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The Magnetic Optical Activity of d → d Transitions. Octahedral Chromium(III), Cobalt(III), Cobalt(II), Nickel(II), and Manganese(II) Complexes[1]

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The utility of magnetic optical activity in the study of the d → d transitions of transition metal complexes is discussed. Magnetic circular dichroism (MCD) data for d → d transitions in a range of octahedral complexes are presented and analyzed. $Mn(H_2O)_6^{2+}$, $Co(H_2O)_6^{2+}$, and $Ni(H_2O)_6^{2+}$ show large effects, while $Co(NH_3)_6^{3+}$, $Co(CN)_6^{3-}$, and the spin-allowed transitions of $Cr(NH_3)_6^{3+}$, $Cr(H_2O)_6^{3+}$, and $Cr(CN)_6^{3-}$, in contrast, exhibit very small MCD. The latter result is tentatively attributed to quenching of orbital angular momentum in the degenerate excited states by vibronic (Jahn–Teller) interactions. A similar diminution was observed in $Co(NH_3)_5Cl^{2+}$, *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$, *cis*- and *trans*-$Co(en)_2Cl_2^+$, $Co(en)_3^{3+}$, $Co(ox)_3^{3-}$, and the spin-allowed transitions of $Cr(en)_3^{3+}$ and $Cr(ox)_3^{3-}$, with the exception of the $^1A_1 \rightarrow {}^1E$ transition at 24,000 cm^{-1} in $Co(ox)_3^{3-}$. Here, a term characteristic of excited-state Zeeman splitting is found and the ^1E magnetic moment obtained is in good agreement with that predicted by ligand-field theory. The spin-forbidden transitions of Cr(III) complexes show huge effects, in some cases greater than the much more intense spin-allowed transitions, which can greatly facilitate the assignment of these transitions.

Introduction

The dispersion of the Faraday effect (magnetic optical activity) through regions of absorption has been studied sporadically for many years.[4] Much of this work has involved the d → d transitions of transition metal complexes, since they occur in the most accessible spectral regions and can show large effects.[5] In the early decades of the century attention was primarily directed at the qualitative dispersion form since contradictory predictions were given by different applications of classical electron theory. The major work in this period was associated with Roberts[6,7] and Cotton.[8–11] Around 1930 the early quantum mechanical theories of the Faraday effect were developed[12–14] and, following this, some attempts were made to classify experimental results on the basis of Serber's theory.[7,15,16] However, at that time neither the instrumentation for accurate experimental work nor the molecular theories necessary for its detailed interpretation existed, and interest was transferred to the low-temperature studies at a single wavelength being made by Becquerel, de Haas, and van den Handel.[4b,17] Very recently the pendulum has swung back, following the resurgence of optical rotatory dispersion and circular dichroism studies of natural optical activity.[18–21] Experimental results for a variety of d → d transitions have been reported by Margerie,[22] Briat,[23,24] Shashoua,[25] Djerassi,[26] Foss,[27] Denning,[28] Yoshiwara and Kearns,[29] and their respective co-workers. Theoretical interest has also been stimulated by the growth of ligand-field theory[30] and by the recent development[4b,31–33] and applications[33–38] of the theory of the Faraday effect in regions of absorption. However, so far there have been few theoretical treatments of the experimental data for d → d transitions[39] and, in particular, no broad

(1) This work was supported in part by the National Science Foundation.
(2) University of Virginia.
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(4) For reviews see: (a) W. Schütz, "Magnetooptik, Handbuch der Experimentalphysik," Vol. 16, Akademische Verlagsgesellschaft, Leipzig, 1936; (b) A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, **17**, 399 (1966).
(5) Transition metal complexes are often paramagnetic, too, and it has frequently been assumed (wrongly) that a direct relation between paramagnetism and the Faraday effect exists.
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(39) Calculations of the magnetic optical activity of d → d transitions have been carried out for: (a) $Co(H_2O)_6^{2+}$ by M. J. Stephen, *Mol. Phys.*, **1**, 301 (1958); (b) $Ti(H_2O)_6^{3+}$, $Cu(H_2O)_6^{2+}$, and $CoCl_4^{2-}$ by S. H. Lin and H. Eyring, *J. Chem. Phys.*, **42**, 1780 (1965); (c) $CoCl_4^{2-}$ by P. J. Stephens, *ibid.*, **43**, 4444 (1965); (d) Co(III) octahedral complexes by P. J. Stephens, *ibid.*, **44**, 4060 (1966); (e) Cr(III), Co(III), Co(II), and Ni(II) octahedral complexes by P. J. Stephens, to be published.

discussion of the general types of information likely to be forthcoming. It is the purpose of this paper to initiate such discussion. We also present new magnetic circular dichroism data and calculations for a selection of metal complexes.

General Discussion

The main features of the theory of the dispersion of magnetooptical rotation (MOR) and magnetic circular dichroism (MCD) through absorption bands[31,40] have been summarized earlier.[4b,35] Here we need only note that the theoretical expressions for the MOR and MCD of a transition each contain three terms, named A, B and C, whose dispersion shapes are shown in Figure 1. A terms are caused by the Zeeman splitting of the ground or excited state and hence occur only when at least one of the states is degenerate. C terms arise from the repopulation of the ground-state sublevels as a result of its Zeeman splitting and can only be present when the ground state is degenerate. The perturbation of the states by the magnetic field, mixing them with other states, is responsible for the B terms. C terms are temperature dependent while A and B terms are independent of temperature. The magnitudes of the terms are determined by the Faraday parameters A, B, and C, defined, for a transition a → j, by[41]

$$A(\mathrm{a} \rightarrow \mathrm{j}) = \frac{1}{2d_\mathrm{a}}\sum[\langle \mathrm{j}|\boldsymbol{\mu}|\mathrm{j}\rangle - \langle \mathrm{a}|\boldsymbol{\mu}|\mathrm{a}\rangle]\cdot Im\{\langle \mathrm{a}|\mathbf{m}|\mathrm{j}\rangle \times \langle \mathrm{j}|\mathbf{m}|\mathrm{a}\rangle\}$$

$$B(\mathrm{a} \rightarrow \mathrm{j}) = \frac{1}{d_\mathrm{a}}\sum Im\left\{\sum_{\mathrm{k}\neq \mathrm{a}}\frac{\langle \mathrm{k}|\boldsymbol{\mu}|\mathrm{a}\rangle}{W_\mathrm{k} - W_\mathrm{a}}\cdot\langle \mathrm{a}|\mathbf{m}|\mathrm{j}\rangle \times \langle \mathrm{j}|\mathbf{m}|\mathrm{k}\rangle + \sum_{\mathrm{k}\neq \mathrm{j}}\frac{\langle \mathrm{j}|\boldsymbol{\mu}|\mathrm{k}\rangle}{W_\mathrm{k} - W_\mathrm{j}}\cdot\langle \mathrm{a}|\mathbf{m}|\mathrm{j}\rangle \times \langle \mathrm{k}|\mathbf{m}|\mathrm{a}\rangle\right\} \quad (1)$$

$$C(\mathrm{a} \rightarrow \mathrm{j}) = \frac{1}{2d_\mathrm{a}}\sum\langle \mathrm{a}|\boldsymbol{\mu}|\mathrm{a}\rangle\cdot Im\{\langle \mathrm{a}|\mathbf{m}|\mathrm{j}\rangle \times \langle \mathrm{j}|\mathbf{m}|\mathrm{a}\rangle\}$$

where **m** and $\boldsymbol{\mu}$ are the electric and magnetic dipole moment operators, d_a is the degeneracy of a, W_a is the energy of a, and the summations are over all transitions degenerate with a → j. In terms containing the αth component of $\boldsymbol{\mu}$, a and j are required to be diagonal in μ_α. A, B, and C are extracted from experimental data by using theoretical expressions which give the MOR and MCD as functions of frequency.[35,36]

We shall here be concerned only with nonempirical applications of the Faraday effect of d → d transitions. These can be categorized as qualitative or quantitative. The principal qualitative application makes use of the presence or absence of A or C terms. A nonzero C term implies a degenerate ground state and the presence of an A term demonstrates that one or both states of the transition are degenerate. B terms are always (in principle) nonzero and lead to no qualitative information. In general, the nature of the ground state of a molecule is known from other data (magnetic susceptibility, esr, etc.) or is obvious from theory, and the use of A or C terms to detect degeneracy here is not likely to prove of wide importance. However, the use of A terms to differentiate between degenerate and nondegenerate transitions from nondegenerate ground states is likely to be of considerable value, particularly for broad bands, where no other direct, unambiguous method exists. One such application has already been reported by Martin, *et al.*, in which the ${}^1A_{1g}(\Gamma_1) \rightarrow {}^1E_g(\Gamma_5)$ d → d transition of $PtCl_4^{2-}$ was identified.[27] We have attempted to make similar use of this technique in tetragonally distorted octahedral Co(III) complexes, as discussed below. Note, however, that the *absence* of an A term does *not* allow the inference of a nondegenerate transition, since the B term may dominate the Faraday effect, making the A term unobservable.

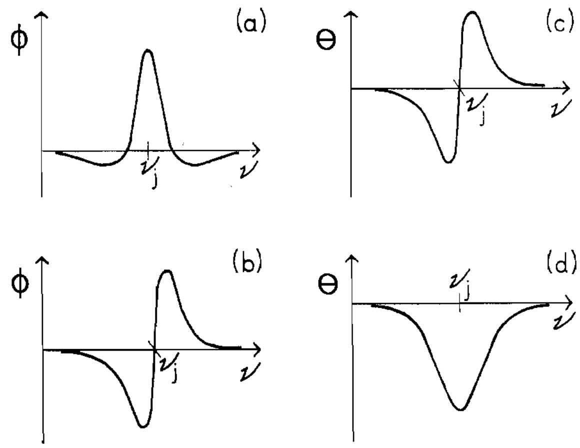

Figure 1.—Qualitative forms of MOR (ϕ) and MCD (Θ): (a) and (c), A term; (b) and (d), B and C terms. ν_j is the transition frequency.

Quantitative applications require detailed calculation of Faraday parameters. These latter depend on matrix elements of $\boldsymbol{\mu}$, diagonal in A and C and off-diagonal in B, and on transition moments of individual Zeeman components of the transition—that is, on the detailed absorption mechanism. For electronically allowed transitions of known symmetry the *relative* magnitudes of the various electric and magnetic dipole matrix elements are given by group theory, and A and C values can be used either to assign transition symmetries (calculating magnetic dipole moments *a priori*) or to determine magnetic moments (knowing the symmetries).[34,36] f → d transitions in rare earth ions,[37] color centers,[42] $\pi \rightarrow \pi$ transitions in porphyrins and phthalocyanines,[35,38] and charge-transfer transitions in $Fe(CN)_6^{3-}$, MnO_4^-, and CrO_4^{2-} [36] have been studied in this way. In electronically forbidden transitions, for example, d → d transitions in centrosymmetric environments, the details of the absorption mechanism are much less understood and in general are not entirely symmetry determined. On the other hand, magnetic

(40) P. J. Stephens, to be published.

(41) These definitions follow ref 35 and 36 and differ by a factor of 3 from those in ref 34, 39c, and 39d. Note that we exclude contributions from magnetic dipole transition moments, which are generally negligible (see Discussion section, part 1).

(42) C. H. Henry, *Phys. Rev.*, **140**, A256 (1965), ref 33, and references therein.

dipole matrix elements for the d^n states are in many cases reliably calculable, owing to their closeness to atomic wave functions, as is well known from paramagnetic resonance and magnetic susceptibility work.[43] The dominant application in this case is hence likely to be to the evaluation of theories of the absorption process between states of known configuration and symmetry. In some simple cases, the relative transition moments of the Zeeman components may be completely symmetry determined, and here magnetic moments can be obtained. In general, the electronic symmetries of such transitions will have been satisfactorily assigned already and it is unlikely that much use can be made of the Faraday effect in making electronic symmetry assignments (except through the qualitative method discussed above). However, if individual vibronic transitions are resolved, the symmetries of the *vibrational* transitions involved can be determined.[39d]

In all cases, B terms are very much more difficult to calculate than A and C terms since they involve contributions from *all* other states of the molecule (including the continuum). While approximate methods of handling this problem may be found, the quantitative use of B terms will remain more difficult than the use of A and C terms.

Following this line of thought, we have studied the MCD of d → d transitions in two classes of complexes with the aim of probing the absorption mechanism. First, we have investigated O_h complexes, where the intensity is supposedly produced by vibronic interactions.[44] Simple theories of these effects have been proposed by Liehr and Ballhausen,[45-47] Koide and Pryce,[48] and Englman.[49] However, the absorption spectrum does not contain sufficient information to provide a stringent test of these theories, and the Faraday effect data should allow a more detailed investigation of their validity. Second, we have examined trigonally distorted octahedral complexes, where two competing mechanisms exist by which d → d transitions are made allowed, namely, through static or vibronic distortions.[50] It is interesting to investigate the sensitivity of the MCD to the relative importance of these two processes. If the former are dominant, we have allowed transitions whose A and C terms may be calculated; if the latter predominate, the MCD should resemble similar O_h complexes. The data could both serve as a qualitative diagnostic tool and substantiate the current theories of these transitions.

The work described here involves room-temperature solutions and is strictly exploratory. As is the case with absorption spectra, only limited information can be obtained from broad, vibrationally unresolved bands. We hope to follow the present work with studies of the more finely resolved bands observable in crystals at low temperatures.

Experimental Results

MCD has been measured by the techniques described in detail in an earlier paper.[36] The results, together with corresponding absorption spectra obtained on a Cary 14, are displayed in Figures 2–19. $[\theta]_M$ is the molar ellipticity, defined as in natural optical activity, per unit magnetic field in the direction of the light beam.[34-36] This sign convention is opposite to that used in earlier MOR work, and with our convention, the Verdet constant of water is negative. Parameters extracted from these data are given in Tables I and II. As before,[35,36] in fitting MCD data we have used both the damped-oscillator model (DOM) and gaussian band shapes. The best fits obtained are shown in the figures. We only give parameters corresponding to the dominant term in the MCD unless A and $(B + C)$ terms are comparable in magnitude. Values given are insensitive to initial parameter choice in the fitting procedure[36] and should be reliable to within

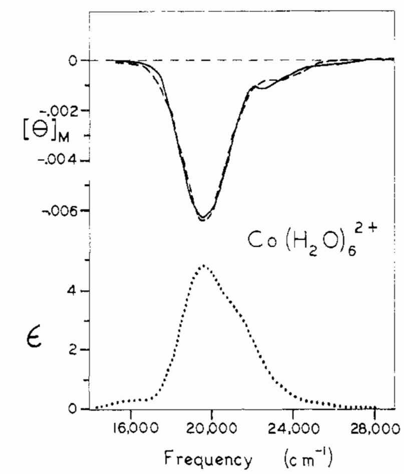

Figure 2.—$[\Theta]_M$, molar ellipticity per unit magnetic field, for $Co(H_2O)_6^{2+}$: solid line, experimental data; dashed line, gaussian best fit; peak-to-peak noise level negligible. ϵ is the molar extinction coefficient.

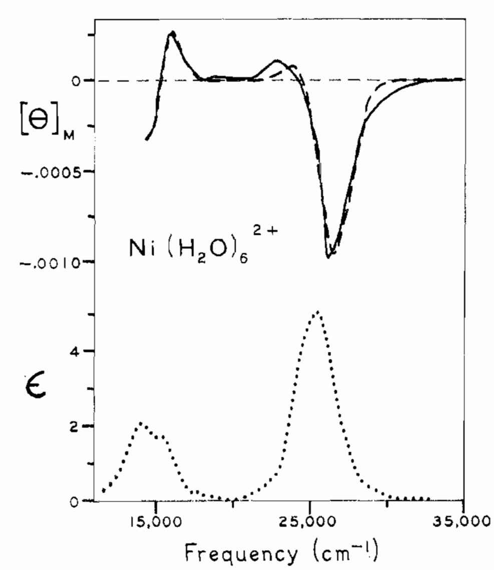

Figure 3.—$[\Theta]_M$ for $Ni(H_2O)_6^{2+}$: solid line, experimental data; dashed line, gaussian best fit; peak-to-peak noise level negligible.

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(47) A. D. Liehr, *Advan. Chem. Phys.*, **5**, 241 (1963).
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(49) R. Englman, *Mol. Phys.*, **3**, 48 (1960); *Advan. Chem. Phys.*, **8**, 13 (1965).
(50) Reference 30, Chapter 8.

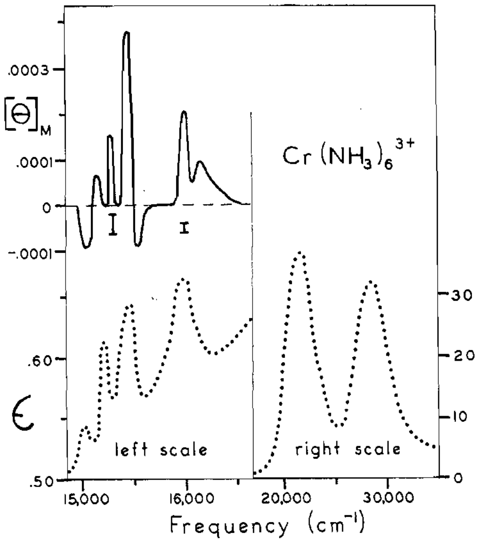

Figure 4.—$[\Theta]_M$ for $Cr(NH_3)_6^{3+}$; vertical bar shows peak-to-peak noise level. MCD unmeasurable in 20,000–30,000-cm^{-1} region.

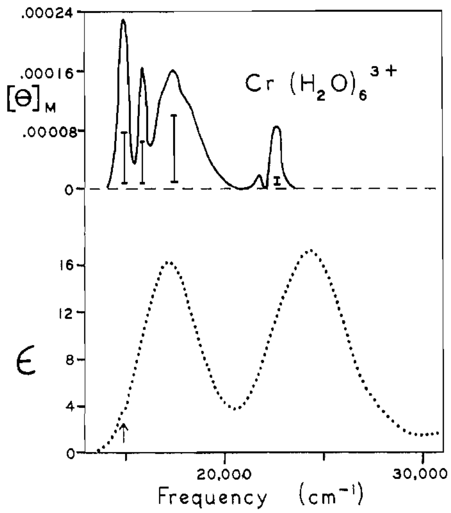

Figure 5.—$[\Theta]_M$ for $Cr(H_2O)_6^{3+}$; vertical bar shows peak-to-peak noise level. MCD unmeasurable above 24,000 cm^{-1}. Vertical arrow indicates shoulder due to spin-forbidden transition.

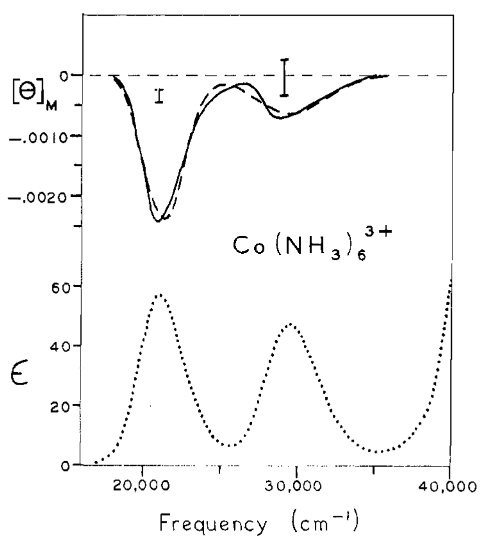

Figure 6.—$[\Theta]_M$ for $Co(NH_3)_6^{3+}$: solid line, experimental data; dashed line, gaussian best fit; vertical bar shows peak-to-peak noise level.

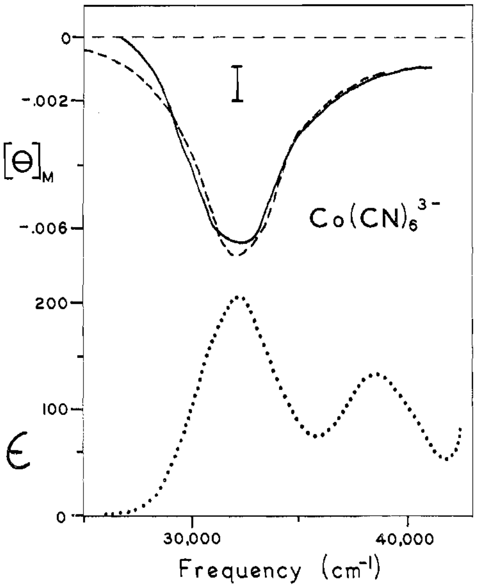

Figure 7.—$[\Theta]_M$ for $Co(CN)_6^{3-}$: solid line, experimental data; dashed line, DOM best fit; vertical bar shows peak-to-peak noise level. MCD unmeasurable above 39,000 cm^{-1}.

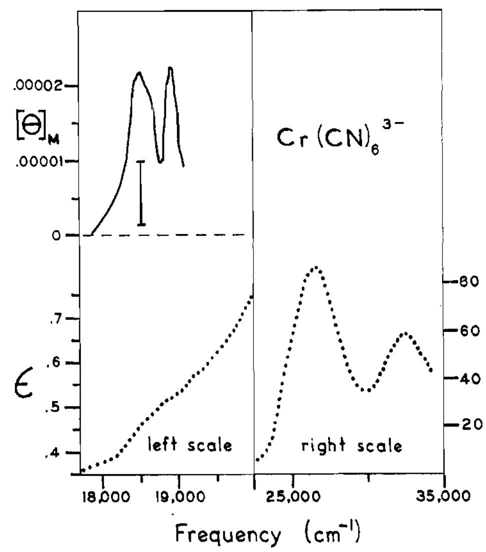

Figure 8.—$[\Theta]_M$ for $Cr(CN)_6^{3-}$; vertical bar shows peak-to-peak noise level. MCD unmeasurable between 20,000 and 35,000 cm^{-1}.

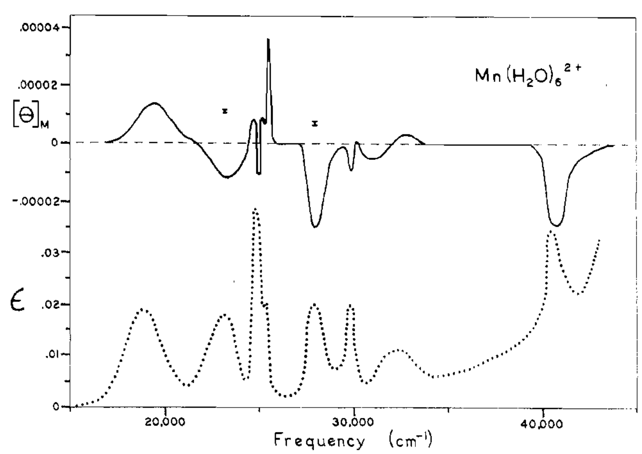

Figure 9.—$[\Theta]_M$ for $Mn(H_2O)_6^{2+}$; vertical bar shows peak-to-peak noise level.

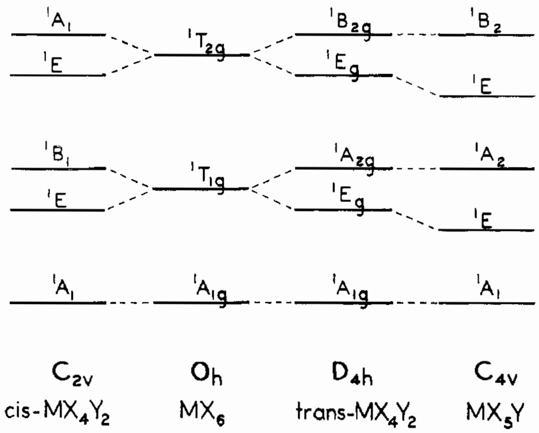

Figure 10.—Splitting of O_h d^6 states in tetragonal Co(III) complexes.

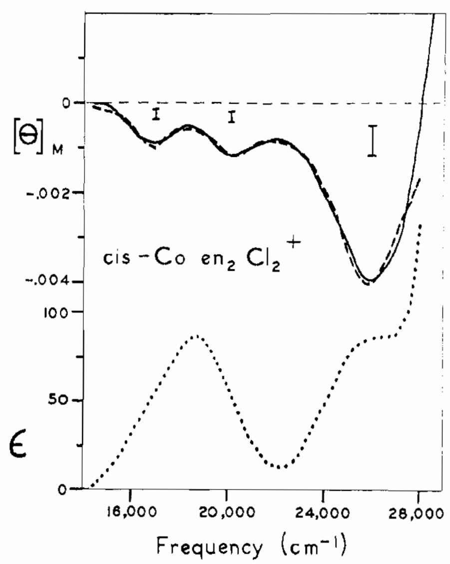

Figure 11.—$[\Theta]_M$ for *cis*-$Co(en)_2Cl_2^+$: solid line, experimental data; dashed line, DOM best fit; vertical bar shows peak-to-peak noise level.

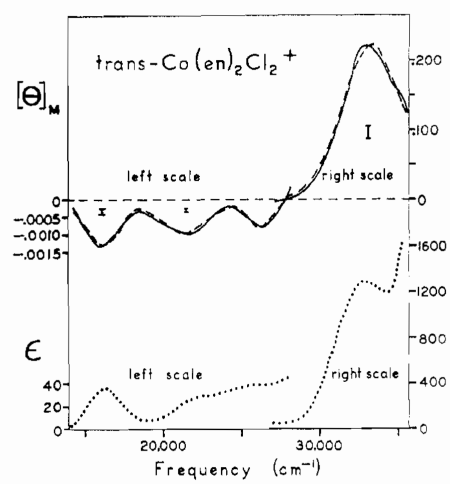

Figure 12.—$[\Theta]_M$ for *trans*-$Co(en)_2Cl_2^+$: solid line, experimental data; dashed line, gaussian best fit; vertical bar shows peak-to-peak noise level.

a factor of 2. Dipole strength values ($D(a \rightarrow j) = (1/d_a)\cdot \Sigma|\langle a|\mathbf{m}|j\rangle|^2$) have been obtained either by numerical integration or by gaussian fitting of absorption data. In some cases where $\mathcal{A}$ terms were expected but not observed, we include upper limits

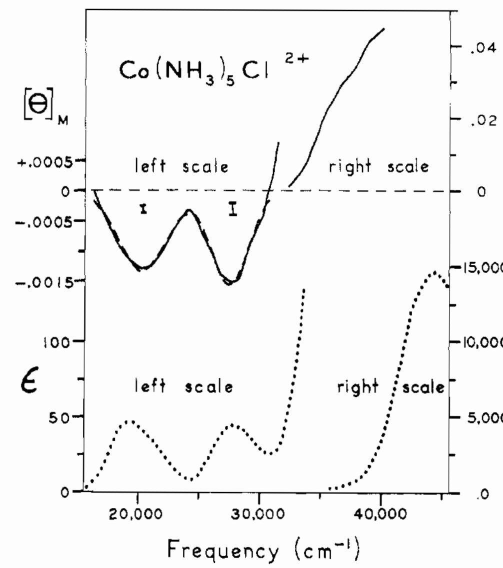

Figure 13.—$[\Theta]_M$ for $Co(NH_3)_5Cl^{2+}$: solid line, experimental data; dashed line, gaussian best fit; vertical bar shows peak-to-peak noise level. MCD was unreliable above 40,000 cm^{-1}.

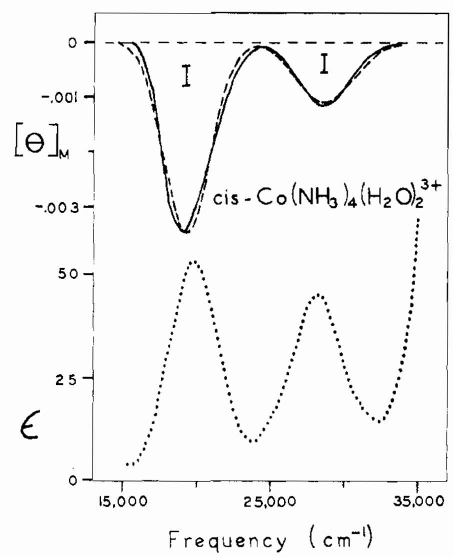

Figure 14.—$[\Theta]_M$ for *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$: solid line, experimental data; dashed line, gaussian best fit; vertical bar shows peak-to-peak noise level.

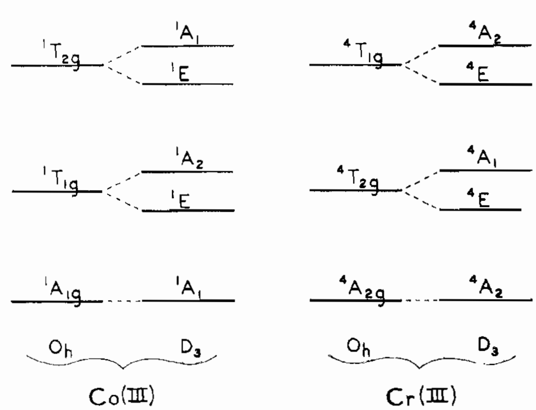

Figure 15.—Splitting of O_h d^n states of Co(III) and Cr(III) in a trigonal field.

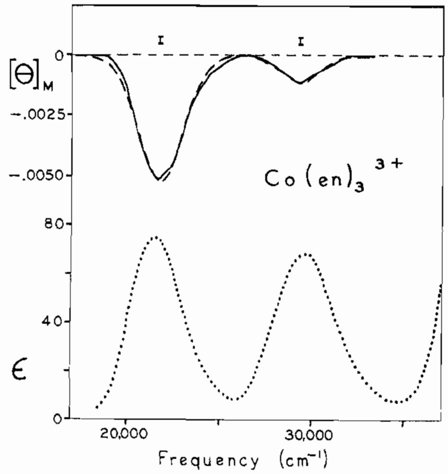

Figure 16.—$[\Theta]_M$ for $Co(en)_3^{3+}$: solid line, experimental data; dashed line, gaussian best fit; vertical bar shows peak-to-peak noise level.

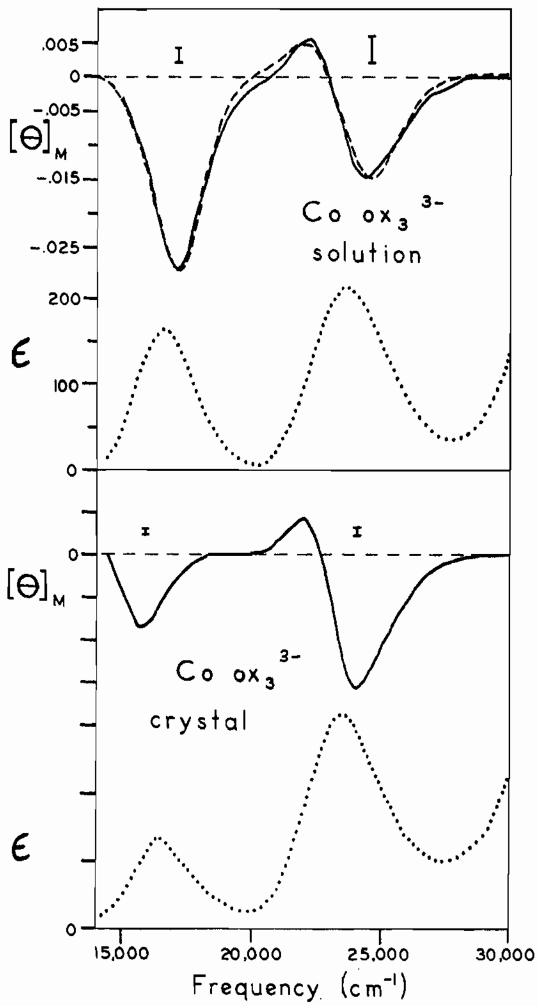

Figure 17.—$[\Theta]_M$ for $Co(ox)_3^{3-}$ solution and Co^{3+}–NaMgAl-$(ox)_3 \cdot 9H_2O$ crystal: solid line, experimental data; dashed line, gaussian best fit; vertical bar shows peak-to-peak noise level. The ordinate scales for the crystal are arbitrary.

for A/D. In other cases, the A-type terms observed may, in fact, arise from overlap of C terms of opposite sign (see below); the A values quoted are then to be construed as "effective" parameters.

The accuracy of the MCD results varies considerably and de-

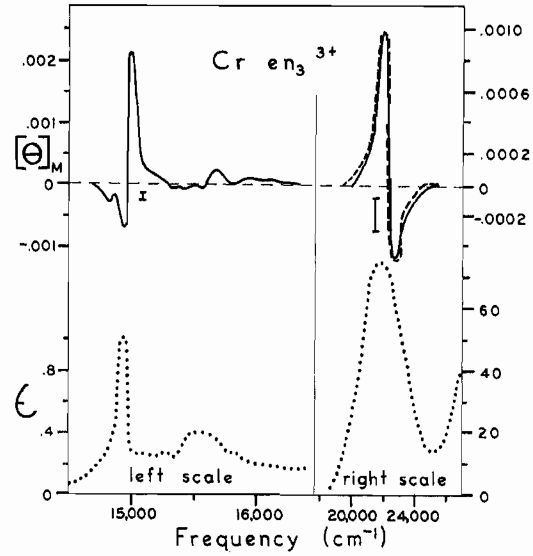

Figure 18.—$[\Theta]_M$ for $Cr(en)_3^{3+}$: vertical bar shows peak-to-peak noise level; solid line, experimental data; dashed line, DOM best fit. MCD unmeasurable above 25,000 cm^{-1}.

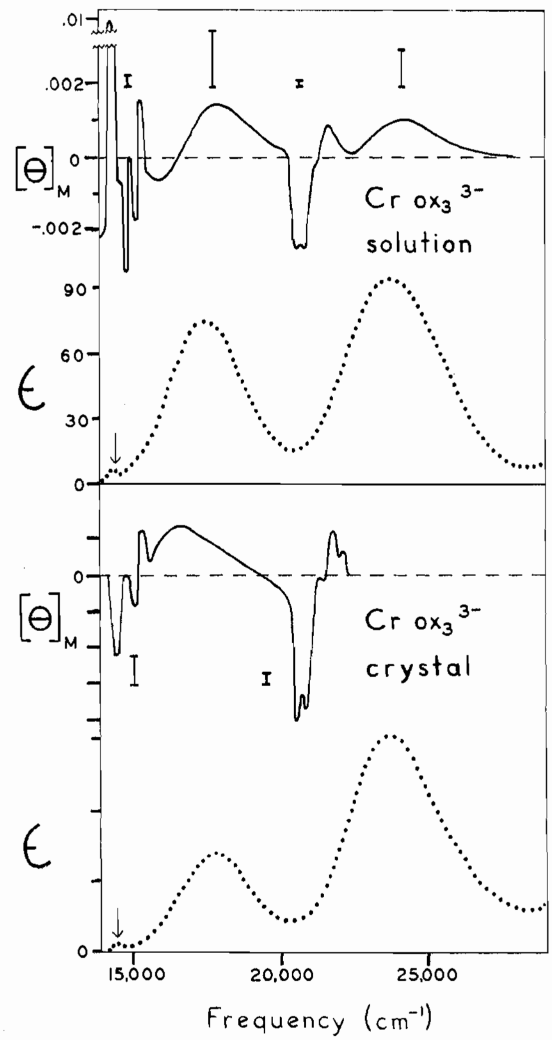

Figure 19.—$[\Theta]_M$ for $Cr(ox)_3^{3-}$ solution and Cr^{3+}–NaMgAl-$(ox)_3 \cdot 9H_2O$ crystal; vertical bar shows peak-to-peak noise level; vertical arrow indicates spin-forbidden absorption. The ordinate scales for the crystal are arbitrary.

Table I[a]

Parameters for Spin-Allowed Transitions and $Mn(H_2O)_6^{2+}$

Complex	Transition	ν_{max}, cm^{-1}	$\lvert[\Theta]_{M_{max}}\rvert/\epsilon_{max}$	A^c	$B + (C/kT)^b$	D^d	A/D	$(B + (C/kT))/D$
$Co(H_2O)_6^{2+}$ [e]	$^4T_{1g} \rightarrow {}^4T_{1g}$	19,600	1×10^{-3}		3.25×10^{-5} [h]	8.95×10^{-3}		3.6×10^{-3}
$Ni(H_2O)_6^{2+}$ [f]	$^3A_{2g} \rightarrow {}^3T_{1g}$	14,000; 15,500	2×10^{-4}	1.49^h		4.54×10^{-3}	0.33	
	$^3A_{2g} \rightarrow {}^3T_{1g}$	25,300	2×10^{-4}	-2.53^h	2.56×10^{-6}	6.19×10^{-3}	−0.41	4.2×10^{-4}
$Cr(NH_3)_6^{3+}$	$^4A_{2g} \rightarrow {}^4T_{2g}$	21,600	$<5 \times 10^{-6}$			5.91×10^{-2}	$<2 \times 10^{-2}$	
	$^4A_{2g} \rightarrow {}^4T_{1g}$	28,500	$<5 \times 10^{-6}$			5.00×10^{-2}	$<2 \times 10^{-2}$	
$Cr(H_2O)_6^{3+}$	$^4A_{2g} \rightarrow {}^4T_{2g}$	17,200	1×10^{-5}		-5.84×10^{-7}	3.08×10^{-2}	$<4 \times 10^{-3}$	-1.9×10^{-5}
	$^4A_{2g} \rightarrow {}^4T_{1g}$	24,300	$<5 \times 10^{-6}$			3.06×10^{-2}	$<7 \times 10^{-2}$	
$Co(NH_3)_6^{3+}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	21,000	4×10^{-5}		1.16×10^{-5}	9.62×10^{-2}	$<2 \times 10^{-2}$	1.2×10^{-4}
	$^1A_{1g} \rightarrow {}^1T_{2g}$	29,500	2×10^{-5}		3.09×10^{-6}	6.81×10^{-2}	$<10^{-1}$	4.6×10^{-5}
$Co(CN)_6^{3-}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	32,100	3×10^{-5}		3.65×10^{-5}	2.58×10^{-1} [h]	$<5 \times 10^{-2}$	1.4×10^{-4}
$Mn(H_2O)_6^{2+}$	$^6A_{1g} \rightarrow {}^4\Gamma_g$	16,000–42,000	$\sim 1 \times 10^{-3}$					
$Co(NH_3)_5Cl^{2+}$	$^1A_1 \rightarrow {}^1A_2, {}^1E_a$	19,000	3×10^{-5}		1.00×10^{-5} [h]	1.01×10^{-1} [h]	$<3 \times 10^{-3}$	1.0×10^{-4}
	$^1A_1 \rightarrow {}^1B_2, {}^1E_b$	27,800	3×10^{-5}		6.56×10^{-6} [h]	7.78×10^{-2} [h]	$<3 \times 10^{-3}$	8.5×10^{-5}
trans-$Co(en)_2Cl_2^+$	$^1A_{1g} \rightarrow {}^1E_g{}^a$	16,200	4×10^{-5}		6.54×10^{-6} [h]	5.50×10^{-2}	$<2 \times 10^{-2}$	1.2×10^{-4}
	$^1A_{1g} \rightarrow {}^1A_{2g}$	22,000	3×10^{-5}		5.48×10^{-6} [h]			
	$^1A_{1g} \rightarrow {}^1B_{2g}, {}^1E_g{}^b$	25,000	2×10^{-5}		1.81×10^{-6} [h]			
cis-$Co(en)_2Cl_2^+$	$^1A_1 \rightarrow {}^1B_1$	17,000	2×10^{-5}		4.00×10^{-6} [i]	1.8×10^{-1} [h] (both bands)		5.0×10^{-5} (both bands)
	$^1A_1 \rightarrow {}^1E_a$	18,700	1×10^{-5}		4.99×10^{-6} [i]			
	$^1A_1 \rightarrow {}^1A_1, {}^1E_b$	26,000	5×10^{-5}		2.48×10^{-5} [i]	1.34×10^{-1} [h]		
cis-$Co(NH_3)_4(H_2O)_2^{3+}$	$^1A_1 \rightarrow {}^1B_1, {}^1E_a$	19,800	6×10^{-5}		2.13×10^{-5}	1.09×10^{-1}	$<4 \times 10^{-2}$	2.0×10^{-4}
	$^1A_1 \rightarrow {}^1A_1, {}^1E_b$	28,200	3×10^{-5}		5.20×10^{-6}	7.46×10^{-2}	$<2 \times 10^{-2}$	7.0×10^{-5}
$Cr(en)_3^{3+}$	$^4A_2 \rightarrow {}^4A_1, {}^4E_a$	21,800	1×10^{-5}	-1.99^i		1.11×10^{-1}	-1.8×10^{-2}	
	$^4A_2 \rightarrow {}^4A_2, {}^4E_b$	28,500	$<1 \times 10^{-5}$			8.11×10^{-2}		
$Cr(ox)_3^{3-}$ [g]	$^4A_2 \rightarrow {}^4A_1, {}^4E_a$	17,500	2×10^{-5}			1.23×10^{-1}	$<8 \times 10^{-3}$	
	$^4A_2 \rightarrow {}^4A_2, {}^4E_b$	23,900	1×10^{-5}			1.45×10^{-1}	$<4 \times 10^{-3}$	
$Co(en)_3^{3+}$	$^1A_1 \rightarrow {}^1A_2, {}^1E_a$	21,500	7×10^{-5}		2.19×10^{-5}	1.20×10^{-1}	$<3 \times 10^{-2}$	1.8×10^{-4}
	$^1A_1 \rightarrow {}^1A_1, {}^1E_b$	29,600	2×10^{-5}		2.84×10^{-6}	9.40×10^{-2}	$<5 \times 10^{-2}$	3.0×10^{-5}
$Co(ox)_3^{3-}$ [g]	$^1A_1 \rightarrow {}^1A_2, {}^1E_a$	16,600	2×10^{-4}		1.23×10^{-4}	2.50×10^{-1}	$<7 \times 10^{-2}$	4.9×10^{-4}
	$^1A_1 \rightarrow {}^1A_1, {}^1E_b$	23,600	7×10^{-5}	-74.7^h	3.22×10^{-5}	3.13×10^{-1}	-2.4×10^{-1}	1.0×10^{-4}

[a] A, B, C, and D values in units of $d^2\beta$, $d^2\beta/cm^{-1}$, $d^2\beta$, and d^2, respectively, where d = Debye unit and β = Bohr magneton. [b] If not otherwise indicated, values are obtained from $\int[\Theta]_M d\nu/\nu$. [c] Values are in units of 10^{-3}, *i.e.*, 1.49 = 1.49×10^{-3}. [d] If not otherwise indicated, values are obtained from $\int \epsilon d\nu$. [e] The MCD was fit as two bands (see Figure 2); $B + (C/kT)$ is for the larger band. D is for both bands. $(B + (C/kT))kT = 6.73 \times 10^{-3}$; $(B + (C/kT))(kT/D) = 0.75\beta$. [f] The MCD refers only to the higher energy component of the 15,000-cm^{-1} band. D is for both bands. [g] Data for solutions only. [h] Value obtained from Gaussian fit. [i] Value obtained from DOM fit.

Table II[a]

Parameters for Cr(III) Spin-Forbidden Transitions

Complex	MCD: ν_{max}, cm^{-1}	MCD: $[\Theta]_M$max	MCD: $B + (C/kT)$	Absorption: ν_{max}, cm^{-1}	Absorption: ϵ_{max}	$[\Theta]_{M_{max}}/\epsilon_{max}$
$Cr(NH_3)_6^{3+}$	15,000–16,500	3.8×10^{-4}		15,220		
				~15,450		$\sim 10^{-3}$
				~16,000		
$Cr(H_2O)_6^{3+}$	14,900	2.3×10^{-4}	-2.68×10^{-7}	14,800	0.5	5×10^{-4}
	15,900	1.7×10^{-4}	-1.59×10^{-7}			
$Cr(CN)_6^{3-}$	18,500	2.1×10^{-5}	-2.08×10^{-8} [b]			
	18,900	2.2×10^{-5}	-9.6×10^{-9} [b]			
$Cr(en)_3^{3+}$	15,000	2.1×10^{-3}		14,950	1.0	2×10^{-3}
	15,200–15,800	2×10^{-4}		15,200–15,800	0.25	8×10^{-4}
$Cr(ox)_3^{3-}$	14,000–15,500	1×10^{-2}		14,350	2.5	4×10^{-3}
	~20,800	-2.5×10^{-3}				

[a] Units and symbols as in Table I. [b] Value obtained from DOM fit.

pends roughly on the ratio of peak MCD to maximum absorption. Thus, in cases such as $Co(H_2O)_6^{2+}$ and $Ni(H_2O)_6^{2+}$ where the peak-to-peak noise level is small or negligible and $[\Theta]_{M_{max}}/\epsilon_{max} \sim 10^{-3}$–$10^{-4}$, the MCD data should be reliable to ±10% or better. On the other hand, in cases where $[\Theta]_{M_{max}}/\epsilon_{max} \lesssim 10^{-5}$, the noise level is high and the results are only semiquantitative. The peak-to-peak noise level is indicated on each figure; $[\Theta]_{M_{max}}/\epsilon_{max}$ values are given in Tables I and II.

Charge-transfer transitions have been studied where easily accessible. Some of the results are shown in Figures 12 and 13. Since, in all cases, the MCD is either uninteresting or unmeasurable, no parameters are given for these transitions.

Table III compares our results for several complexes with those of other groups. The sensitivity of our instrument is seen to be considerably greater than of the other apparatus. Since Yoshiwara and Kearns[29] detect no "anomalies" in $Ni(H_2O)_6^{2+}$, their results for $Cr(H_2O)_6^{3+}$ and $Co(NH_3)_6^{3+}$ (which exhibit smaller MCD) are probably spurious. Our data for $Co(H_2O)_6^{2+}$ agree quantitatively with those of Schérer and Cordonnier[10] and Shashoua[25] and qualitatively with the results of Roberts,[6] Briat,[24] and Schooley, Bunnenberg, and Djerassi.[26] Qualitative agreement with the work of Roberts and Adams[7] is found for $Ni(H_2O)_6.^{2+}$

All measurements were made at 26 ± 2°, and we are not able to separate B and C terms experimentally, the quantity obtained from fitting or integrating MCD data being $B + (C/kT)$. However, there are two alternative ways in which we can plausibly distinguish B and C terms without temperature-dependence data. First, from theory, it is known in certain cases that C must be zero, and then $B + (C/kT) = B$. This is the case for Co(III)

TABLE III[a]

Complex	Transition freq, cm^{-1}	This work[b]	Roberts, *et al.*[c]	Schérer, *et al.*[d]	Briat, *et al.*[e]	Shashoua[f]	Schooley, *et al.*[g]	Yoshiwara and Kearns[h]
$Cr(H_2O)_6^{3+}$	17,000	*						*
	24,000	?						×
$Mn(H_2O)_6^{2+}$	16,000–42,000	*				×		
$Co(NH_3)_6^{3+}$	21,000	*			×			*
	30,000	*			×			×
$Co(H_2O)_6^{2+}$	19,600	*	*	*	*	*	*	*
	21,500	*	×	×	*	*	×	×
$Ni(H_2O)_6^{2+}$	25,000	*	*			×	×	×

[a] * or × indicates MCD or MOR "anomaly" observed or not observed, respectively. [b] Durrum–Jasco CD, $H \sim 45,000$ gauss. [c] References 6 and 7; home-made instrument, $H \sim 11,000$ gauss. [d] References 9 and 10; home-made instrument, $H \sim 50,000$ gauss. [e] References 23 and 24; home-made instrument, $H \sim 4200$ gauss. [f] Reference 25; home-made instrument, $H \sim 10,000$ gauss. [g] Reference 26 and C. Djerassi, private communication, Dec 1966; Jouan Dichrograph, $H \sim 8500$ gauss. [h] Reference 29; Rudolph polarimeter, $H \sim 2500$ gauss.

complexes and, to a first approximation, for the spin-allowed transitions in Cr(III) and Ni(II) complexes. The second criterion uses the magnitude of the effect. The ratio of MCD maxima for B and C terms is $B(kT/C)$. If we suppose that the matrix elements of $\mathbf{m}$ and $\boldsymbol{\mu}$ entering into B and C are of the same order of magnitude, this ratio is $\sim kT/\Delta E$, where ΔE is an average energy denominator in B. At room temperature $kT \sim 200\ cm^{-1}$ and ΔE may be reasonably estimated as $\sim 10,000\ cm^{-1}$. Then $B(kT/C) \sim 1/50$. Both B and C are roughly proportional to D. Hence, for a transition of given intensity, C terms should be some 50 times greater than B terms; or, $(B + (C/kT))/D$ and $[\Theta]_{M_{max}}/\epsilon_{max}$ are 50 times greater for a pure C term than for a pure B term. Exceptions must be made if there are electronic states $<<10,000\ cm^{-1}$ above the ground state contributing B terms through interaction with the ground state. For example, in $Co(H_2O)_6^{2+}$, spin–orbit splitting of the ground $^4T_{1g}$ multiplet puts excited states $<1500\ cm^{-1}$ above the ground Kramers doublet. $B(kT/C)$ is then expected to be of order unity. While these arguments are very crude, it appears to be the case that $(B + (C/kT))/D$ and $[\Theta]_{M_{max}}/\epsilon_{max}$ are considerably larger in $Co(H_2O)_6^{2+}$ and in the spin-forbidden transitions in $Mn(H_2O)_6^{2+}$ and Cr(III) complexes, where C terms are expected theoretically, than in all other transitions, where C should be zero or small. Thus, in the cases where $(B + (C/kT))/D$ is large and there are no low-lying excited states, we can neglect B terms and put $B + (C/kT) = C/kT$. Temperature-dependence studies will of course allow these arguments to be tested more critically.

Our samples were obtained from the following sources: $Co(H_2O)_6^{2+}$, $Ni(H_2O)_6^{2+}$, and $Cr(H_2O)_6^{3+}$ solutions were made from Fisher Certified reagent grade $CoSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, and $KCr(SO_4)_2 \cdot 12H_2O$, respectively, without further purification. Crystalline samples of the following compounds were supplied by Lektor Erik Larsen and were used without further purification: $Co(NH_3)_6Cl_3$, $[cis\text{-}Co(NH_3)_4(H_2O)_2]_2(SO_4)_3 \cdot 3H_2O$, *trans*-$Co(en)_2Cl_2Cl$, $Co(en)_3Cl_3$, $Cr(NH_3)_6Cl_3 \cdot 3H_2O$, $K_3Cr(ox)_3 \cdot 3H_2O$, $Cr(en)_3Cl_3 \cdot 3H_2O$, $K_3Cr(CN)_6$. Dr. R. Dingle also supplied us with a crystalline sample of $K_3Cr(CN)_6$. $Mn(ClO_4)_2 \cdot 6H_2O$ and $K_3Co(CN)_6$ were obtained from City Chemical Corp., the former being used without further purification, the latter being recrystallized once from water. Dr. R. D. Feltham supplied us with a sample of *cis*-$Co(en)_2Cl_2Cl$ which was recrystallized once from water. $Co(NH_3)_5ClCl_2$ was obtained from K & K Laboratories, Inc., and was recrystallized twice from water. $K_3Co(ox)_3 \cdot 3H_2O$ was made by a standard method.[51] The extinction coefficients of the ions studied generally agreed well with literature values. All solution measurements (ϵ and $[\Theta]_M$) were made in pure water. The host crystals $(NaMgAl(ox)_3 \cdot 9H_2O)$ containing $Cr(ox)_3^{3-}$ and $Co(ox)_3^{3-}$ were prepared in the manner described by Piper and Carlin.[52a] It is known[52b] that $Co(ox)_3^{3-}$ is not stable in solution. Our solutions of this ion were prepared immediately before running and, in fact, we did this as a general rule with all compounds to minimize possible contamination with other species. In the case of $Co(ox)_3^{3-}$, the similarity of the crystal and solution MCD in the 21,000–27,000-cm^{-1} region strongly suggest that the solution MCD is due to $Co(ox)_3^{3-}$.

(51) J. C. Bailar, Jr., and E. M. Jones, *Inorg. Syn.*, **1**, 37 (1939).
(52) (a) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **35**, 1809 (1961); (b) L. Hin-Fat and W. C. E. Higginson, *J. Chem. Soc., Sect. A*, 298 (1967).

Discussion

1. Octahedral Complexes.—The gross ligand-field theoretical assignments of the spin-allowed transitions observed are well known[53–55] and are given in Table I. The splitting of the 20,000-cm^{-1} band of $Co(H_2O)_6^{2+}$ (Figure 2) has been variously attributed to overlap with $^4T_{1g} \rightarrow {}^4A_{2g}$[56,57] or quartet → doublet transitions,[55] spin–orbit coupling,[58,59] and Jahn–Teller effects.[57] Likewise, the double peak of the 15,000-cm^{-1} band of $Ni(H_2O)_6^{2+}$ (Figure 3) may be due either to spin–orbit coupling[60,61] or to the simultaneous presence of a $^3A_{2g} \rightarrow {}^1E_g$ transition.[57,62,63] It should also be noted that the ground $^4T_{1g}$ state of $Co(H_2O)_6^{2+}$ is very substantially split by spin–orbit coupling, the ground state being a Kramers doublet.[56]

In the limit where spin–orbit coupling is zero, A, B, and C are independent of spin and only *orbital* degeneracy contributes to A and C terms. Then, for example, C would be zero for the spin-allowed transitions of Cr(III) and Ni(II) complexes. In the actual case, if the spin–orbit splitting is much less than the band width and, in the ground state, than kT, in general the MCD of spin-allowed transitions should to a first approximation be unmodified and still independent of spin. A specific exception is the case where the ground state is spin-degenerate and orbitally nondegenerate. In a transition to an orbitally degenerate state spin–orbit splitting of the excited state causes the C terms of the split components of the transition no longer to cancel and gives rise to MCD changing in sign through the

(53) Reference 30, Chapter 10.
(54) D. S. McClure, *Solid State Phys.*, **9**, 399 (1959).
(55) C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).
(56) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.* (London), **A206**, 173 (1951).
(57) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).
(58) C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).
(59) S. Koide, *Phil. Mag.*, **4**, 243 (1959).
(60) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959).
(61) C. J. Ballhausen and A. D. Liehr, *Mol. Phys.*, **2**, 123 (1959).
(62) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).
(63) Reference 43, Chapter 11.

band. In some cases this may mimic an A term; however, the effects are separable since genuine A terms are temperature independent. If the spin–orbit splitting is much smaller than the band width, the MCD will be much less than the C terms of the individual components but can still be comparable to the contributions of A and B terms present in the zero spin–orbit coupling limit. This effect in fact dominates the MCD of certain color centers in alkali halide crystals.[42] Here, it could be of importance in Cr(III) and Ni(II) complexes.

$Co(H_2O)_6^{2+}$ is expected to show C terms and large B terms, the ground state being degenerate and close to other spin–orbit components of the $^4T_{1g}$ multiplet. In agreement with this, $[\Theta]_{M\max}/\epsilon_{\max}$ and $(B + (C/kT))/D$ for the 20,000-cm^{-1} band are large and $(B + (C/kT))kT/D = 0.75\beta$ is of the correct order of magnitude. Temperature-dependence measurements are required to separate the B and C terms. The A term also expected for the transition is presumably swamped by the B and C terms (*cf.* $Fe(CN)_6^{3-}$ [36]). The component transitions of the whole 20,000-cm^{-1} band contribute in differing relative magnitude to absorption and MCD. This would be expected qualitatively for any of the proposed assignments, and it would require a very sophisticated calculation to differentiate between them on the basis of the MCD.

A-Type terms are observed for both bands in $Ni(H_2O)_6^{2+}$ (Figure 3) and could be due either to genuine A terms caused by excited-state Zeeman splitting or to overlapping C terms, as discussed above. Temperature-dependence studies would allow these alternatives to be distinguished. The A term of the 15,000-cm^{-1} band appears to be associated with the higher energy peak (~15,500 cm^{-1}) in absorption. Unfortunately we were not able to measure the MCD below 14,300 cm^{-1} and thus to cover the lower energy peak. Measurements through the whole band may allow discrimination between the conflicting assignments of the two peaks.

The $[\Theta]_{M\max}/\epsilon_{\max}$ ratios for the spin-allowed bands of $Cr(NH_3)_6^{3+}$, $Cr(H_2O)_6^{3+}$, $Cr(CN)_6^{3-}$, $Co(NH_3)_6^{3+}$, and $Co(CN)_6^{3-}$ (Figures 4–8) are 10–100 times smaller than in $Ni(H_2O)_6^{2+}$. Also, despite all bands being assigned to orbitally degenerate transitions, in no case[64] do we find evidence of A terms. Upper limits to A/D values, given in Table I, lie between 10^{-1} and $10^{-3}\beta$. It thus appears, unexpectedly, that there is very considerable quenching of orbital angular momentum in the excited states of these d^3 and d^6 complexes.[65] We are not able at this point to provide a detailed explanation of this phenomenon. The most likely cause, however, is the dynamic Jahn–Teller effect which has recently been shown to cause quenching of certain operators, including orbital angular momentum.[66–69] Jahn–Teller instability is presumably less in the Co(II) and Ni(II) complexes; this might be rationalized in terms of both their stronger spin–orbit coupling (which counteracts the distorting force) and the nature of the states involved. The excited state of the 25,000-cm^{-1} band of $Ni(H_2O)_6^{2+}$ belongs predominantly to the $t_{2g}^4e_g^4$ configuration, Jahn–Teller splitting of which should be weaker than of configurations with unfilled e_g shells, such as give rise to the $^4T_{1g}$ and $^4T_{2g}$ Cr(III) and $^1T_{1g}$ and $^1T_{2g}$ Co(III) states.

The C- and A-type terms observed in $Co(H_2O)_6^{2+}$ and $Ni(H_2O)_6^{2+}$ provide information against which to test the vibronic theory of the transitions. Detailed calculations to this end are presented in a forthcoming paper.[39e]

Yoshiwara and Kearns[29] suggested that the Faraday effect of d → d transitions is related to the magnetic dipole contribution to the transition moment since they only observed "anomalous" MOR dispersion for magnetic-dipole-allowed transitions. As discussed above, however, their results are probably incorrect and our MCD data show no correlation with magnetic-dipole selection rules. It can also be shown quantitatively that this contribution is too small to explain the observed MCD.[39e]

The d → d bands of $Mn(H_2O)_6^{2+}$ (Figure 9) all arise from spin-forbidden $^6A_{1g} \rightarrow {}^4\Gamma_g$ transitions. These should exhibit C terms, and the large $[\Theta]_{M\max}/\epsilon_{\max}$ ratios are consistent with this expectation. The spin-forbidden transitions of Cr(III) complexes are discussed in part 4 below.

2. Tetragonal Complexes.—In tetragonal Co(III) complexes of the form CoX_5Y and *cis*- and *trans*-CoX_4Y_2,[70] the O_h d → d transitions are split as shown in Figure 10. The assignments of these transitions and quantitative correlation of the splittings with the nature of X and Y have been extensively discussed.[31,71–76] The generally accepted assignments of the transitions we have studied are indicated in Table I. It was hoped that the MCD would serve to confirm assignments to degenerate transitions through the occurrence of A terms. Unfortunately, in all cases only B terms are observed, and no qualitative inferences can be made. As in $Co(NH_3)_6^{3+}$, the magnitude of $[\Theta]_{M\max}/\epsilon_{\max}$ is quite small and upper limits to A/D values for degenerate transitions are in the range 4×10^{-2}–$10^{-3}\beta$. This again indicates quenching of angular momentum in the excited states and suggests the intrusion of dynamic Jahn–Teller effects.

(64) There appears to be an A term in the 22,000-cm^{-1} band of $Cr(NH_3)_6^{3+}$ but the effect is too small to be unambiguous.

(65) An alternative possibility is that transitions made allowed by different vibrations give rise to contributions of opposite signs, the net effect being nearly zero. However, this seems unlikely as a general explanation.

(66) H. M. McConnell and A. D. McLachlan, *J. Chem. Phys.*, **34**, 1 (1961).

(67) F. S. Ham, *Phys. Rev.*, **138**, A1727 (1965).

(68) M. D. Sturge, *ibid.*, **140**, A880 (1965).

(69) W. C. Scott and M. D. Sturge, *ibid.*, **146**, 262 (1966).

(70) *cis*-CoX_4Y_2 is generally treated as having tetragonal symmetry although it is strictly only C_{2v}; see, for example, reference 30, pp 106–108.

(71) C. J. Ballhausen and W. Moffitt, *J. Inorg. Nucl. Chem.*, **3**, 178 (1956).

(72) J. S. Griffith and L. E. Orgel, *J. Chem. Soc.*, 4981 (1956).

(73) D. S. McClure, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 498.

(74) F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

(75) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

(76) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709, 1524 (1965).

However, there are several features of the observed MCD which are worth noting. First, in *cis*- and *trans*-$Co(en)_2Cl_2^+$ (Figures 11 and 12) the d → d bands are much better resolved in MCD than in absorption, presumably owing to different vibrational dependence of the two phenomena. It is possible that the location of transitions in tetragonal complexes can be better carried out with MCD. However, the MCD of $Co(NH_3)_5Cl^{2+}$ and *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$ (Figures 13 and 14) show no more splitting than the absorption spectra. Second, the relative magnitudes of absorption and MCD in the "$^1T_1$" and "$^1T_2$" bands vary considerably, the difference between *cis*- and *trans*-$Co(en)_2Cl_2^+$ being particularly striking. While very difficult to treat theoretically, variations in $[\Theta]_{M\,max}/\epsilon_{max}$ or B/D might be of some empirical stereochemical value, as are the absorption spectra alone.[77] However, such usage would need to be based on a much wider variety of data.

The chloro complexes all exhibit charge-transfer bands: at 44,000 cm^{-1} in $Co(NH_3)_5Cl^{2+}$, 31,000 and 44,000 cm^{-1} in *cis*-$Co(en)_2Cl_2^+$, and 33,000 and 40,500 cm^{-1} in *trans*-$Co(en)_2Cl_2^+$. Conflicting interpretations of these transitions have been given,[78,79] among which MCD can in principle distinguish. However, MCD was found only in the 33,000-cm^{-1} band of *trans*-$Co(en)_2Cl_2^+$ and the 44,000-cm^{-1} band of $Co(NH_3)_5Cl^{2+}$, and apparently consists of B terms alone.

3. Trigonal Complexes.—Among the simplest and most studied trigonal metal complexes are the tris-oxalate and tris-ethylenediamine compounds of Co(III) and Cr(III). These are of D_3 symmetry, in which the O_h d^n states are split as shown in Figure 15. In fact, the splitting is small and is not observed in the room-temperature solution spectra, which closely resemble those of similar O_h complexes. However, the loss of centrosymmetry renders the d → d transitions formally allowed and no longer solely dependent on vibronic interactions for intensity. For the oxalates, polarized crystal spectra[80] have shown that the static distortion is the major factor governing the d → d intensities. The situation for the ethylenediamines has been less clear[81,82] but it now appears that, at least in $Co(en)_3^{3+}$,[83,84] vibronic effects are of dominant importance.

The MCD of $Co(en)_3^{3+}$ (Figure 16) is very similar in appearance to that of $Co(NH_3)_6^{3+}$, $[\Theta]_{M\,max}/\epsilon_{max}$ being of the same absolute and relative magnitude for the two bands. The upper limits of A/D for the two bands are ~3 and 5 × 10^{-2}, again indicating quenching of the excited-state angular momenta.[84a] The resemblance to $Co(NH_3)_6^{3+}$ is expected if the bands are vibronic in origin.

$Co(ox)_3^{3-}$ (Figure 17), on the other hand, exhibits a very different MCD, particularly in the 24,000-cm^{-1} band. $[\Theta_{M\,max}]/\epsilon_{max}$ is also an order of magnitude greater. This indicates a gross change in the nature of the transitions and is consistent with the adoption of a static intensity mechanism. The MCD of the Co^{3+}–$NaMgAl(ox)_3 \cdot 9H_2O$ crystal with light propagating along the trigonal axis (Figure 17) provides additional evidence for this: the qualitative difference from the solution shows that the MCD is anisotropic, in accord with the operation of D_3 selection rules. Quantitatively, the decrease of the MCD of the 17,000-cm^{-1} band relative to the 24,000-cm^{-1} band (which remains essentially unchanged in appearance) in going from solution to crystal is expected, since in the latter the $^1A_1 \rightarrow {}^1A_2$ transition is forbidden and cannot contribute to the MCD.

The magnitude of A/D for a spin-allowed $A_1 \rightarrow E$ transition in D_3 symmetry in solution is calculated to be (Appendix) $-\mu/2$, where μ is the E state orbital magnetic moment (defined in the Appendix). From the MCD data we obtain $\mu_a \lesssim 0.1\beta$ and $\mu_b = +0.48\beta$, where a and b denote the 17,000- and 24,000-cm^{-1} bands, respectively. If it is assumed that the ^1E_b states are simply correct linear combinations of O_h $^1T_{2g}$ states, unperturbed by the reduction in symmetry, we find (Appendix) μ_b to be very close to that observed. It thus appears for this transition that simple ligand-field theory gives a good account of the excited-state angular momentum and that the trigonal field does not drastically affect μ_b. However, for the $^1A_1 \rightarrow {}^1E_a$ transition, considerable quenching is again present, as in the other Co(III) complexes.

The MCD of the spin-allowed bands of $Cr(en)_3^{3+}$ (Figure 18) resemble $Cr(NH_3)_6^{3+}$ in magnitude ($[\Theta]_{M\,max}/\epsilon_{max} \sim 10^{-5}$–$10^{-6}$) but not, in the 22,000-cm^{-1} band, in appearance. The observed A-term shape could arise in several ways: it might be due to the Zeeman splitting of the $^4A_2 \rightarrow {}^4E_a$ transition or to B terms of opposite sign belonging to $^4A_2 \rightarrow {}^4E_a$ and $^4A_2 \rightarrow {}^4A_1$, or to overlapping C terms (split by spin–orbit coupling), or to a vibronically allowed A term which is not totally quenched as in $Cr(NH_3)_6^{3+}$. These alternatives could be distinguished by MCD measurements along the trigonal axis and as a function of temperature. Here we merely note that the calculation of A/D on the basis of the first mechanism using O_h functions to evaluate matrix elements of $\boldsymbol{\mu}$ gives (Appendix) $A/D = \beta/4$, which is not very close to that observed (-0.018β). However, the discrepancy may be due to quenching effects, and this alternative cannot be definitely excluded.

$Cr(ox)_3^{3-}$ (Figure 19) presents a similar MCD to $Cr(en)_3^{3+}$ in its spin-allowed bands. Here, however, we also have the MCD along the trigonal axis from

(77) See, for example: F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950); ref 74; T. M. Dunn, R. S. Nyholm, and S. Yamada, *J. Chem. Soc.*, 1564 (1962).

(78) H. Yamatera, *J. Inorg. Nucl. Chem.*, **15**, 50 (1960).

(79) K. Nakamoto, J. Fujita, M. Kobayashi, and R. Tsuchida, *J. Chem. Phys.*, **27**, 439 (1957).

(80) T. S. Piper and R. L. Carlin, *ibid.*, **35**, 1809 (1961).

(81) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **33**, 98 (1960).

(82) Reference 30, pp 186, 193, 217, 239.

(83) R. Dingle, *Chem. Commun.*, 304 (1965).

(84) R. Dingle and C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **35**, No. 12 (1967).

(84a) NOTE ADDED IN PROOF.—The MCD of the lowest vibronic transitions in the 22,000-cm^{-1} band of $Co(en)_3^{3+}$ was recently measured by R. G. Denning [*Chem. Commun.*, 120 (1967), and private communication]; no A terms were observed, and this was attributed to the Jahn–Teller effect.

measurements on Cr^{3+}–$NaMgAl(ox)_3 \cdot 9H_2O$ (Figure 19). This indicates that in the 17,000-cm^{-1} band the apparent A term is in fact a superposition of B terms of opposite sign; the disappearance of the *lower* energy MCD component (of negative sign) is consistent with the absorption spectra of Piper and Carlin,[80] which demonstrate that the $^4A_1$ state lies below ^4E_a. We estimate upper limits of ~ 4–8×10^{-3} for A/D of genuine A terms, again indicating substantial quenching of angular momentum in the excited states.

Since bona fide A terms are so rare in these complexes, the one found in the $^1A_1 \rightarrow {}^1E_b$ $Co(ox)_3^{3-}$ transition is of particular interest. Not only is an account of the quenching mechanism for other transitions required, but it is also necessary to explain why this particular A term is unquenched. At present we can offer no solution to this problem.

The spin-forbidden transitions of $Cr(en)_3^{3+}$ and $Cr(ox)_3^{3-}$ are discussed in the following section.

4. Spin-Forbidden Cr(III) Transitions.—The huge MCD found in spin-forbidden Cr(III) transitions constitutes the most dramatic result of this work. Where observed, $[\Theta]_{M\max}/\epsilon_{\max} \sim 10^{-3}$, comparable with $Co(H_2O)_6^{2+}$ and $Mn(H_2O)_6^{2+}$ and $\gtrsim 10^2$ times greater than in the spin-allowed Cr(III) transitions. In some cases (15,000–16,000-, 14,900-, 14,900–16,000-, and 14,300-cm^{-1} bands of $Cr(NH_3)_6^{3+}$, $Cr(H_2O)_6^{3+}$, $Cr(en)_3^{3+}$, and $Cr(ox)_3^{3-}$, respectively) the transitions are clearly seen in absorption; more frequently, however, little or no absorption is observed corresponding to the MCD.

Clearly, MCD can greatly aid in the detection and assignment of spin-forbidden Cr(III) transitions. Thus, for example, the 15,900-cm^{-1} MCD of $Cr(H_2O)_6^{3+}$ (Figure 5) undoubtedly belongs to a spin-forbidden transition hidden in absorption under the red tail of the $^4A_{2g} \rightarrow {}^4T_{2g}$ band. The solution results, however, are only indicative of this potential and are not adequate for detailed assignments, which must await low-temperature crystal measurements.

The magnitude of the MCD can be attributed to two distinct effects. First, since the ground state is $^4A_{2g}$, spin-forbidden transitions can exhibit C terms, unlike the spin-allowed transitions. As discussed in the previous section, $[\Theta]_{M\max}/\epsilon_{\max}$ is expected to be some 50 times greater for C terms than for B terms. Second, since the transitions take place within the nonbonding quartet–doublet t_{2g}^3 configuration, they are very sharp. (In Cr^{3+}–$NaMgAl(ox)_3 \cdot 9H_2O$ the half-widths of the spin-forbidden transitions at 77°K are 10–100 cm^{-1}.[80]) While peak values of B and C terms in $[\Theta]_M$ and peak values of ϵ are inversely proportional to the band width for given B, C, and D, A terms vary as the inverse square of the width; hence, for given A, $[\Theta]_{M\max}/\epsilon_{\max}$ increases inversely as the width. Consequently, for narrow transitions, A terms can contribute to $[\Theta]_M$ in comparable magnitude to C terms. The observed MCD are therefore presumably a mixture of A and C terms. Temperature-dependence measurements would allow the A and C terms to be unscrambled.

It is perhaps worth emphasizing that, in order for the MCD of spin-forbidden transitions to be much enhanced relative to that of spin-allowed transitions, either the ground state must be spin-degenerate but orbitally nondegenerate or the spin-forbidden transitions must be much sharper than the spin-allowed transitions. In the majority of cases (and particularly in organic molecules) neither of these criteria is satisfied, and it is then not to be expected that MCD will act as a probe for spin-forbidden transitions. Preliminary measurements by us on several systems seem to bear this out.

Conclusions

Our work indicates that considerable insight into d → d transitions may be expected from their MCD. At the present stage, it is clear that MCD is a very direct and sensitive tool for investigating, on the one hand, the angular momentum of d^n states and, on the other hand, the nature of Cr(III) spin-forbidden transitions. MCD data can also lead to information on the intensity-gaining mechanisms in various types of d → d transitions. We hope shortly to extend this work, especially to the study of vibrationally resolved spectra at low temperatures, from which more detailed information should follow.

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Appendix

A/D for Spin-Allowed A → E Transitions in D_3 Symmetry

A/D for a spin-allowed $A_1 \rightarrow E$ transition in D_3 symmetry is calculated by the method described in previous papers.[34,36] We use Griffith's definitions of basis functions,[85] when $\langle A_1|m_x|E_x\rangle = \langle A_1|m_y|E_y\rangle = 2^{-1/2}\langle A_1||m||E\rangle$; $\langle E_x|\mu_z|E_y\rangle = \langle E||\mu||E\rangle$, whence we obtain $A/D = -i\langle E||\mu||E\rangle/2 = -\mu/2$, where we define $\mu = i\langle E||\mu||E\rangle = i\langle E_x|\mu_z|E_y\rangle$. If the A_1 and E states are spin-degenerate and spin–orbit coupling is negligible, $\boldsymbol{\mu}$ is the orbital contribution to the total magnetic moment alone, $-\beta\mathbf{L}$; if spin–orbit coupling is appreciable and A_1 and E are representations of the D_3 double group, $\boldsymbol{\mu} = -\beta(\mathbf{L} + 2\mathbf{S})$. Note that our result for A/D applies to a solution where the molecules are randomly oriented, not to an oriented crystal.

Since the energy levels of $Co(ox)_3^{3-}$ closely resemble those of an O_h complex, to a zeroth approximation the ^1E_b x and ^1E_b y states are simply linear combinations of $^1T_{2g}$ states, as given by Griffith.[86] Then $\mu = i\langle T_2\xi|\mu_z|{}^1T_2\eta\rangle$, where the basis function definitions are those of Griffith[85] and z now refers to the O_h coordinate system.

(85) Reference 43, Table A16, pp 390–391.
(86) Reference 43, Table A17, p 392.

In the strong-field limit, $\mu = -\beta/2$. However, as pointed out by Griffith,[87] the $^1T_2(t_{2g}^5e_g)$ state of low-spin d^6 ions is subject to extensive configuration interaction. We have therefore evaluated μ in the intermediate-field situation, diagonalizing the whole (7 × 7) $^1T_{2g}$ matrix[88] for a range of Δ and B values. The results show that μ increases uniformly as Δ decreases and B increases (*i.e.*, as configuration interaction increases), being $+0.57\beta$ for $\Delta = 18{,}000$ cm^{-1}, $B = 600$ cm^{-1}, $+0.95\beta$ for $\Delta = 18{,}000$ cm^{-1}, $B = 800$ cm^{-1}, and $+0.45\beta$ for $\Delta = 20{,}000$ cm^{-1}, $B = 600$ cm^{-1}. For $Co(ox)_3^{3-}$ $\Delta \sim 18{,}000$ cm^{-1}, $B \sim 540$ cm^{-1},[89] and hence the calculated μ value is close to that observed experimentally ($+0.48\beta$). The sensitivity of μ to configuration interaction is noteworthy. The effects of the D_3 perturbation on the wave functions are hard to evaluate but should be small.

The calculation of A/D for a spin-allowed $A_2 \rightarrow E$ transition in D_3 symmetry follows that above for $A_1 \rightarrow E$. Defining $\mu = i\langle E||\mu||E\rangle = i\langle E_x|\mu_z|E_y\rangle$, $A/D = -\mu/2$. For the $^4A_2 \rightarrow {}^1E_a$ transition of Cr(III), assuming ^4E_a to be unperturbed linear combinations of $^4T_{2g}$ O_h states (which are not subject to configuration interaction), we find $\mu = -\beta/2$, whence $A/D = \beta/4$.

(87) Reference 43, Section 11.6.1, pp 312–313.
(88) Reference 43, Table A29, p 412.
(89) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., Oxford, 1962, Table 11, pp 110–111.

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Electronic and Infrared Spectral Study of Chromium(III) Derivatives of the Type $[Cr(NCS)_4\cdot(ligand)_2]^-$

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A series of complexes of the type $R^+[Cr(NCS)_4L_2]^-$ [$R^+ = K^+$, NH_4^+, $(C_2H_5)_4N^+$, cholinium$^+$, $(CH_3)_3PH^+$, $(C_2H_5)_3PH^+$, $(n\text{-}C_4H_9)_3PH^+$, $(CH_3)_2(C_6H_5)PH^+$, or $(C_2H_5)_2(C_6H_5)PH^+$; L = NH_3, pyridine, $^1/_2$(2,2′-bipyridyl), $^1/_2$(*o*-phenylenebisdimethylarsine), $(CH_3)_3P$, $(C_2H_5)_3P$, $(n\text{-}C_4H_9)_3P$, $(CH_3)_2(C_6H_5)P$, $(C_2H_5)_2(C_6H_5)P$, or $(C_2H_5)(C_6H_5)_2P$] have been prepared, several for the first time, and studied in the 10,000–40,000- and the 4000–70-cm^{-1} regions. From the position of the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition in the electronic spectra of these complexes, the relative positions of the ligands (L) in the spectrochemical series have been deduced. In general, tertiary phosphines have slightly higher ligand field strengths than nitrogen-donor ligands. Methylphosphines have higher ligand field strengths than other alkylphosphines, whereas phenyl substituents lower the ligand field strengths of phosphines. The complex anions are all believed to have *trans*-octahedral structures, with the exceptions of the pyridine, 2,2′-bipyridyl, phenyldiethylphosphine, and *o*-phenylenebisdimethylarsine complexes, which have *cis*-octahedral structures. Assignments for the CN, CS, CrN, and CrL stretching vibrations and for the NCS bending vibration are given. In the case of the salts of the type $R^+[Cr(NCS)_4(NH_3)_2]^-$ the fully deuterated species were also studied in order to differentiate between the Cr–NH_3 stretching mode and the NCS bending mode. Metal–phosphorus stretching vibrations are believed to lie near 300 cm^{-1} in the case of trimethyl- and triethylphosphine derivatives. Assignments of the skeletal bending modes in the above complexes and in those of the type $M(NCS)_6^{3-}$ (M = V, Cr, or Fe) are also given.

Introduction

In an attempt to obtain more information about the factors influencing ligand field strengths, we have studied a series of complexes containing the octahedral anions $[Cr(NCS)_4L_2]^-$, where L is an amine, a tertiary phosphine, or (in one case) a tertiary arsine. It is of interest to establish how Dq varies with the nature of the substituent on the ligand atom. Chromium(III) complexes are particularly suited to such a study (a) because the first spin-allowed ligand field band $^4T_{2g} \leftarrow {}^4A_{2g}$ is a direct measure of the ligand field splitting parameter ($10Dq$) and (b) because although, in principle, this band should be resolved into two or three components in ligand fields lower than octahedral, the magnitude of this splitting is not usually large enough to observe without the use of polarized radiation. Where the ligand field strengths of the coordinated ligands are widely disparate, as for ammonia and halide ions, the $^4T_{2g}$ term *is* clearly split, but in the present series of complexes using ligands of comparable ligand field strengths, this is not the case.

The infrared spectra of the anions have been recorded down to 70 cm^{-1} in order to locate low-lying skeletal modes.

The above anions could, of course, exist as two possible stereochemical isomers, *i.e.*, *cis* or *trans* forms. The different selection rules pertaining to the vibrational modes of the two isomers usually permit the establishment of the isomeric form which crystallizes out. Moreover, in the case where L = NH_3, three salts of the anion $[Cr(NCS)_4L_2]^-$ have been the subject of full X-ray analyses;[1] in all three cases, the anion has the *trans*-octahedral structure, the thiocyanate group being nitrogen bonded. In the ammonium and pyridinium salts, the thiocyanate groups are coplanar

(1) Y. Takéuchi and Y. Saito, *Bull. Chem. Soc. Japan*, **29**, 319 (1957).