Values are calcualted for the one-electron self-exchange rate constants of Br_2, Br_2^- and I_2, I_2^-. Knowledge of these self-exchange rate constants should allow the prediction of the rates of other electron-transfer reactions involving these halogens. An immediate example is the prediction that the reaction of $Cr^{II}EDTA^{2-}$ with I_2 should be very fast and either diffusion or substitution controlled.

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Registry No. $Fe^{II}(EDTA)^{2-}$, 15651-72-6; I_2, 7553-56-2; I_3^-, 14900-04-0; $Fe^{II}(CyDTA)^{2-}$, 34446-90-7; Br_2, 7726-95-6; Br_3^-, 14522-80-6; $Mn^{II}(EDTA)^{2-}$, 52279-49-9; $Fe^{III}(CyDTA)^-$, 52305-99-4.

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Magnetic Circular Dichroism of Cobalt(II) Complexes

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Absorption and magnetic circular dichroic (MCD) spectra of d → d transitions of hexa-, penta-, and tetracoordinate high-spin Co(II) complexes have been measured and their zeroth and first moments determined. Octahedral complexes exhibit a single major negative MCD band at a frequency corresponding to that of their absorption maxima. Tetrahedral complexes display a strong negative and a weaker positive band. The MCD spectra of pentacoordinate complexes of various geometries consist of several negative and, in some instances, an additional positive band. B and C components of the zeroth moment have also been differentiated through measurements of the temperature dependence of the absorption and MCD spectra of $CoSO_4$ in water–ethylene glycol and of $Co(py)_2Br_2$ and $Co(Et_4dien)Cl_2$ in Plexiglas. These complexes exemplify both the three coordination geometries considered and the three classes of MCD spectra observed. The results obtained indicate that each type of coordination generates a characteristic MCD spectrum which appears to be rather insensitive both to distortions of the coordination sphere of the metal ion and to the presence of chelate rings, each of which lower the symmetry of the complex. MCD seems to provide an additional and important method to classify and predict the overall structure of Co(II) complexes.

Introduction

The coordination geometry of many simple Co(II) complexes has been determined on the basis of spectral,[2a] epr,[2b] and magnetic[3] measurements; however, frequently such determinations have proven difficult for Co(II) complexes liganded with bulky or rigid groups or for Co(II)-substituted metalloenzymes.[4] Recent instrumental developments and theoretical advances[5,6] have suggested that MCD might provide an additional approach to study the structure of such metal complexes. The magnetic circular dichroic spectra of $Co(H_2O)_6^{2+}$,[7,8] $CoCl_4^{2-}$, $CoBr_4^{2-}$, and CoI_4^{2-},[9] have been described previously, and a detailed calculation on the MCD of $CoCl_4^{2-}$ and its temperature dependence has been published.[10] MCD measurements on $CoCl_4^{2-}$ in Cs_3ZnCl_5 have also been used to detect weak bands due to spin-forbidden transitions.[11] We have now examined the MCD spectra of Co(II) complexes of known structures for comparison with those of analogous complexes where the structure is thus far unknown.

Experimental Section[12]

Me_6tren,[13] POA,[14] $Co(Me_6tren)Br_2$,[13] $Co(Et_4dien)Cl_2$,[15] $Co(terpy)Cl_2$,[16] $Co(DPVM)_2$,[17] and $Co(py)_2Br_2$[18] were synthesized as described in the literature. All other complexes were made by mixing appropriate solutions of the ligand with either $CoSO_4$ or $Co(NO_3)_2$ at the desired pH.

The experimental conditions for the solutions used to measure the absorption and MCD spectra are as follows: $Co(H_2O)_6^{2+}$, 5.0×10^{-2} *M* $CoSO_4$ in water;[19] $Co(DMSO)_6^{2+}$, 5.0×10^{-2} *M* $Co(NO_3)_2$ in DMSO;[20] $Co(NH_3)_6^{2+}$, 5.0×10^{-2} *M* $Co(NO_3)_2$ in 6 *M* NH_3;[19] $Co(trien)(H_2O)_2^{2+}$, 1.0×10^{-1} *M* $CoSO_4$ in 2.0×10^{-1} *M* trien at pH 8;[21] $Co(trien)(H_2O)OH^+$, 1.5×10^{-2} *M* $CoSO_4$ in 2.0×10^{-1} *M* trien at pH >13;[21] $Co(glygly)_2$, 3.3×10^{-2} *M* $CoSO_4$ in 2.0×10^{-1} *M* glygly at pH 9 and $Co(glyglyH_{-1})_2^{2-}$ at pH >13;[22] $Co(OH)_4^{2-}$, 3.2×10^{-3} *M* $CoSO_4$ in 50% NaOH;[23] $Co(SCN)_4^{2-}$, 5.0×10^{-2} *M* $CoSO_4$ with 0.1 *M* KSCN in acetone;[24] $Co(DPVM)_2$, 1.6×10^{-2} *M*

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(12) Abbreviations used: Me_6tren; tris(2-dimethylaminoethyl)-amine; POA, *N*-2-picolyloxamide; Et_4dien, *N,N,N',N'*-tetraethyldiethylenetriamine; terpy, 2,2′:6′,2″-terpyridine; DPVM, dipivaloylmethane; py, pyridine; trien, triethylenetetramine; glygly, glycylglycine; his, histidine; DMSO, dimethyl sulfoxide.

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in benzene; $Co(hisH_{-1})_2{}^{2-}$; 6.0×10^{-3} *M* $Co(NO_3)_2$ in 1.0 *M* DL-his at pH >13;[25] $Co(py)_2Br_2$, 5.0×10^{-4} *M* in acetone; $Co(Me_6tren)Br_2$, 4.5×10^{-3} *M* in acetonitrile; $Co(Et_4dien)Cl_2$, 5.0×10^{-3} *M* in $CHCl_3$; $Co(terpy)Cl_2$, 1.0×10^{-3} *M* in DMF; $Co(POAH_{-1})_2$, 1.0×10^{-2} *M* $CoSO_4$ and 5.0×10^{-2} *M* POA in 0.2 *M* borate buffer, at pH 10.[14]

In the measurements of oxygen-sensitive materials, solutions were prepared under nitrogen, the cuvette compartment was purged with this gas, and during measurements the cuvettes themselves were sealed to avoid oxidation. The intense, yellow-brown color, characteristic of cobalt-oxygen adducts,[26] was not observed in any instance.

Temperature dependence of the absorption and MCD spectra of one known octahedral, tetrahedral, and trigonal-bipyramidal complex each were examined. $CoSO_4$, 5.0×10^{-2} *M* in a water-ethylene glycol (1:9 v/v) mixture served as an example of octahedral geometry while $Co(py)_2Br_2$ and $Co(Et_4dien)Cl_2$, dissolved in Plexiglas, represented tetrahedral and distorted trigonal-bipyramidal compounds, respectively. These solid solutions were prepared by adding a concentrated $CHCl_3$ solution of the respective complexes to a solution of polymethacrylate (Plexiglas) dissolved in 1,2-dichloroethane. The viscous mixture was poured into a glass ring and then left at room temperature until evaporation of the solvent resulted in a film of about 0.5-mm thickness. For spectral measurements circular disks of the film, 1 cm in diameter, were fitted to the brass sample holder. The spectra obtained for these materials indicate that this procedure does not alter the structure of the complexes dissolved in Plexiglas.

The absorption spectra were measured with a Cary 14 spectrophotometer and their corresponding MCD spectra with a Cary Model 61 spectropolarimeter equipped with a Varian superconducting V4145 magnet and a V4106 power supply at magnetic fields varying from 40 and 45 kG. The magnetic fields were calibrated by using the conversion factor of 0.6 A/kG given by the manufacturer and/or by means of a standard $Co(H_2O)_6{}^{2+}$ solution, with molar ellipticity per unit field of $[\theta]_M{}^{510\,\mathrm{nm}} = -6.1 \times 10^{-3}$ deg cm^2 dmol^{-1} G^{-1}.[7] Signal:noise ratios were excellent for all measurements throughout the spectral ranges examined. In addition, the instrument was calibrated in the CD mode with *d*-10-camphorsulfonic acid.[27]

The temperature dependence of the visible absorption and MCD spectra were studied using a channeled and bored brass block inserted in the sample chamber of the superconducting solenoid. Nitrogen gas held at the various discrete temperatures was flushed through the block until equilibrium was attained at the temperature desired. Temperature measurements were made with an iron-constantan thermocouple calibrated against air at 23°, ice water, Dry Ice-acetone, and liquid nitrogen. The thermocouple output was monitored with a Westronics recorder.

Molar absorptivities are given in M^{-1} cm^{-1}, and molar magnetic ellipticities, $[\theta]_M$, in deg cm^2 dmol^{-1} G^{-1} were calculated from the equation $[\theta]_M = 100\theta/bMH$ where θ is the ellipticity measured directly in degrees $[\theta = 3300(A_R - A_L)]$, *b* is the path length in centimeters, *M* is the molar concentration, and *H* is the magnetic field in units of gauss. All MCD measurements were made with the magnetic field parallel to and in the direction of the light beam.

The experimental absorption and MCD curves were analyzed by means of two computer programs written for an IBM 360 computer. The first program, based on the method of moments,[28] uses relations 1 and 2, where $n = 0$ or 1 for the zeroth and first moments, respec-

$$\langle\epsilon\rangle_n = \int\frac{\epsilon}{\nu}(\nu - \nu_0)^n \, d\nu \qquad (1)$$

$$\langle[\theta]_M\rangle_n = \int([\theta]_M/\nu)(\nu - \nu_0)^n \, d\nu \qquad (2)$$

tively, and ν_0 is defined as the frequency which makes $\langle\epsilon\rangle_1 = 0$. IBM subroutine QSF[29] is the central part of this program. The second program is a version of Marquad's nonlinear least-squares program[30] which was modified to fit the absorption and MCD spectra with gaussian curves using eq 3 for absorption and eq 4 for the MCD spectra,[6,31]

$$\epsilon = \sum_i \epsilon_{\max,i} \exp[-(\nu - \nu_{0,i})^2/\Delta\nu_i{}^2] \qquad (3)$$

$$[\theta]_M = \sum_j C_j(\nu_{0,j} - \nu)/\Delta_j{}^3 \exp\left[\frac{-(\nu - \nu_{0,j})^2}{\Delta_j{}^2}\right] + \sum_l C'_l \exp\left[\frac{-(\nu - \nu_{0,l})^2}{\Delta_l{}^2}\right] \qquad (4)$$

where *i*, *j*, and *l* are the index numbers of absorption bands and biphasic and monophasic MCD bands, respectively, $\epsilon_{\max,i}$ is the maximal molar absorptivity at the frequency $\nu_{0,i}$, $\Delta\nu_i$ is the bandwidth, and *C*, *C''*, and Δ are the corresponding constants defining the MCD bands. Complete MCD spectra could not be obtained in some cases, precluding direct integration. In these instances eq 3 and 4 were used to fit the spectra to full curves to allow integration and determination of zeroth and first moments according to eq 1 and 2. While these equations are of the same basic form as those used in the rigid-shift approximation,[31] this method of analysis is impractical since the Co(II) spectra are composed of many overlapping electronic transitions.

Results

We have studied the absorption and MCD spectra of hexa-, penta-, and tetracoordinate Co(II) complexes in order to examine the extent by which MCD can contribute to structure determinations of complexes in solution. As a basis of comparison we have chosen compounds whose structures are known from X-ray diffraction studies. However, since complexes in the solid state and in solution often differ in their coordination number and geometry, great care was taken in the selection of suitable materials for comparative studies. Complexes such as $Co(H_2O)_6{}^{2+}$, $Co(py)_2Br_2$, $Co(DPVM)_2$, $Co(Me_6tren)Br_2$, and $Co(Et_4dien)Cl_2$, whose reflectance and solution absorption spectra are very similar in regard to maxima, represent nearly ideal standards for comparisons. Other complexes such as $Co(DMSO)_6{}^{2+}$, $Co(NH_3)_6{}^{2+}$, $Co(SCN)_4{}^{2-}$, and $Co(terpy)Cl_2$ for which sufficient data are known to allow a structural assignment in solution can also be used for comparative purposes. Only tentative structures have been postulated for the additional compounds studied, *i.e.*, $Co(trien)(H_2O)_2{}^{2+}$, $Co(trien)(H_2O)(OH)^+$, $Co(glygly)_2$, $Co(glyglyH_{-1})_2{}^{2-}$, $Co(hisH_{-1})_2{}^{2-}$, and $Co(POAH_{-1})_2$.

The MCD spectra for the cobalt complexes studied fall into three general categories. Complexes of known octahedral geometry, *e.g.*, $Co(H_2O)_6{}^{2+}$, $Co(NH_3)_6{}^{2+}$, and $Co(DMSO)_6{}^{2+}$ exhibit an absorption maximum of low intensity centered near 20,000 cm^{-1} (500 nm). The corresponding MCD spectra exhibit a pronounced band of negative ellipticity at this frequency (Figures 1 and 2). Qualitatively similar in shape, though higher in intensity, are the MCD spectra of $Co(glygly)_2$ at pH 8, $Co(trien)(H_2O)_2{}^{2+}$, and $Co(trien)(H_2O)(OH)^+$ (Figures 2 and 3) for which distorted octahedral geometry may be expected, based upon their absorption spectra.

The second group encompasses complexes with absorption maxima from 15,600 to 18,000 cm^{-1} and molar absorptivities from 40 to 2000 M^{-1} cm^{-1}. The MCD spectrum of $Co(py)_2Br_2$, known to be tetrahedral,[32] is illustrative of this class of compounds (Figure 4). It exhibits a negative band in the low-frequency region of the MCD spectrum and a smaller positive band at higher frequencies. The patterns of the MCD spectra of $Co(OH)_4{}^{2-}$, $Co(DPVM)_2$, and $Co(SCN)_4{}^{2-}$ are similar (Figures 4-6). Overall, the MCD spectra of this second category of complexes are 10-100 times more intense than those of the first. $Co(DPVM)_2$ is an exception since it is known to be tetrahedral by X-ray diffrac-

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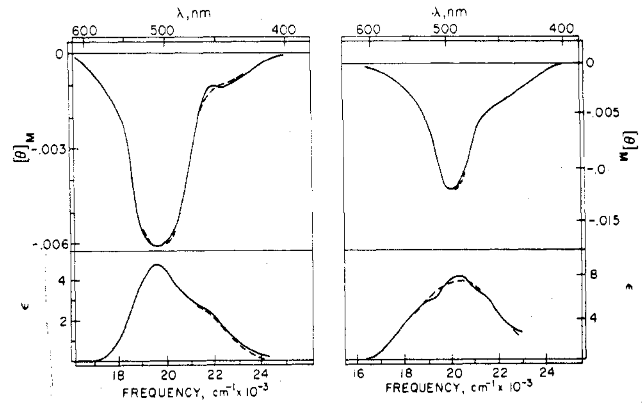

Figure 1. Absorption and MCD spectra of $Co(H_2O)_6^{2+}$ (left) and $Co(NH_3)_6^{2+}$ (right); ——, experiment; - - - -, best gaussian fit.

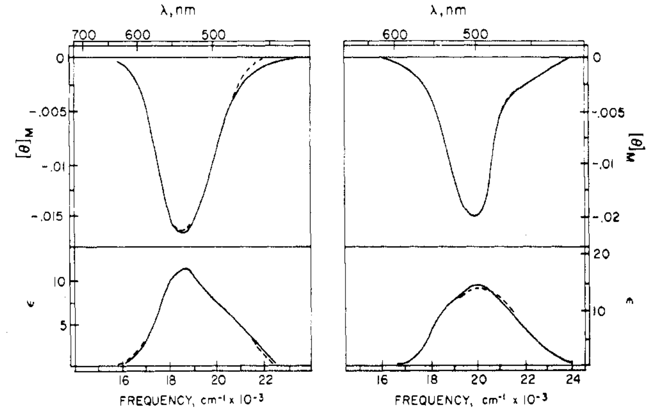

Figure 2. Absorption and MCD spectra of $Co(DMSO)_6^{2+}$ (left) and $Co(glygly)_2$ at pH 0 (right): ——, experiment; - - - -, best gaussian fit.

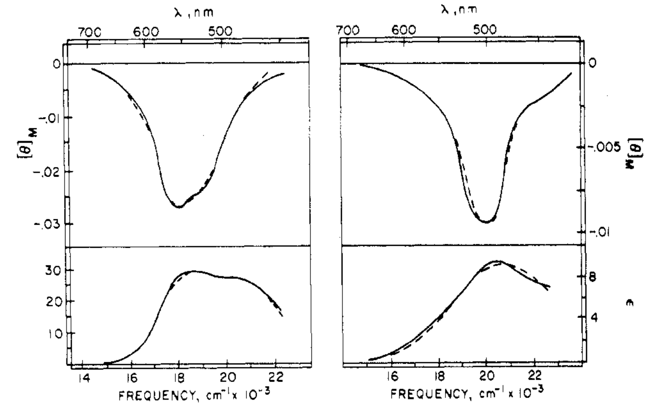

Figure 3. Absorption and MCD spectra of $Co(trien)(H_2O)(OH)^+$ at pH >13 (left) and $Co(trien)(H_2O)_2^{2+}$ at pH 8 (right): ——, experiment; - - - -, best gaussian fit.

tion,[33] and its MCD and absorption bands are less intense and are at higher frequency.

The third group, exemplified by the pentacoordinate complexes $Co(Me_6tren)Br_2$,[34] $Co(Et_4dien)Cl_2$,[35] and Co(terpy)-Cl_2[36] exhibit two distinct bands in the visible absorption spectrum with molar absorptivities ranging from 50 to 150 M^{-1} cm^{-1}. Two bands of negative ellipticity and, in some

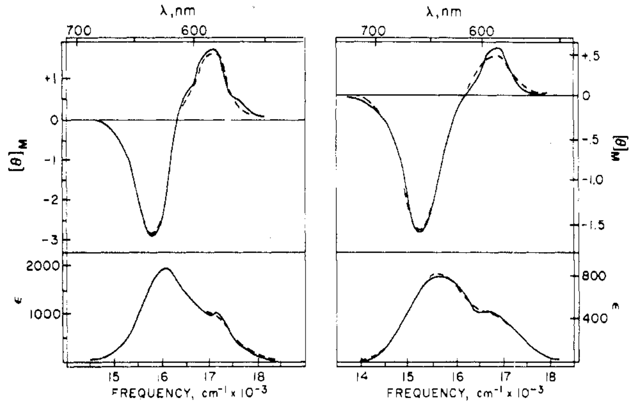

Figure 4. Absorption and MCD spectra of $Co(SCN)_4^{2-}$ in acetone (left) and $Co(py)_2Br_2$ in acetone (right): ——, experiment; - - - -, best gaussian fit.

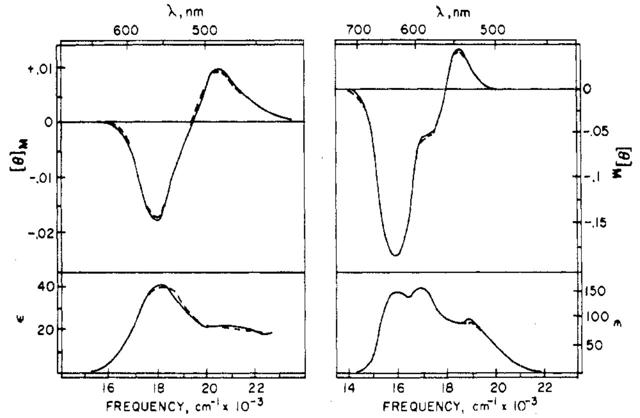

Figure 5. Absorption and MCD spectra of $Co(DVPM)_2$ in benzene (left) and $Co(OH)_4^{2-}$ in 50% NaOH (right): ——, experiment; - - - -, best gaussian fit.

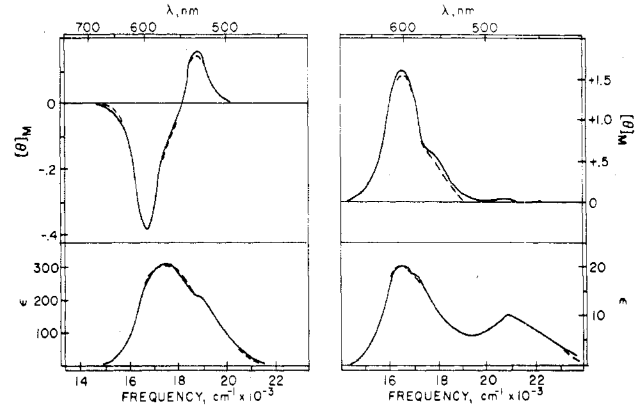

Figure 6. Absorption and MCD spectra of $Co(hisH_{-1})_2^{2-}$ at pH >13 (left) and $Co(glyglyH_{-1})_2^{2-}$ at pH >13 (right): ——, experiment; - - - -, best gaussian fit.

instances, one positive MCD band are observed which coincide with absorption maxima. Similarly, the absorption and MCD bands of $Co(POAH_{-1})_2$ are found at 16,300 and 21,200 cm^{-1} in borate buffer, pH 10 (Figures 7 and 8).

MCD parameters are best obtained by the method of moments,[6,28] which does not require a detailed knowledge of the number, position, or shape of the bands. However, this method can only be used when data are available over the entire spectral range of the transitions examined so that integration can be performed.

Where complete spectra were not available, the curve-fitting procedure described by Stephens, *et al.*,[6,31] was employed

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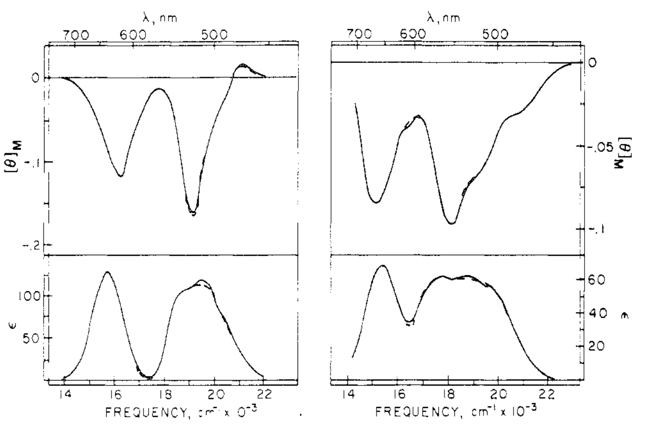

Figure 7. Absorption and MCD spectra of $Co(Me_6tren)Br_2$ in acetonitrile (left) and $Co(Et_4dien)Cl_2$ in $CHCl_3$ (right): ——, experiment; - - - -, best gaussian fit.

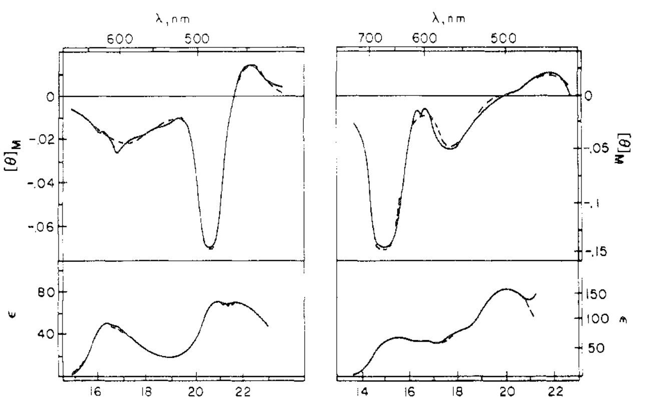

Figure 8. Absorption and MCD spectra of $Co(POAH_{-1})_2$ in borate buffer at pH 10 (left) and $Co(terpy)Cl_2$ in DMF (right): ——, experiment; - - - -, best gaussian fit.

to separate overlapping bands or to obtain functions which, in turn, served to generate complete spectra allowing integration.

In the curve-fitting procedure, the number of bands must be assigned. Additionally, several assumptions are made, since three parameters, related to their position (ν_0), their height (ϵ_{max}, C, or C'), and their width ($\Delta\nu$ and Δ) have to be identified inductively before they can progressively be changed by the iteration procedure to obtain the best fit. In many instances both methods were employed (Tables I and II) with comparable results. Values of ν_0, $\langle\epsilon\rangle_0$, and the ratios $\langle[\theta]_M\rangle_0/\langle\epsilon_0\rangle$ and $\langle[\theta]_M\rangle_1/\langle\epsilon_0\rangle$ are given in Tables I-III.

The values of the zeroth and first moments of compounds whose structures have not yet been determined by X-ray diffraction are included in the tables under the appropriate group of compounds of known structure and analogous MCD spectra. The absorption and MCD spectra, calculated from the parameters of the gaussian fit, are displayed in Figures 1-8 to demonstrate the quality of the "best fit" obtained.

B and C components of $\langle[\theta]_M\rangle_0$ can be differentiated by measuring the temperature dependence of the absorption and MCD spectra over a sufficiently wide range and by plotting $\langle[\theta]_M\rangle_0/\langle\epsilon\rangle_0$ *vs.* $1/T$. Such measurements have been performed for Co(II), in water–ethylene glycol (1:9 v/v), $Co(py)_2Br_2$, and $Co(Et_4dien)Cl_2$, the latter two in Plexiglas, each exemplifying one of the three types of MCD spectra described above (Figure 9).

The band positions and contours of the MCD and absorption spectra of $Co(py)_2Br_2$ and $Co(Et_4dien)Cl_2$ in the solid

Table I. Parameters for Regular and Distorted Octahedral Co(II) Complexes[a]

	ν_0, cm⁻¹	$\langle\epsilon\rangle_0$	$10^3\langle[\theta]_M\rangle_0/\langle\epsilon\rangle_0$, β cm	$\langle[\theta]_M\rangle_1/\langle\epsilon\rangle_0$, β
$Co(H_2O)_6{}^2$ [b]	20,200	0.76	−1.3	−25
	(20,200)	(0.76)	(−1.3)	(−25)
$Co(NH_3)_6{}^{2+}$	(20,100)	(1.5)	(−1.1)	(−22.6)
$Co(DMSO)_6{}^{2+}$	18,800	2.1	−1.2	−22.4
	(18,800)	(2.0)	(−1.25)	(−23.0)
$Co(glygly)_2$ [c]	19,900	2.8	−0.79	−14.3
	(19,800)	(3.4)	(−0.58)	(−11.8)
$Co(trien)(H_2O)_2{}^{2+}$	(20,400)	(2.4)	(−0.62)	(−12.5)
$Co(trien)(H_2O)OH^+$	(18,500)	(8.2)	(−0.57)	(−11.1)
$CoSO_4$ [d]	20,200	1.7	−0.70	−16.6

[a] Values in parentheses are those obtained from integration of gaussian fits. [b] Structure has been determined by X-ray diffraction analysis. [c] At pH 8.0. [d] In water–ethylene glycol (1:9 v/v).

Table II. Parameters for Regular and Distorted Tetrahedral Co(II) Complexes[a]

	ν_0, cm⁻¹	$10^{-1}\langle\epsilon\rangle_0$	$10^4\langle[\theta]_M\rangle_0/\langle\epsilon\rangle_0$, β cm	$\langle[\theta]_M\rangle_1/\langle\epsilon\rangle_0$, β
$Co(DPVM)_2$ [b]	(19,800)	(9.8)	(−0.082)	(−9.1)
$Co(OH)_4{}^{2-}$	17,300	3.6	−5.3	−8.3
	(17,300)	(3.5)	(−5.4)	(−8.3)
$Co(py)_2Br_2$ [b]	15,900	10	−7.4	−11.0
	(15,900)	(9.9)	(−7.0)	(−10.1)
$Co(hisH_{-1})_2{}^{2-}$	17,900	5.5	−3.8	−6.0
	(17,900)	(5.5)	(−3.8)	(−6.0)
$Co(SCN)_4{}^{2-}$	16,350	20	−2.5	−3.5
	(16,300)	(20)	(−2.7)	(−3.6)

[a] Values in parentheses are those obtained from integration of gaussian fits. [b] Compounds whose structures have been determined by X-ray diffraction analysis.

Table III. Parameters for Pentacoordinated Co(II) Complexes[a]

	ν_0, cm⁻¹	$10^{-1}\langle\epsilon\rangle_0$	$10^4\langle[\theta]_M\rangle_0/\langle\epsilon\rangle_0$, β cm	$\langle[\theta]_M\rangle_1/\langle\epsilon\rangle_0$, β
$Co(Me_6tren)Br_2$ [b]	15,600	1.5	−8	−12.6
	19,400	1.5	−6.7	−13.3
$Co(Et_4dien)Cl_2$ [b]	15,300	0.7	−14	−22.8
	18,500	1.5	−9.3	−17.3
$Co(POAH_{-1})_2$	16,900	0.7	−6.2	−8.9
	21,200	1.2	−2.7	−5.5
$Co(terpy)Cl_2$ [b]	15,700	1.3	−12	−19.2
	19,500	2.6	−1.4	−2.3

[a] From gaussian fits. [b] Compounds whose structures have been determined by X-ray diffraction analysis.

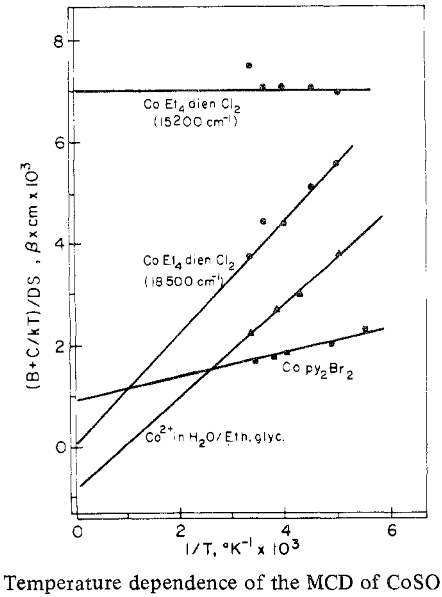

Figure 9. Temperature dependence of the MCD of $CoSO_4$ in H_2O–ethylene glycol (1:9 v/v) and $Co(py)_2Br_2$ and $Co(Et_4dien)Cl_2$ in Plexiglas.

matrix were identical with those of their solutions. Apparently the nature of the medium or its physical state minimally affects the geometry of these complexes.

In contrast, the absorption spectrum of Co^{2+} in water-ethylene glycol differs from that in aqueous solution. The mixed solvent shifts the absorption maximum of $Co(H_2O)_6{}^{2+}$ from 513 to 516 nm with absorptivities of 4.8 and 7.8 M^{-1} cm^{-1}, respectively. Since the absorption spectrum of Co(II) in water-ethylene glycol is similar to that obtained for Co(II) in ethanol, λ_{max} 517 nm, ϵ_{max} 8.3 M^{-1} cm^{-1},[37] ethylene glycol may have replaced some of the water molecules coordinated to Co(II), distorting the octahedral structure. Variations in intensity of the absorption spectra of $Co(py)_2Br_2$ and $Co(Et_4dien)Cl_2$ examined as a function of temperature are small when studied as solid solutions in Plexiglas. Such solid solutions in an inert, transparent matrix seem to be a convenient means to examine the temperature dependence of MCD spectra.

Values of $\langle[\theta]_M\rangle_0$ and $\langle\epsilon\rangle_0$ were calculated at each temperature by the methods described above. The results obtained from the plots of Figure 9 are given in Table IV. $\langle[\theta]_M\rangle_0$ values for Co^{2+} in water-ethylene glycol and/or $Co(py)_2Br_2$ in Plexiglas both contain a *B* and a *C* component. In contrast, $\langle[\theta]_M\rangle_0$ for $Co(Et_4dien)Cl_2$ at 15,200 cm^{-1} is predominantly the *B* component whereas that at 18,500 cm^{-1} consists primarily of the *C* component.

Discussion

Divalent cobalt forms numerous high-spin complexes of different structures. Compounds with octahedral and tetrahedral geometry are most numerous, but trigonal-prismatic,[38] trigonal-bipyramidal, and square-pyramidal[39] complexes have been observed. The versatility of Co(II) to adapt to such different environments makes this ion especially suitable for a study correlating the structure with the electronic properties of its complexes both in models and in cobalt-substituted metalloenzymes.[40]

A large number of spectral methods of variable-information content can serve as approaches to the determination of molecular structures. X-Ray diffraction is thus far unique in allowing the definitive description of coordination complexes in the crystalline state, and their optical properties, in turn, can serve as a means of comparison with complexes of as yet unknown structure. Spectral methods reflecting electronic properties are inferential, though the joint use of a number of different spectral approaches has generally proven useful in arriving at tentative structural conclusions. Such measurements gain additional value when the geometry of a complex in the crystalline state differs from that which it assumes in solution.

While the full potential of MCD is not completely apparent as yet, its value in gauging both the electronic properties and geometry of complexes has long been recognized.[5,7] Significant advances in both theory and instrumental development have rendered the method increasingly useful only relatively recently.

Two computer programs, one based upon the method of moments and the other using a nonlinear least-squares curve-fitting procedure, served to determine the values of zeroth and first moments of the absorption and MCD spectra. Reproducibility of the experimental data was excellent, and, hence, any possible errors in these values are most likely due to the assumptions underlying the curve-fitting procedure. The method of moments could not be employed directly in all instances because of band overlaps and/or because the complete spectrum was not available. However, wherever both procedures could be used, the deviations are relatively small (Tables I–III) giving confidence in the results of the curve-fitting procedure when the method of moments could not be applied directly.

Table IV. $\langle[\theta]_M{}^B\rangle_0/\langle\epsilon\rangle_0$ and $\langle[\theta]_M{}^C\rangle_0/\langle\epsilon\rangle_0$ for $CoSO_4$ in Water–Ethylene Glycol (1:9 v/v) and $Co(py)_2Br_2$ and $Co(Et_4dien)Cl_2$ in Plexiglas Obtained from the Temperature Dependence of Their Absorption and MCD Spectra

Compd	Geometry	ν_0, cm^{-1}	$\langle[\theta]_M{}^B\rangle_0/\langle\epsilon\rangle_0$, β cm	$\langle[\theta]_M{}^C\rangle_0/\langle\epsilon\rangle_0$, β
$CoSO_4{}^a$	ψ-O_h	24,000	$+2.8 \times 10^{-4}$	−0.20
$Co(py)_2Br_2$	$C_{2v}{}^b$	17,400	-2.7×10^{-4}	−0.53
$Co(Et_4dien)Cl_2$	ψ-$D_{3h}{}^c$	15,200	-2.2×10^{-4}	0
		18,500	0	−0.24

[a] In H_2O–ethylene glycol. [b] See ref 32. [c] See ref 35.

The temperature dependence of the absorption and MCD spectra for three of the compounds exhibiting pseudooctahedral, tetrahedral, and trigonal-bipyramidal geometry was examined in mixed solvents and in solid solutions of Plexiglas. Such measurements allow a separation of the *B* and *C* components of the Faraday effect. However, a majority of the complexes examined could not be investigated in this manner, because of either their sensitivity to oxygen or their insolubility in a solvent suitable for such measurements. Since only one compound of each geometry was studied, definitive conclusions regarding the effects of symmetry on the *B* and *C* values cannot be drawn as yet. More detailed studies of these and of analogous compounds are therefore indicated.

Phenomenologically, the MCD spectra of Co(II) complexes studied thus far appear to be characteristic for hexa-, penta-, and tetracoordination. Compounds of each of these types of coordination display similar MCD spectra, regardless of distortions from regular structures or the presence of chelate rings. Surprisingly, only the overall geometry of the coordination sphere of Co(II) complexes seems to be important for the shape of the MCD signal, although the values of the Faraday parameters clearly indicate that differences between complexes of each kind are present.

In the following discussion the characteristic MCD features of the different types of Co(II) complexes will be detailed.

Octahedral Complexes. The complexes known to be octahedral, $Co(H_2O)_6{}^{2+}$,[7] $Co(NH_3)_6{}^{2+}$, and $Co(DMSO)_6{}^{2+}$, exhibit a negative dispersion near 500 nm apparently diagnostic for this geometry. The structures of $Co(trien)(H_2O)_2{}^{2+}$ [21] and $Co(glygly)_2$[22] have been thought to be pseudooctahedral based upon their absorption spectra. The present MCD measurements are consistent with this view. The molar absorptivity of $Co(trien)(H_2O)OH^+$ is unusual, and on this basis it has been thought to be a mixture of octahedral and pentacoordinate complexes.[21] Its MCD spectrum does not resemble that of the five-coordinated compounds (see below) but coincides closely with that of pseudooctahedral complexes, as indicated by the overall shape of the MCD signal and the values of $\langle[\theta]_M\rangle_0/\langle\epsilon\rangle_0$ (Table I). It is conceivable, of course, that pentacoordination of a small fraction of this compound could escape detection.

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The Faraday effect for the octahedral complexes observed at about 20,000 cm^{-1} results from the interaction of the magnetic field with the states involved in the $^4T_{1g} \rightarrow {}^4T_{1g}$ (P), $^2T_{1g}$ transition. The strictly octahedral complexes Co($H_2O)_6^{2+}$, Co(DMSO)$_6^{2+}$, and Co(NH$_3$)$_6^{2+}$ have values of $\langle[\theta]_M\rangle_0/\langle\epsilon\rangle_0$ ranging from -1.1×10^{-3} to -1.3×10^{-3} β cm.

For the other hexacoordinated Co(II) complexes with lower symmetry, *i.e.*, Co(trien)(H$_2$O)$_2^{2+}$, Co(trien)(H$_2$O)OH$^+$, Co(glygly)$_2$, and CoSO$_4$ in water-ethylene glycol, quenching of the orbital angular momentum of the ground state is expected, which would be reflected in a lower value of the *C* term and in a higher value of the *B* term, relative to those found for the highly symmetrical compounds. Based on the temperature dependence of CoSO$_4$ in water-ethylene glycol, $\langle[\theta]_M{}^B\rangle_0/\langle\epsilon\rangle_0$ is 2.8×10^{-4} β cm, while $\langle[\theta]_M{}^C\rangle_0/\langle\epsilon\rangle_0$ is -0.2 β.

Tetrahedral Complexes. Co(DPVM)$_2$[33] and Co(py)$_2$Br$_2$[32] are known to be tetrahedral from X-ray analysis and Co(SCN)$_4^{2-}$,[24] Co(OH)$_4^{2-}$,[23] and Co(hisH$_{-1}$)$_2^{2-}$ [25] are thought to have the same geometry based on their spectral properties.

The visible absorption band of tetrahedral Co(II) complexes is due to the $^4A_2 \rightarrow {}^4T_1$ (P) transition. The $^4T_1$ (P) state splits further into four sublevels E$'$, $^3/_2$ U$'$, E$''$, and $^5/_2$ U through spin-orbit coupling.[41] Neither the absorption nor the MCD spectra of the tetrahedral complexes measured in solution are sufficiently resolved to identify each of the spin-orbit components of the transition.

The MCD of Co(py)$_2$Br$_2$ is temperature dependent with $\langle[\theta]_M{}^B\rangle_0/\langle\epsilon\rangle_0 = -2.7 \times 10^{-4}$ β cm and $\langle[\theta]_M{}^C\rangle_0/\langle\epsilon\rangle_0 = -0.053$ β, respectively (Table IV).

Five-Coordinated Co(II) Complexes. In Co(Me$_6$tren)Br$_2$, the Co(II) ion is in a nearly trigonal-bipyramidal environment,[34] whereas Co(Et$_4$dien)Cl$_2$ deviates significantly from this symmetry,[35] although pentacoordination is maintained. The structure of Co(terpy)Cl$_2$ is also known to be distorted trigonal bipyramidal from X-ray diffraction,[36] and pentacoordination for Co(POAH$_{-1}$)$_2$ has been inferred from both spectral and magnetic data.[14] The MCD spectra of all these complexes are very similar (Figures 6 and 7) and are in agreement with the proposed structures.

The energy level diagram proposed for trigonal-bipyramidal Co(II) complexes[39] assigns the two absorption bands in the visible spectrum in ~16,000 and ~19,000 cm^{-1} to the $^4A_2$ (F) $\rightarrow {}^4A_2$ (P) and $^4A_2$ (P) $\rightarrow {}^4E$ (P) transitions, respectively. However, lowering of the ligand field symmetry would be expected to split the ^4E (P) state into two nondegenerate sublevels.[42] The temperature dependence of the MCD of Co(Et$_4$dien)Cl$_2$ in Plexiglas clearly identifies the 15,200-cm^{-1} band as a pure *B* term (Figure 8), but a *C* term is suggested for the 18,500-cm^{-1} band.

Co(glyglyH$_{-1}$)$_2^{2-}$ at High pH. The spectrum and magnetic moment of the blue Co(glyglyH$_{-1}$)$_2^{2-}$ complex at pH >12 have been accounted for by the assumption that it is a mixture of 70% high-spin and 30% low-spin Co(II).[22] The possibility of pentacoordinated Co(II) had also been discussed.[14] However, the MCD spectrum of Co(glyglyH$_{-1}$)$_2^{2-}$ (Figure 6) does not resemble that of any of the high-spin octahedral, tetrahedral, or five-coordinated complexes studied so far. In the absence of suitable comparisons, the absorption of the Co(II) coordination sphere in Co(glyglyH$_{-1}$)$_2^{2-}$ cannot be assigned as yet. Nevertheless the MCD results are not consistent with any of the structures suggested[14,22] and exemplify the potential of MCD in structure studies.

Conclusion

The systematic study of high-spin Co(II) complexes exhibiting different microsymmetries shows that MCD is valuable in classifying and predicting overall geometry of the coordination sphere of Co(II). MCD spectra are apparently less sensitive to distortions than are absorption spectra and, hence, permit ready qualitative comparisons with suitable models of known geometry. This approach will prove particularly important when applying the data obtained for simple Co(II) complex ions to the determination of the overall geometry of Co(II) at the active site of metalloenzymes.[40]

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Registry No. Co(H$_2$O)$_6^{2+}$, 15276-47-8; Co(NH$_3$)$_6^{2+}$, 14695-95-5; Co(DMSO)$_6^{2+}$, 26745-61-9; Co(glygly)$_2$, 52239-54-0; Co(trien)(H$_2$O)$_2^{2+}$, 29871-98-5; Co(trien)(H$_2$O)(OH)$^+$, 16404-29-8; Co(DVPM)$_2$, 13986-53-3; Co(OH)$_4^{2-}$, 24640-11-7; Co(py)$_2$Br$_2$, 14024-83-0; Co(hisH$_{-1}$)$_2^{2-}$, 52248-67-6; Co(SCN)$_4^{2-}$, 18904-81-9; Co(Me$_6$tren)Br$_2$, 52225-43-1; Co(Et$_4$dien)Cl$_2$, 15609-41-3; Co(POAH$_{-1}$)$_2$, 52278-82-7; Co(terpy)Cl$_2$, 14854-50-3; Co(glyglyH$_{-1}$)$_2^{2-}$, 52278-83-8.

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