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Magnetic Circular Dichroism of $Cu(acac)_2$, $Fe(acac)_3$, and $Co(acac)_3$

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The magnetic circular dichroism (MCD) spectra of $Cu(acac)_2$, $Fe(acac)_3$, and $Co(acac)_3$ have been measured; they are shown in Fig. 1.

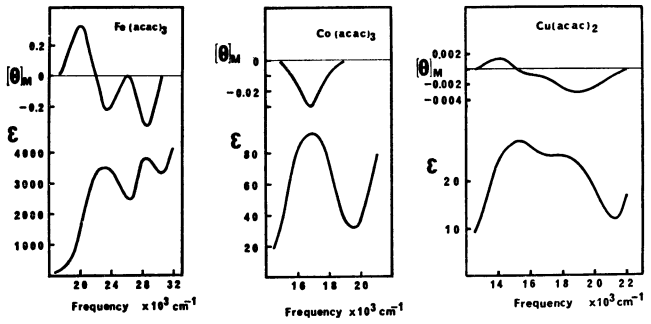

Fig. 1. The experimental MCD and absorption spectra of $Fe(acac)_3$, $Co(acac)_3$, and $Cu(acac)_2$. $[\theta]_M$ is the molar ellipticity per unit magnetic field. ε is the molar extinction coefficient. MCD has been measured by the techniques described in detail in an earlier paper.[5,8]

There has been considerable discussion concerning the assignment of bands appearing in the visible region of the spectrum of bis(acetylacetonato)copper(II), $Cu(acac)_2$, but no final solution to the problem has yet appeared.[1-4] One of the present authors (H.K) has studied the MCD of some Cu^{2+} complexes and found that the B-term of the MCD parameters is dominant in the MCD of the Cu^{2+} complexes at room temperature.[5] According to the analysis, the MCD line shape of $Cu(acac)_2$ suggests two possible assignments: the order of the energy levels is $|xz, yz \gg |x^2\text{-}y^2 \gg |z^2 \gg |xy>$ or $|z^2 \gg |x^2\text{-}y^2 \gg |xz, yz \gg |xy>$, where the locations of the x and y axes are in the plane and along the C_2 axes. However, in order to understand the high-frequency shift of the peak with a large negative MCD band from the maximum point of the absorption band, it is reasonable to assume a positive MCD band in the 16500 cm^{-1} region. Therefore, we propose this order of energy levels; $|xz, yz \gg |x^2\text{-}y^2 \gg |z^2 \gg |xy>$ on the basis of the MCD analysis.[5] Assuming the transition energies to be 14500, 16500, and 18500 cm^{-1} for the $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$, and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively, we have calculated the oscillator strengths and the Faraday parameter B (Table 1). The zeroth moment of the MCD satisfies the relation:[6]

$$\int_{band}([\theta]_M/\nu)d\nu = -33.53(B + C/kT)$$

The values of $(B+C/kT)$ are extracted by simple numerical integrations of the experimental data. By estimating the line shape, we have obtained the experimental values shown in Table 1. The estimated values of B for the lower two bands depend on the estimation of the line shape. However, the order of magnitude is in very good agreement with the calculated ones; these results support the present assignment.

The MCD spectra of $Co(en)_3^{3+}$ and $Co(ox)_3^{3+}$, which are of a D_3 symmetry, were studied by McCaffery and his co-workers.[7] The MCD of $Co(acac)_3$ (Fig. 1) is very similar in appearance to the MCD of the 17000 cm^{-1} band of $Co(ox)_3^{3+}$. $[\theta]_{M_{max}}/\varepsilon_{max}$ is 2×10^{-4}, which is of the same order of magnitude as the value for the $^1A_1 \rightarrow {}^1E_a$ band of $Co(ox)_3^{3+}$. The resemblance to $Co(ox)_3^{3+}$ shows that the static distortion is the major factor governing the d-d intensities. Since the ground state, $^1A_1$, is nondegenerate, the MCD of the 16800 cm^{-1} band of $Co(acac)_3$ shows that the Faraday B-term is absolutely dominant. However, the maximum contribution of an A-term to MCD, $[\theta^A]_{M_{max}}$, is given by $3\sqrt{3}\omega_{ja}{}^{(0)}A/4\Gamma_{ja}{}^2\hbar$. The magnitude of A/D for the $^1A_1 \rightarrow {}^1E$ transition in a D_3 symmetry in solution is theoretically given as $1/2\beta k$, where $k(>0)$ is the orbital angular momentum reduction factor. The value of D is obtained from $\int\varepsilon d\nu$. Then, $A(^1A_1 \rightarrow {}^1E_a)$ is $0.098\beta k$ (in Debye^2 unit). Using the experimental values of $\omega_{ja} \simeq 16800$ cm^{-1} and $\Gamma_{ja} \simeq 4000$ cm^{-1}, we obtain $[\theta^A]_{M_{max}} = 0.0028k$. This value is about 10% of $[\theta]_{M_{max}}$. Therefore, we cannot estimate the magnitude of the quenching of the excited-state angular momentum.

The ground state of $Fe(acac)_3$ is $^6A_1$. In such a case, where the ground state is spin-degenerate and orbitally nondegenerate, the spin-orbit splitting of the orbitally degenerate excited state causes the C terms of the split components of the transition no longer to cancel and gives rise to a MCD changing in sign

Table 1. Oscillater strengths and faraday parameter B for $Cu(acac)_2$

f^{Obs}	B^{Obs} a)	Energy (cm^{-1})	Assignment	f^{Cal}	B^{Cal} a)
3×10^{-4}	-0.6×10^{-5}	14500	$^2B_{1g} \rightarrow {}^2A_{1g}$	5×10^{-4}	-0.4×10^{-5}
1×10^{-4}	-0.2×10^{-5}	16500	$^2B_{1g} \rightarrow {}^2B_{2g}$	1×10^{-4}	-0.2×10^{-6}
3×10^{-4}	1.9×10^{-5}	18500	$^2B_{1g} \rightarrow {}^2E_g$	5×10^{-4}	0.8×10^{-5}

a) In units of $\beta\times$Debye^2/cm^{-1}.

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through the band.[7,8] However, the bands of moderate intensity at about 23000 and 29000 cm^{-1} can plausibly be assigned to allowed charge-transfer transitions, $^6A_{1g} \rightarrow {}^6T_{1u}$ ($^6A_1 \rightarrow {}^6E + {}^6A_2$). The magnitude of spin-orbit spliting is determined by $\langle {}^6A_{1g}|H_{so}|{}^6T_{1u}\rangle$, which is reduced to one-electron matrix elements, $\langle d|H_{so}|L\rangle$ for the $d^5L^2 \rightarrow d^6L$ transition and $\langle L'|H_{so}|d\rangle$ for the $d^5 \rightarrow L'd^4$ transition. These two-center integrals are small; therefore, the C-term must be negligible. The magnitude of A/D for the $^1A_1 \rightarrow {}^1E$ transition in a D_3 solution is given by $\langle E||\mu||E\rangle i/\sqrt{6} \propto \beta$. Therefore, the expected MCD is of the β-type (which is defined in Ref. 9); this contradicts the observed one. Therefore, the observed MCD must be the B-term; it shows the existence of three bands, at 20000, 24000, and 28500 cm^{-1}. Hanazaki and his co-workers[10] predicted the existence of three bands, a transition to $V_1(E)$, $V_1(A_2)$ at 17000 cm^{-1} with $f=0.007$, a transition to $V_6(E)$ at 24000 cm^{-1} with $f=0.095$, and a transition to $V_8(E)$, $V_4(A_2)$ at 26500 cm^{-1} with $f=0.039$. The present MCD analysis supports their assignments. A much more detailed analysis of the B-term would confirm our assignments. MCD studies of the solvent effects of some copper β-diketonates are now in progress in our laboratory.

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