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Polarized Crystal Spectra for $2[d,l\text{-Co(en)}_3\text{Cl}_3]\cdot\text{NaCl}\cdot6\text{H}_2\text{O}$ in the Region of the Spin-Forbidden Ligand Field Transitions

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Spin-forbidden ligand field transitions in octahedral complexes may be classified into two categories: the first involving excited states belonging to the same configuration as the ground state (intraconfigurational transitions) and the second involving excited states belonging to a different configuration from the ground state (interconfigurational transitions). The low-energy $^4A_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$, and $^2T_{2g}$ transitions of the $t_{2g}{}^3$ configuration in Cr(III) complexes belong to the first category and are characterized by sharp lines, often accompanied by considerable vibrational structure. Quite naturally the spectra of Cr(III) complexes have been extensively investigated both theoretically and experimentally.[1-3] Such studies have provided a fairly detailed description of the transitions and the low-lying doublet states. The low-energy $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^3T_{2g}$ transitions of the $t_{2g}{}^6 \rightarrow t_{2g}{}^5e_g{}^1$ configurations in diamagnetic Co(III) complexes belong to the second category, and in contrast to the spectra of Cr(III), such transitions have been observed only as weak, broad featureless bands in solution and in crystals.[1,2,4,5] Few details are available concerning the nature of these transitions or their associated excited states because of the difficulties in extracting information from the broad bands. This note reports some polarized single-crystal absorption measurements at liquid helium temperatures for the racemic double salt $2[d,l\text{-Co(en)}_3\text{Cl}_3]\cdot\text{NaCl}\cdot6\text{H}_2\text{O}$. This salt is convenient since large hexagonal crystals may be grown easily, and the threefold axis of the $\text{Co(en)}_3{}^{3+}$ chromophore lies parallel to the optic axis of the crystal.[5,6]

Experimental Section

The $2[d,l\text{-Co(en)}_3\text{Cl}_3]\cdot\text{NaCl}\cdot6\text{H}_2\text{O}$ crystals used in this study were grown as described in the literature.[6] The crystallographic details have been published.[5,6] Crystals with well-developed (0001) or $\{11\bar{2}0\}$ faces, 1–3 mm thick, were studied in the region 10 500–20 000 cm^{-1} using a Cary 14 spectrophotometer equipped with a red-sensitive (S-1) photomultiplier and calcite polarizers in both the sample and reference beams. Several specimens were also examined at higher resolution using a Zeiss-Jena 2-m grating spectrograph (dispersion ca. 7 Å mm^{-1} in the region of interest). Spectra were obtained at 300, 77, ca. 5, and 1.65 K. For the 1.65-K spectra, crystals were immersed in liquid helium cooled below the λ point by pumping. The temperature was determined from the vapor pressure of the liquid helium and also from a calibrated carbon resistor. Molar absorptivities for the crystal spectra were determined relative to ϵ at 10 530 cm^{-1}, which was taken to be zero. Absorptivities were computed from baseline-corrected absorbances ($A_{\bar{\nu}}$ and $A_{10530\ \text{cm}^{-1}}$), the formula weight (fw), the crystal thickness (t in cm), and the density (d) calculated from the crystal cell parameters,[5] by means of the expression $\epsilon = (A_{\bar{\nu}} - A_{10530\ \text{cm}^{-1}})\text{fw}/1000td$. The uncertainty in ϵ is within ca. ±5%.

A search for emissions from crystals at 77 K was also made from 9000 to 14 000 cm^{-1} using a GaAs type photomultiplier (RCA Sel 4832) and a sensitive amplifier (10^{-10}-A photocurrent detection limit). Excitation was from a He–Ne laser or a conventional high-intensity visible source which together with appropriate filters covered the range 14 000–22 000 cm^{-1}. However no emissions were found in spite of a careful search.

Results and Discussion

Figure 1 presents polarized crystal spectra for $2[d,l\text{-Co(en)}_3\text{Cl}_3]\cdot\text{NaCl}\cdot6\text{H}_2\text{O}$ at 1.65 K, and Table I summarizes the absorption data in the region of the spin-forbidden ligand field transitions of $\text{Co(en)}_3{}^{3+}$. In addition, studies of several thin crystals also revealed the band origin and several vibrational components for the lowest energy singlet ligand field transition $^1A_{1g} \rightarrow {}^1T_{1g}$ (maximum at 21 550 cm^{-1}). Both the energy and polarization of these bands agreed favorably with that reported by Dingle and Ballhausen.[5,7]

Table I. Spectral Data for $2[d,l\text{-Co(en)}_3\text{Cl}_3]\cdot\text{NaCl}\cdot6\text{H}_2\text{O}$ Crystals

Crystal orientation	$10^3\ \bar{\nu}$, cm^{-1} (ϵ,[a] $\text{M}^{-1}\ \text{cm}^{-1}$)	
	$^1A_{1g} \rightarrow {}^3T_{1g}$	$^1A_{1g} \rightarrow {}^3T_{2g}$
	300 K	
Axial	13.60 (0.82)	*c*
σ	13.60 (0.73)	*c*
π	14.08 (0.41)[b]	*c*
Soln[d]	13.99 (0.34)	*c*
	1.65 K	
Axial	13.83 (0.73)	18.18 (2.1)
σ	13.79 (0.74)	18.18 (2.2)
π	14.53 (0.44)[b]	18.18 (2.4)

[a] ϵ values are relative to $\epsilon_{10530\ \text{cm}^{-1}} = 0$. [b] shoulder; ϵ is for the $\bar{\nu}$ given. [c] Unresolved. [d] Aqueous solution of $d,l\text{-Co(en)}_3\text{Cl}_3$ (9.86×10^{-2} M, 10.000-cm cell).

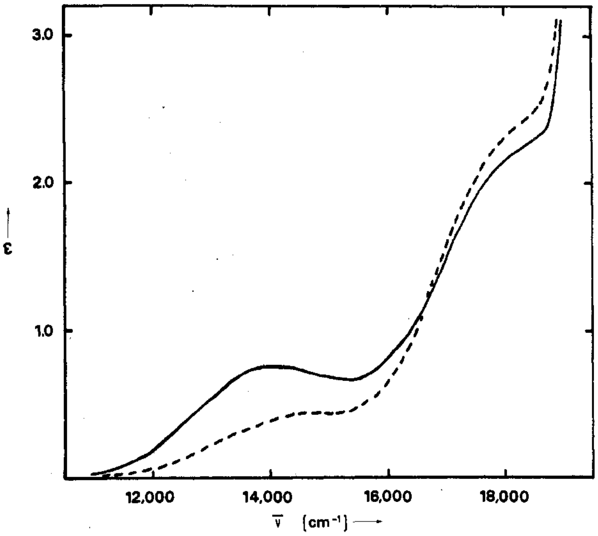

Figure 1. Polarized single crystal spectra for $2[d,l\text{-Co(en)}_3\text{Cl}_3]\cdot\text{NaCl}\cdot6\text{H}_2\text{O}$ at 1.65 K: ——, σ or axial polarization; - - -, π polarization.

The two spin-forbidden bands have been assigned (in O_h) as $^1A_{1g} \rightarrow {}^3T_{1g}$ (lower energy) and $^1A_{1g} \rightarrow {}^3T_{2g}$ (higher energy).[4,5] However in contrast to the earlier studies absorption by crystals in this region is not isotropic. The $^1A_{1g} \rightarrow {}^3T_{1g}$ band is observed more strongly in the σ polarization (perpendicular to the molecular C_3 axis), and while the difference is less, the $^1A_{1g} \rightarrow {}^3T_{2g}$ band is stronger in the π polarization (parallel to the molecular C_3 axis). Furthermore, the axial spectra and the σ spectra are identical to within experimental error. This finding establishes an electric dipole mechanism for absorption and rules out a magnetic dipole mechanism for these weak bands.[1]

The intensities and polarization of the spin-forbidden bands can be traced, via spin–orbit coupling, to the spin-allowed singlet ligand field transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, whose absorption maxima are located[5] at 21 350 and 29 400 cm^{-1}, respectively. Assuming O_h local symmetry about the Co(III) ion to a first approximation, diagonalization of the appropriate spin–orbit matrices[8] for the T_{1g} and T_{2g} states of the $t_{2g}{}^5e_g{}^1$ configuration (ignoring contributions from higher energy configurations) provides spin–orbit eigenvectors which contain $^1T_{1g}$ and $^1T_{2g}$ components. The "singlet character" (SC) in the $^3T_{1g}$ and $^3T_{2g}$ states is proportional to the square of the coefficients of the $^1T_{1g}$ and $^1T_{2g}$ components in the normalized spin–orbit eigenvectors. These squared coefficients are given in eq 1 and 2, calculated for $\zeta = 600\ \mathrm{cm}^{-1}$, $^1T_{1g} =$

$$\text{SC in } {}^3T_{1g} \propto 9.38 \times 10^{-4}({}^1T_{1g}) + 5.56 \times 10^{-4}({}^1T_{2g}) \qquad (1)$$

$$\text{SC in } {}^3T_{2g} \propto 8.63 \times 10^{-3}({}^1T_{1g}) + 2.74 \times 10^{-4}({}^1T_{2g}) \qquad (2)$$

$21\,350\ \mathrm{cm}^{-1}$, $^1T_{2g} = 29\,400\ \mathrm{cm}^{-1}$, $^3T_{1g} = 13\,500\ \mathrm{cm}^{-1}$, and $3T_{2g} = 17\,750\ \mathrm{cm}^{-1}$ (the energy splitting of the T_{1g} and T_{2g} spin–orbit components of the $^3T_{1g}$ and $^3T_{2g}$ states was negligibly small ($\sim 300\ \mathrm{cm}^{-1}$) compared to the bandwidths of the broad $^3T_{1g}$ and $^3T_{2g}$ bands). Since the $^1T_{1g}$ and $^1T_{2g}$ transitions have comparable oscillator strengths, eq 1 and 2 predict the $^3T_{2g}$ band will be the more intense of the two, in agreement with experiment. Further, by assuming the *relative* intensities of the σ and π absorptions for the $^1T_{1g}$ and $^1T_{2g}$ bands in the crystal can be approximated by relative values of the molar absorptivities at the 21 350- and 29 400-cm^{-1} maxima, the following relations are obtained[5,9]

$$I_\pi({}^1T_{1g}) = 1.3 I_\sigma({}^1T_{1g})$$

$$I_\sigma({}^1T_{2g}) = 1.3 I_\sigma({}^1T_{1g})$$

$$I_\pi({}^1T_{2g}) = 0 \quad \text{(see ref 9)}$$

When these relative intensities are weighted by the squared coefficients of eq 1 and 2, the polarization ratios, I_π/I_σ, for the $^3T_{1g}$ and $^3T_{2g}$ bands are estimated to be 0.73 and 1.26. These ratios may be compared with the observed $\epsilon_\pi/\epsilon_\sigma$ ratios for the $^3T_{1g}$ and $^3T_{2g}$ bands of 0.59 and 1.09, respectively. The agreement is probably satisfactory in view of the approximations involved.

Finally it may be remarked that the broadness of the $^3T_{1g}$ and $^3T_{2g}$ bands and their lack of structure even at 1.65 K indicate efficient coupling of numerous vibrations in the solid with the electronic excited states. Lattice phonons, internal $\mathrm{Co(en)_3}^{3+}$ modes, and vibrations of lattice water all can contribute, providing a high density of vibrational states. Such a dense manifold of states in the excited state may account for the lack of observed emissions, since a coupling of these states with the vibrationally excited states of the ground state can provide an efficient pathway for a nonradiative relaxation.[10] The lack of observed emissions due to a large Stokes shift ($>5000\ \mathrm{cm}^{-1}$) placing the emissions outside the region investigated cannot be ruled out however. The broadness of the spin-forbidden bands indicates that the potential surfaces for the ground and excited states are quite different. This, together with the antibonding character of states arising from the $t_{2g}{}^5e_g{}^1$ configuration, makes a large shift quite plausible. Better experiments are needed to clarify this point.

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Registry No. $2[d,l\text{-Co(en)}_3\text{Cl}_3]\cdot\text{NaCl}$, 59109-92-1.

References and Notes

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(8) J. S. Griffith, "The Theory of Transition-Metal Ions", Cambridge University Press, Cambridge, England, 1964, Table A37, p 422.

(9) The polarization of the $^1T_{1g}$ band can be traced to the difference in oscillator strengths of the formally allowed $^1A_1 \rightarrow {}^1E(\sigma$ polarized) and $^1A_1 \rightarrow {}^1A_2(\pi$ polarized) transitions in the lower symmetry (D_3) of the $\mathrm{Co(en)_3}^{3+}$ complex. In contrast, the $^1T_{2g}$ band is allowed only in the σ polarization. However, the experimental spectra[5,7] reveal some π-polarized absorption for the $^1T_{2g}$ band, though it is considerably weaker than the σ absorption. The π absorption has been rationalized in terms of vibronic coupling or site symmetry effects in the crystal, the former probably predominating.[5,7] Since the details of the origin of the π intensity for $^1T_{2g}$ are not fully understood and since the π intensity is forbidden (neglecting strong site influences), $I_\pi({}^1T_{2g})$ is taken as zero in the arguments advanced here.

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