} = -15.36, M_{zx} = 0).
Curves – theory; points – experiment.

It should be mentioned that the observed behavior of the MCD signal strongly depends on the M_{yz} / M_{xy} ratio. When this value is high, the sign change occurs at a low temperature and is clearly seen. The decrease of the M_{yz} / M_{xy} ratio shifts the signal sign change to higher temperatures. Since the temperature increase results in the diminishing of the MCD C-term, the sign change at high temperature looks like the disappearance of the corresponding lines from the

spectrum. To illustrate this, we modeled a signal behavior at 494 nm. The result is shown in Fig. 3. At low temperatures, the signal is negative and relatively strong. The temperature increase leads to a diminishing of the absolute value of this MCD signal and at 20 K it almost disappears because the positive and negative contributions cancel each other. The further temperature growth results in the change of the signal sign, however, the intensity of this signal becomes negligible. This agrees well with the experimental data.

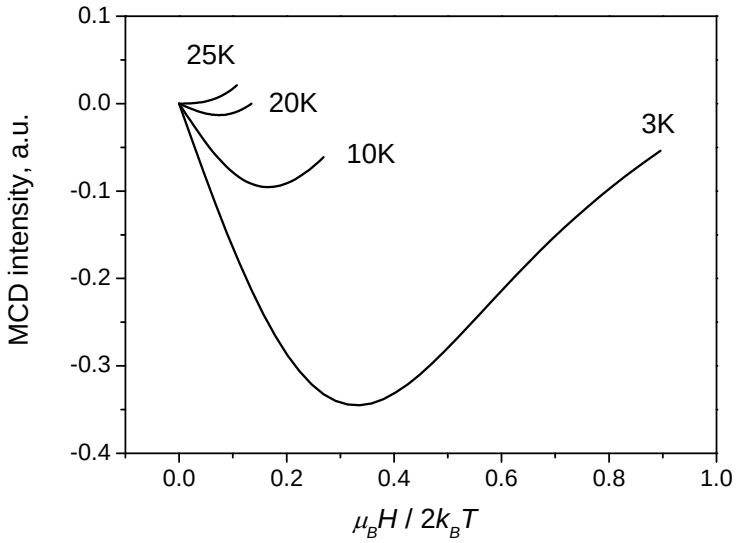

Fig. 3. Theoretical simulation of the MCD magnetization curves at 494 nm. Parameters are shown in the caption of Fig. 2.

4. Conclusions

In this paper, the MCD analysis of the $[Co_2(\mu\text{-}H_2O)(\mu\text{-}OAc)_2(OAc)_2(tmen)_2]$ exchange coupled dimer is presented. The analysis is based on the assumption that weak exchange interaction does not change the optical properties of the interacting ions and affects the saturation magnetization behavior only. This analysis differs from that used in [10] where the MCD signal was simulated using the collective states of the dimeric complex. Some interesting features of the signal behavior were found. However, the main conclusion of [10] remains the same: the observed feature of the MCD behavior, namely, the disappearance of some lines with increasing magnetic field and the appearance again with the opposite sign, is caused by the overlap of the different electronic transitions.

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