cobalt(III) center is reduced directly.

The faster rate for the complexes for which the chemical mechanism has been postulated could hardly be explained on the basis of direct electron transfer into cobaltIII) orbitals since their acceptor properties are not expected to change by changing the substituents in the pyridine ring. This expectation is based on the insensitivity of the rates of reaction of the cobalt(III) complexes to the nature of the pyridine ligand when the reductant is too weak to reduce the ligands.[13,17,18] Rate constants for internal electron transfer in the ion pairs $Co(NH_3)_5L^{n+}|Fe(CN)_6^{4-}$ are in the narrow range $(1.0–5.0) \times 10^{-2}$ M^{-1} s^{-1} for L = py, bpa, bpy, bpyMe$^+$, nicotinamide, and isonicotinamide, to be contrasted with the wider range $(1.2–27) \times 10^7$ M^{-1} s^{-1} for the analogous reductions by MV$^+$.[19] $Fe(CN)_6^{4-}$ is too weak a reductant to respond to variations in the acceptor abilities of the bound ligands, and the range of rates is taken to be a measure of the effect of the pyridine ring substituents on the acceptor properties of the cobalt(III) orbitals. Therefore, the considerably larger range of rates for MV$^+$ is interpreted on the basis of an additional reaction pathway at the upper rate range, namely, the increasing ability of the ligand to act as the primary electron acceptor.

Additional evidence for the proposed mechanistic assignment comes from a comparison between MV$^+$ and $*Ru(bp)_3^{2+}$ as reductants toward the pyridine complexes. The ratios of the rate constants for $*Ru(bp)_3^{2+}$ to the rate constants for MV$^+$ are in the range 11–14 for the cobalt complexes reacting via the direct mechanism, whereas the ratios are in the range 3–6 for the complexes reacting via the chemical mechanism. If all the complexes underwent reaction by the same mechanism, the reactivity ratio of $*Ru(bp)_3^{2+}$ to MV$^+$, based on the Marcus theory, would be expected to be independent of the cobalt(III) complex. The fact that two different ranges of reactivitiy ratios are observed supports the suggestion that two distinct mechanisms, reduction of the cobalt(III) center or reduction of the pyridine ligand, are operative in the present systems.

Finally, it is noteworthy that the rates of reduction of the (pyridine)pentaamminecobalt(III) complexes by MV$^+$ exhibit a general tendency toward increasing as the length of the pyridine ligand increases.[20] For the direct reduction of the cobalt(III) center via the pyridine ligand, the opposite trend is observed and expected on theoretical grounds.[21] Therefore, we consider these observations, although the argument is indirect, as a reinforcement of the dual mechanistic assignment proposed for the reduction of the (pyridine)pentaamminecobalt(III) complexes by MV$^+$ and $*Ru(bp)_3^{2+}$.

Acknowledgment. This research was supported by the National Science Foundation under Grant CHE-7909253.

Registry No. MV$^+$, 25239-55-8; $Ru(bp)_3^{2+}$, 15158-62-0; $Co(NH_3)_5py^{3+}$, 31011-67-3; $Co(NH_3)_5bpa^{3+}$, 38671-05-5; $Co(NH_3)_5bpyMe^{4+}$, 66290-41-3; $Co(NH_3)_5bpy^{3+}$, 53879-90-6; $Co(NH_3)_5bpe^{3+}$, 61177-69-3.

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(18) We also wanted to obtain the rate constants for the reduction of the pyridine complexes by $Ru(NH_3)_6^{2+}$. Experiments with $Co(NH_3)_5py^{3+}$ confirmed the literature value. However, the reaction with $Co(NH_3)_5bpy^{3+}$ displayed an autocatalytic behavior, even at pH 7.0. Moreover, we found that added free bpy had a catalytic effect on the $Co(NH_3)_5py^{3+}–Ru(NH_3)_6^{2+}$ reaction. Therefore, these studies did not yield the desired rate constants.

(19) The range of rates for $*Ru(bp)_3^{2+}$, $(1.7–11) \times 10^9$ M^{-1} s^{-1}, is about as narrow as the range for $Fe(CN)_6^{4-}$. However, at the upper range of the $*Ru(bp)_3^{2+}$ reactions, the rate constants are approaching the diffusion-controlled limit within a factor of 3.

(20) Note that because of its higher positive charge the complex $Co(NH_3)_5bpMe^{4+}$ cannot be compared, without first making an electrostatic correction, with the other complexes.

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Optical Activity of Tetrahedral Dihalo[(−)-α-isosparteine]cobalt(II) Complexes

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The absorption and circular dichroism spectra of the tetrahedral halide complexes $[Co(l\text{-}\alpha\text{-isp})X_2]$ have been recorded over the range of the d–d transition manifold, 2000–20 000 cm^{-1}. An interaction between the C–H stretching vibration transitions of the organic ligand and the electronic d–d transitions of the metal ion is observed in the optical activity near 2900 cm^{-1}. The spectra are discussed in terms of the dynamic ligand-polarization mechanism for d–d transition probabilities.

Introduction

Hitherto, the investigation of the optical activity of chiral transition-metal complexes has been confined largely to the type of chelated coordination compound first optically resolved by Werner.[1] These enantiomers are mainly six-coordinate complexes of the M(III) ions with a d^3 or spin-paired d^6 configuration, which affords an orbitally nondegenerate ground state, and with ligands at a position in the spectrochemical series that corresponds to d–d absorption in the readily accessible visible or quartz UV region. The principal features of the d–d absorption and circular dichroism (CD) spectra of the dihedral (D_3) tris-chelate transition-metal complexes were early established,[2,3] and the first quantum-mechanical interpretation of d-electron optical activity, employing crystal field theory, was based upon the CD spectra of these complexes.[4]

Crystal field theory proved to have a limited application to the analysis of d–d optical activity. A pseudoscalar crystal field, required for a first-order d–d rotational strength, was found[5] to give a vanishing contribution in a chiral complex with octahedral coordination, while the corresponding second-order approach gave crystal field d–d rotational strengths at variance with the observed CD spectra of D_3 tris-chelate complexes.[6] An alternative treatment of d–d optical activity, based upon

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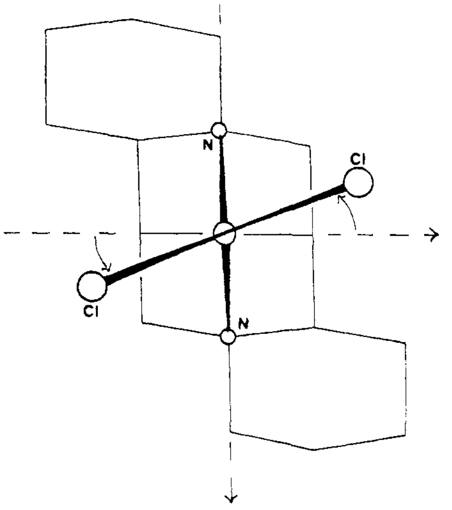
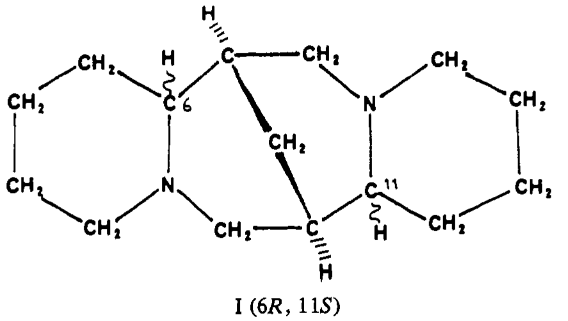


Figure 1. Projection of the molecular structure of [Co(*l*-α-isp)Cl_2] on the plane perpendicular to the C_2 (*Z*) axis. The projections of the NCoN and the ClCoCl planes are distorted from orthogonality by 19.2°.

the dynamic polarization of the ligands by the potential of the leading electric moment of the d–d transition, necessarily an even multipole, provides a less limited analysis of the CD spectra of chiral six-coordinated complexes of cobalt(III), whether tris chelate[7] or hexa-unidentate,[8] as in the case[9] of (*R*)-(+)-*all-cis*-$[Co(NH_3)_2(H_2O)_2(CN)_2]^+$.

As yet, few studies have been reported of the d-electron optical activity of chiral transition-metal complexes with tetrahedral coordination. The main quasi-tetrahedral chiral complexes at present well characterized belong to the $[M^{II}(diamine)X_2]$ series, where M(II) is a transition-metal ion of the first long period, X is a halide or pseudohalide ion, and the diamine is chiral and ditertiary. The diamines employed[10-14] are (−)-sparteine (*l*-sp) (I) and its epimers, (−)-α-isosparteine (*l*-α-isp) (II) and (+)-β-isosparteine (*d*-β-isp) (III), or their antipodes, together with[15] (*R*)-(+)-*N,N,N′,N′*-tetramethyl-1,2-propylenediamine (*R*-Me_4pn). The molecular structures of [Cu(*l*-β-isp)Cl_2],[16] [Co(*l*-sp)Cl_2],[17] [Co(*l*-α-isp)Cl_2],[18] and [Co(*R*-Me_4pn)Cl_2],[15] determined by X-ray crystallography, show that the coordination is tetrahedral, although the molecular and chromophoric $[MN_2Cl_2]$ symmetry at the highest is C_2 (Figure 1).



I (6*R*, 11*S*)
II (6*R*, 11*R*)
III (6*S*, 11*S*)

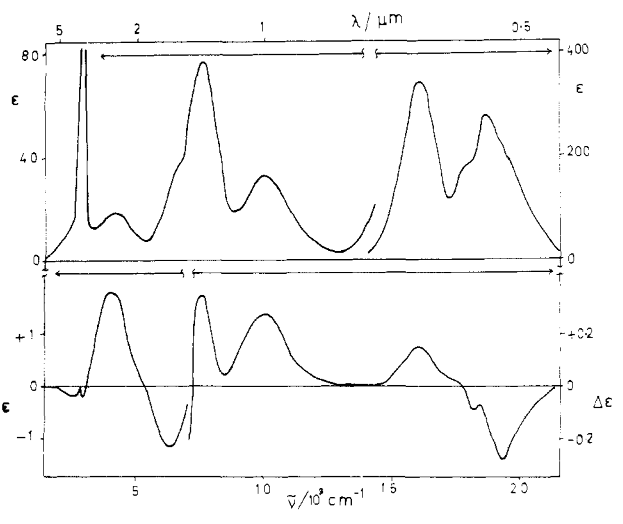


Figure 2. Absorption (upper curve) and circular dichroism (lower curve) spectra of [Co(*l*-α-isp)Cl_2] in $CHCl_3$ or $CDCl_3$ solution over the d–d transition range.

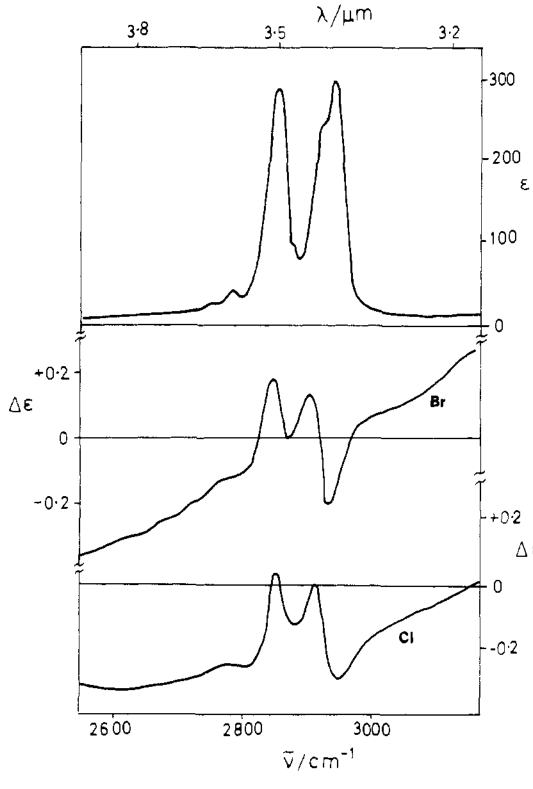


Figure 3. Absorption (top curve) and circular dichroism (lower curves) spectra of [Co(*l*-α-isp)Br_2] and [Co(*l*-α-isp)Cl_2] in $CDCl_3$ solution over the frequency region of the C–H stretching vibrations of the (−)-α-isosparteine ligand.

The present work reports the preparation and the absorption and CD spectra of [Co(*l*-α-isp)Cl_2] (IV) and the corresponding bromo and iodo complexes over the frequency region (2000–20 000 cm^{-1}) of the d–d manifold (Figure 2). The study aims to extend the measurement and the analysis of d–d optical activity to chiral complexes with coodination polyhedra other than octahedral. Owing to the smaller ligand field of tetrahedral cobalt(II), relative to octahedral cobalt(III), two of the three main d–d band systems of IV and its analogues lie in

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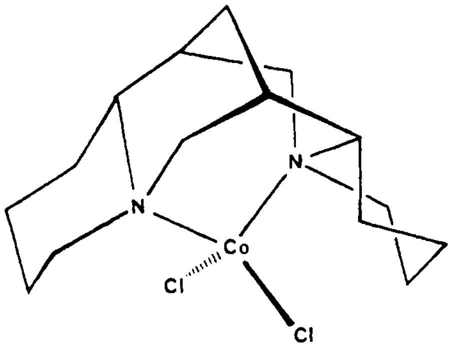

IV

the IR wavelength region. The recent development of CD spectrophotometers for the IR region with a sensitivity adequate for the detection of vibrational optical activity[19-21] allows a comprehensive characterization of the relatively stronger d–d electronic optical activity of IV and analogous complexes. From IRCD studies of the complexes $[M(l\text{-sp})Cl_2]$, M = Co(II), Ni(II), Zn(II), a Fano-type[22,23] interaction in the optical activity has been observed[24] between the C–H stretching vibration transitions of the organic ligand and the d–d electronic transitions. A similar interaction is found in the IRCD spectrum of complex IV and its bromo analogue (Figure 3).

Experimental Section

Materials. (−)-Sparteine (Sigma Chemical Co.) was converted into (−)-α-isosparteine by the procedure of Winterfeld and Rauch[25] as modified by Leonard and Beyler.[26] The dihalo[(−)-α-isosparteine]cobalt(II) complexes were obtained by the method described for the preparation of the corresponding (−)-sparteine analogues.[10] The analytical data for the $[Co(l\text{-}\alpha\text{-isp})X_2]$ complexes are recorded in Table I.

Spectra. Absorption spectra were obtained with a Cary 17 spectrophotometer (0.5–2.5 μm) and a Perkin-Elmer 621 grating instrument (2.0–5.0 μm), and the circular dichroism spectra were measured with a Jasco J40C (0.5–1.0 μm) and a laboratory-constructed IRCD instrument (0.7–5.0 μm) previously described.[21] The spectra recorded (Figures 2 and 3, Tables II and III) refer to chloroform and to deuteriochloroform solutions of the $[Co(l\text{-}\alpha\text{-isp})X_2]$ complexes.

Results and Discussion

The absorption and CD spectra of the dihalo complexes $[Co(l\text{-}\alpha\text{-isp})X_2]$ over the range of the d–d manifold divide into three regions, characterized by the dissymmetry ratio of Kuhn,[3] $g = \Delta\epsilon/\epsilon$. The g ratio differs by an order of magnitude among the three regions, having the $|g|$ values ca. 8×10^{-2} (2000–7000 cm^{-1}), ca. 4×10^{-3} (7000–12 000 cm^{-1}), and ca. 4×10^{-4} (15 000–20 000 cm^{-1}) for the chloro complex IV (Figure 2), and similar values over the corresponding frequency regions for the bromo and iodo complexes (Table III). The absorption and CD in each of the three regions correspond to the low-symmetry components of the tetrahedral cobalt(II) d–d transitions, $^4A_2 \rightarrow {}^4T_2(F)$, $^4T_1(F)$, and $^4T_1(P)$, respectively. Over the band areas of an absorption feature as a whole, the g factor represents the ratio of the rotational strength to the dipole strength of the transition, $g = 4R/D$. The rotational strength, R, is given by the scalar product of the magnetic dipole, **m**, and the electric dipole, μ, transition moment, while the dipole strength, D, corresponds to the square modulus of the latter moment, $|\mu|^2$. A substantial g ratio ($g > 10^{-2}$) indicates that the corresponding transition has a large magnetic moment, with generally, but not necessarily, a small electric dipole moment.[27]

Table I. Analytical Data (%) with Calculated Values in Parentheses

complex	C	H	N	halogen
$[Co(l\text{-}\alpha\text{-isp})Cl_2]$	49.4 (49.5)	7.2 (7.2)	7.4 (7.7)	19.6 (19.5)
$[Co(l\text{-}\alpha\text{-isp})Br_2]$	39.2 (39.7)	5.7 (5.8)	6.0 (6.2)	34.6 (35.3)
$[Co(l\text{-}\alpha\text{-isp})I_2]$	33.6 (32.9)	4.9 (4.8)	5.1 (5.1)	45.7 (46.4)

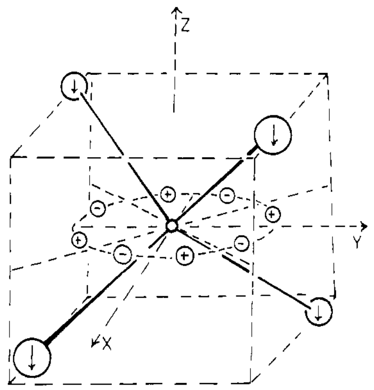

Figure 4. Coulombic correlation of the z component of the electric dipole induced in each of the coordinated ligand atoms by the electric hexadecapole moment, $H_{xy(x^2-y^2)}$, of the $d_{x^2-y^2} \rightarrow d_{xy}$ transition in a chirally distorted tetrahedral metal complex of D_2 or lower symmetry.

The lowest energy tetrahedral cobalt(II) transition, $^4A_2 \rightarrow {}^4T_2(F)$, is made up, together with two equivalent orthogonal excitations, of the single d-orbital promotion, $d_{x^2-y^2} \rightarrow d_{xy}$, which has a magnetic dipole (m_z = 2 Bohr magnetons) and an electric hexadecapole, $H_{xy(x^2-y^2)}$, as the leading transition moments.[7] The field of the electric 2^4-pole transition moment, $H_{xy(x^2-y^2)}$, in a complex with regular tetrahedral coordination produces no overall constructive correlation of the electric dipoles induced in each of the coordinated ligand atoms, but a D_2 or lower symmetry distortion of the complex affords a constructive correlation, giving a nonvanishing resultant-induced electric dipole (Figure 4). The resultant represents the first-order ligand-polarization electric dipole moment of the d–d transition, and it has z polarization in the isotropic ligand polarizability approximation.[28] The electric dipole transition moment, located in the ligands, is given by the expression

$$\mu_z^{dd'} = -H_{xy(x^2-y^2)}^{dd'} \sum_{L} [\bar{\alpha}(L)] G_{xyz(x^2-y^2)}^{L} \qquad (1)$$

where the sum is taken over the ligand atoms or groups, L, each with the mean electric-dipole polarizability, $\bar{\alpha}(L)$, at the d–d transition frequency.

In eq 1, the geometric tensor, $G_{xyz(x^2-y^2)}^{L}$, contains the angular and radial factors governing the potential between the electric hexadecapole, $H_{xy(x^2-y^2)}$, and the z component of an electric dipole, μ_z, centered on the ligand atom or group, L, namely

$$G_{xyz(x^2-y^2)}^{L} = 315XYZ(Y^2 - X^2)/2R^{11} \qquad (2)$$

where X, Y, Z refer to the Cartesian coordinates of the ligand group, L, in the tetrahedral coordinate frame at a distance, R, from the metal ion at the origin (Figure 4). As the geometric tensor of eq 2 vanishes for regular tetrahedral coor-

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Table II. Absorption and Circular Dichroism Spectra of the Complex [Co(l-α-isp)Cl_2] in $CDCl_3$ Solution and the Observed Dipole Strengths, D (10^{-38} cgsu, esu^2 cm^2), and Rotational Strengths, R (10^{-40} cgsu, esu cm erg G^{-1}), together with the D and R Values, in the Same Respective Units, Calculated for the Component d-d Transitions of the [CoN_2Cl_2] Chromophore[a]

CD			abs			from $^4A_2(e^4t_2^3)$		
$\nu/10^3$ cm^{-1}	$\Delta\epsilon_{max}$	R	$\nu/10^3$ cm^{-1}	ϵ_{max}	D	R_{calcd}[f]	D_{calcd}[f]	confign
2.6	−0.29	−1.1	2.9[b]	300[b]	d	−0.71	0.04	x
4.1	+1.46	+7.6	4.1	24	3.6	+19.5	1.1	y $^4T_2(e^3t_2^4)$
6.5	−1.20	−5.9	6.4[c]	30[c]	4[e]	−18.8	1.0	z
7.7	+0.31	+0.65	7.6	75	13	0	33	$^4T_1(e^3t_2^4)$
10.0	+0.24	+0.94	10.0	32	6			
16.1	+0.16	+0.26	16.0	335	27			
19.1	−0.29	−0.38	18.4	275	26			

[a] The calculated values refer to the bond distances and bond angles of the [CoN_2Cl_2] group from the crystal structure of the complex,[18] to the expectation values, $\langle r^2\rangle = 0.366$ Å^2 and $\langle r^4\rangle = 0.443$ Å^4, appropriate for a dipositively charged cobalt ion, and to the mean polarizability values, $\bar{\alpha}(N) = 1.50$ Å^3 and $\bar{\alpha}(Cl^-) = 3.50$ Å^3. [b] Mean value for the symmetric (2855 cm^{-1}) and antisymmetric (2940 cm^{-1}) stretching vibration modes of the CH_2 groups in the organic ligand (Figure 3). [c] Shoulder absorption (Figure 2). [d] The electronic d-d transition is overlaid by the vibrational C-H stretching-mode absorption. [e] By Gaussian analysis from the shoulder absorption (Figure 2). [f] Minimum estimates for an effective dipositively charged cobalt ion in the complex (see text).

Table III. Absorption and Circular Dichroism Spectra of [Co(l-α-isp)Br_2] over the 0.5-5.0-μm Range and of [Co(l-α-isp)I_2] over the 0.5-2.0-μm Wavelength Range in $CDCl_3$ and $CHCl_3$ Solutions, Respectively, with the Observed Dipole Strengths, D (10^{-38} cgsu, esu^2 cm^2), and Rotational Strengths, R (10^{-40} cgsu, esu cm erg G^{-1})

CD			abs		
$\nu/10^3$ cm^{-1}	$\Delta\epsilon_{max}$	R	$\nu/10^3$ cm^{-1}	ϵ_{max}	D
		[Co(l-α-isp)Br_2]			
2.5	−0.37	−1.2	2.9[a]	295[a]	4.0[a]
3.6	+1.55	+7.9	3.7	17	3.5
6.2	−1.84	−6.8	6.3[b]	25[b]	
7.4	+0.29	+0.72	7.3	98	16
9.7	+0.56	+2.40	9.7	44	7.5
15.4	+0.21	+0.31	15.8	380	34
18.4	−0.41	−0.56	18.0	345	29
		[Co(l-α-isp)I_2]			
5.2	−2.88	−14.0	5.2[b]	40[b]	
7.0[b]	−0.1[b]		6.9	119	25
9.2	+1.08	+4.05	9.2	59	11
14.7	+0.31	+0.55	15.2	495	41
17.4	−0.70	−1.66	17.2	505	40

[a] Mean value for the symmetric and antisymmetric CH_2 stretching-vibration modes of the organic ligand (Figure 3). [b] Shoulder absorption.

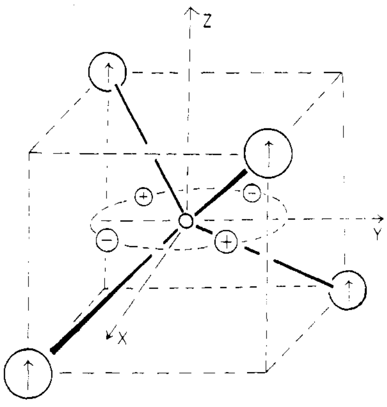

Figure 5. Coulombic correlation of the z component of the electric dipole induced in each of the coordinated ligand atoms by the electric quadrupole moment, θ_{xy}, of the $d_{z^2} \rightarrow d_{xy}$ transition in a tetrahedral metal complex.

dination, the minor angular distortions of the coordinated ligand atoms in the [CoN_2Cl_2] chromophore of complex IV from the tetrahedral positions (Figure 1) give the $d_{x^2-y^2} \rightarrow d_{xy}$ transition, and the two equivalent excitations producing the $^4T_2$(F) cobalt(II) excited state, only a small first-order electric dipole transition moment from eq 1. The electric dipole transition moment in the ligand atoms is collinear with the zero-order magnetic dipole transition moment of the cobalt(II) ion, however, giving each of the three components of the tetrahedral $^4A_2 \rightarrow {}^4T_2$(F) cobalt(II) transition in IV and its analogues a large rotational strength, while the corresponding dipole strength is small. Thus the g ratio is large for each of the three CD bands over the 2000–7000-cm^{-1} region of IV (Figure 2, Table II) and of its bromo analogue (Table III).

In the cubic description, the higher energy d–d transitions of a tetrahedral cobalt(II) complex, $^4A_2 \rightarrow {}^4T_1$(F) and $^4T_1$(P), derive a nonzero transition probability from the one-electron promotion, $d_{z^2} \rightarrow d_{xy}$, and two equivalent orthogonal excitations. Both the $^4T_1$(F) and the $^4T_1$(P) excited states are represented by linear combinations of one-electron ($e^3t_2^4$) and two-electron ($e^2t_2^5$) excited configurations, and promotions from the ground configuration ($e^4t_2^3$) to the two-electron excited configuration have a vanishing transition probability in a radiation field. The leading moment of the one-electron excitation, $d_{z^2} \rightarrow d_{xy}$, is the xy component of an electric quadrupole, θ_{xy} but there is no accompanying magnetic dipole moment in this case nor that of the equivalent orthogonal excitations.

The constructive correlation of the electric dipoles induced in each coordinated ligand atom or group by the field of the d–d quadrupole transition moment, θ_{xy}, is an optimum in four-coordinate complexes at regular tetrahedral coordination for a given metal–ligand bond length[28] (Figure 5). The resultant first-order electric dipole transition moment, located in the ligand atoms, is relatively large in this case, and it is given by the expression

$$\mu_z^{dd'} = -\theta_{xy}^{dd'} \sum_{L} [\bar{\alpha}(L)] G_{xyz}^{L} \qquad (3)$$

The geometric tensor governing the potential between the z component of an electric dipole in a ligand atom, L, and the xy component of an electric quadrupole has the form

$$G_{xyz}^{L} = -15XYZ/R^7 \qquad (4)$$

where X, Y, and Z represent the Cartesian coordinates of the ligand, L, in the tetrahedral frame centered on the metal ion, with a metal–ligand bond length, R (Figure 5).

Steric distortions from regular tetrahedral coordination reduce the first-order electric dipole transition moment induced in the ligands by the potential of the d–d electric quadrupole moment (eq 3 and 4), but the moment remains substantial in complexes such as IV where the angular distortions are not large. In addition, the distortions limit the validity of the cubic description, and the allowed and the forbidden magnetic dipole d–d transitions become mixed to a degree dependent, among other factors, upon the inverse of the energy separation between the allowed and the forbidden magnetic dipole transition types. The magnetic dipole allowed d–d transitions of IV and its bromo and iodo analogues, with ${}^4A_2 \rightarrow {}^4T_2(F)$ tetrahedral cobalt(II) parentage, lie in the 2000–7000-cm^{-1} region, and the *g* ratios of the higher energy band systems, those with ${}^4A_2 \rightarrow {}^4T_1(F)$, ${}^4T_1(P)$ tetrahedral parentage in the 7000–12 000 and 15 000–20 000-cm^{-1} region, respectively, reflect the reduced mixing of allowed and forbidden magnetic dipole d–d transitions with increasing energy separation (Figure 2, Tables II and III).

A detailed treatment of the absorption and CD spectra of complex IV and its analogues requires quantitative information as to the degree of mixing of the d–d transition types or, what is equivalent, of the particular composition of the d-electron states. Such information is provided in principle by the angular overlap model[29] in which the independent-systems assumption of crystal field theory and the ligand-polarization treatment is relaxed and weak covalency between the metal ion and the ligand is taken into account. Angular overlap calculations based upon the molecular structure of IV, determined by X-ray crystallography,[18] and the parameters $e_\sigma(N) = 4200$, $e_\sigma(Cl) = 3690$, $e_\pi(Cl) = 1080$, and $B(\text{Racah}) = 730$ cm^{-1} satisfactorily reproduce the frequencies of the d-electron transitions of complex IV. Other angular overlap parameter sets are found to reproduce adequately the observed frequencies in the spectrum of complex IV, but in no case, as yet, are the corresponding transition probabilities, the observed rotational and dipole strengths, satisfactorily explained. In particular, the theoretical mixing of the adjacent components of the ${}^4T_2(F)$ and ${}^4T_1(F)$ excited states given by the present angular overlap calculations is too large.

General observations, not dependent upon the extent of the mixing between the components of the tetrahedral cobalt(II) excited d-electron states in complex IV, are that eq 1 and its analogues for the two other components of the ${}^4A_2 \rightarrow {}^4T_2(F)$ tetrahedral transition give the correct order of magnitude and the signs of the three major CD bands observed over the 2000–7000-cm^{-1} region and that eq 3 and its analogues for the other two components of the ${}^4A_2 \rightarrow {}^4T_1(e^3t_2{}^4)$ configurational excitation account for a substantial fraction of the total dipole strength measured over the 7000–20 000-cm^{-1} region (Table II). For both regions, the bond lengths and bond angles of the $[CoN_2Cl_2]$ chromophore employed to evaluate the appropriate geometric tensors (eq 2 and 4) had the values determined[18] by the X-ray analysis of the crystal structure of complex IV. The Cartesian coordinate frame to which eq 2 and 4 refer is not symmetry determined in quasi-tetrahedral complexes of lower than D_2 point symmetry. Accordingly the *Z* axis was taken as the C_2 axis of complex IV, and the bisectors of the larger and the smaller dihedral angles between the NCoN and the ClCoCl planes were chosen as the *X* and *Y* axis, respectively, so that the $[CoN_2Cl_2]$ chromophore is taken essentially as a perturbed D_2 system (Figures 1 and 4).

The electric multipole transition moments of eq 1 and 3 were obtained by the method of Griffith.[30] In units of the electronic charge, the values are

$$\langle d_{x^2-y^2}|H_{xy(x^2-y^2)}|d_{xy}\rangle = \langle r^4\rangle(2/21) \tag{5}$$

and

$$\langle d_{z^2}|\theta_{xy}|d_{xy}\rangle = -\langle r^2\rangle\{2/[7(3^{1/2})]\} \tag{6}$$

The radial expectation values for a 3d electron of cobalt were calculated from double-exponent wave functions[31] for the range from the dipositively charged ion to the neutral atom, representing the limiting effective charge state of the cobalt atom in complex IV and its analogues. The values of $\langle r^2\rangle$ obtained are 0.569 and 0.366 Å^2 for neutral and dipositively charged cobalt, respectively, and the corresponding $\langle r^4\rangle$ values are 0.835 and 0.443 Å^4, respectively. The calculated dipole and rotational strengths recorded (Table II) are based upon the radial expectation values for dipositively charged cobalt. The corresponding values for neutral cobalt increase the theoretical rotational and dipole strengths of the ${}^4A_2 \rightarrow {}^4T_2(F)$ components by a factor of 1.9 and 3.5, respectively, and increase the total dipole strength of the ${}^4A_2 \rightarrow {}^4T_1(e^3t_2{}^4)$ components by the factor of 2.4. The mean polarizability values[32] employed in the calculations are 1.50 and 3.50 Å^3 for the nitrogen and the chloride ligand, respectively.

A comparison of the calculated with the corresponding observed rotational and dipole strengths of complex IV (Table II) indicates that the degree of mixing between the components of the ${}^4A_2 \rightarrow {}^4T_2(F)$ and the ${}^4A_2 \rightarrow {}^4T_1(e^3t_2{}^4)$ transitions is surprisingly small, in view of the large perturbations from tetrahedral symmetry in the $[CoN_2Cl_2]$ chromophore. Most of the rotational strength remains localized in the magnetic dipole allowed components of the ${}^4A_2 \rightarrow {}^4T_2(F)$ set, and the major part of the dipole strength is restricted to the electric quadrupole allowed components of the ${}^4A_2 \rightarrow {}^4T_1(e^3t_2{}^4)$ manifold, for which the ligand-polarization intensity mechanism is particularly effective.

More approximate ligand-polarization estimates of rotational and dipole strength are feasible for the corresponding bromo and iodo complexes $[Co(l\text{-}\alpha\text{-isp})X_2]$ in the absence of a X-ray crystal structure in these cases, on the assumption that the significant changes from complex IV are an increase in the metal–halide bond length, R_{MX}, and in the mean polarizability of the halide, $\bar{\alpha}(X)$. With a common set of corresponding bond angles in the chromophore $[CoN_2X_2]$, the contribution of the halide ligands to the sums of eq 1 and 3 are proportional to $[\bar{\alpha}(X)]R_{MX}{}^{-6}$ and to $[\bar{\alpha}(X)]R_{MX}{}^{-4}$, respectively (eq 2 and 4). The tetrahedral cobalt(II) bond lengths,[33] Co–Br = 2.39 and Co–I = 2.53 Å, and the mean polarizabilities,[32] $\bar{\alpha}(Br^-) = 5.02$ and $\bar{\alpha}(I^-) = 7.61$ Å^3, give the total dipole strength over the components of the ${}^4A_2 \rightarrow {}^4T_1(e^3t_2{}^4)$ manifold the ratios 1:1.21:1.77 in the series of complexes $[Co(l\text{-}\alpha\text{-isp})X_2]$ for X = Cl$^-$, Br$^-$, I$^-$, respectively, compared with the corresponding observed ratios 1:1.19:1.64 (Tables II and III). The ratios expected for the rotational strengths of the ${}^4A_2 \rightarrow {}^4T_2(F)$ components in the $[Co(l\text{-}\alpha\text{-isp})X_2]$ series, 1:0.98:1.05, for X = Cl$^-$, Br$^-$, I$^-$, respectively, are less satisfactory, although the observed rotational strengths measure only the residual CD absorption resulting from the overlap on the frequency ordinate of the larger intrinsic rotational strengths with opposed signs (Tables II and III).

The lowest energy component of the tetrahedral ${}^4A_2 \rightarrow {}^4T_2(F)$ d-electron transition of complex IV and its bromo analogue overlap the frequency region of the C–H stretching vibration fundamentals of the (−)-α-isosparteine ligand (II), and the particular CD line shape observed near the frequencies of the symmetric (2855 cm^{-1}) and the antisymmetric (2940 cm^{-1}) stretching modes of the CH_2 group in ligand II indicate that the electronic and the vibrational transitions are coupled (Figure 3). An interaction between the superposed electronic and vibrational transitions is not evident in the isotropic absorption spectrum, but the CD associated with the C–H stretching fundamentals of IV is enhanced by a factor of ~20 relative to the purely vibrational CD observed over the corresponding region in the IRCD spectrum[24] of $[Zn(l\text{-sp})Cl_2]$,

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and the CD band shapes differ in the two cases.

The general theory of the interference effects in CD spectra resulting from the superposition of a sharp transition upon a broad continuous excitation has been investigated for chiral molecules with C_2 point symmetry.[23] The application of the theory to IV, and analogous complexes with C_2 symmetry, indicates that the line-shape function, L_{CD}, expected for the CD spectra in the region of the frequency ν_{01} of a C–H stretching fundamental has the form

$$L_{CD} = \rho(\epsilon^2 + \delta^2)^{-1}\{R_{01} + \epsilon[\mu_{01}\cdot\mathbf{m}_{dd} + \mu_{dd}\cdot\mathbf{m}_{01}] + \epsilon^2 R_{dd}\} \quad (7)$$

where ρ is the state density of the broad manifold of the d–d transition, with the rotational strength, R_{dd}, in the frequency region of the sharp vibrational transition, with the rotational strength, R_{01}. In eq 7, ϵ and δ are dimensionless scaled quantities, respectively representing the frequency region centered upon ν_{01} and the width, $\Delta\nu_{01}$, of the vibrational fundamental, in units of the potential, V_{ev}, between the electronic and the vibrational transition charge distributions, namely

$$\epsilon = hc(\bar{\nu} - \bar{\nu}_{01})/V_{ev} \quad (8)$$

$$\delta = hc\Delta\bar{\nu}_{01}/2V_{ev} \quad (9)$$

The coupling term, V_{ev}, corresponds to the Coulombic potential between the electric hexadecapole moment of the d–d transition (Figure 4) and the electric dipole of the C–H stretching vibration transition, governed by a geometric tensor analogous to that of eq 2.

The rotational strength of the C–H stretching vibration transitions, R_{01}, measured by the CD band areas observed for the d^{10} complex $[Zn(l\text{-sp})Cl_2]$ over the 2800–3000-cm^{-1} region,[24] is small and makes only a minor contribution to the CD line shape found for the analogous cobalt(II) complexes over the same wavenumber region (Figure 3). The first of the two cross terms in eq 7, $[\mu_{01}\cdot\mathbf{m}_{dd}]$, is the more important, since the C–H stretching transition and the d–d transition are primarily electric dipole and magnetic dipole allowed, respectively. This term contributes a dispersive line shape to the CD curve,[23] as is particularly evident in the case of complex IV and its bromo analogue in the region of both the symmetric and the antisymmetric stretching modes of the CH_2 groups in ligand II, at 2855 and 2940 cm^{-1}, respectively (Figure 3). The final term of eq 7, dependent upon the rotational strength of the d–d transition, contributes an interference feature to the CD line shape, a resonance or an antiresonance, dependent upon the positive or the negative sign of the ratio R_{01}/R_{dd}, with an amplitude proportional to the magnitude of that ratio.[23] A comparison of the CD spectra of the zinc(II) and cobalt(II) complexes $[M^{II}(l\text{-sp})Cl_2]$ over the 2800–3000-cm^{-1} range[24] shows that the ratio is small, $\sim 10^{-2}$, and the interference features are not so evident as the dispersion effect arising from the first cross term of eq 7 (Figure 3).

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Registry No. $Co(l\text{-}\alpha\text{-isp})Cl_2$, 71392-82-0; $Co(l\text{-}\alpha\text{-isp})Br_2$, 79357-60-1; $Co(l\text{-}\alpha\text{-isp})I_2$, 79390-70-8.

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Ligand Control of the Mechanism of Photosensitization by Copper(I) Compounds[1]

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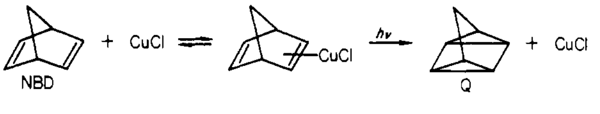
Formation of a ground-state complex between $CuBr(py)(PPh_3)$ (py is pyridine) and norbornadiene (NBD) occurs upon mixing the compounds in benzene. Irradiation of the complex with 313-nm light generates the valence isomer quadricyclene (Q) with moderate observed quantum efficiency. This efficiency varies with the nature and concentration of excess ligands present in solution. Spectral studies reveal that this behavior arises from the creation of new Cu(I) species whose sensitization properties differ from those of $CuBr(py)(PPh_3)$. Thus a sufficient excess of triphenylphosphine converts the parent compound to $CuBr(PPh_3)_3$. The latter species functions as an effective sensitizer for Q production but by a pathway involving bimolecular interaction of photoexcited $CuBr(PPh_3)_3$ with ground-state NBD. These results demonstrate that the mechanism of sensitization by Cu(I) can be controlled by the judicious addition of ligands to the system.

Introduction

Recent work from this laboratory has established that copper(I) compounds can sensitize the photoisomerization of norbornadiene (NBD) to quadricyclene (Q) via two distinct mechanisms.[2] The first, summarized in eq 1, features the



(1)

formation of a ground-state copper(I)–norbornadiene complex that, upon the absorption of a photon, generates the highly strained Q molecule. Simple CuX salts[3] and $Cu[HB(pz)_3]CO$[4] function as sensitizers in this manner. An alternative pathway followed by $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$[5] is depicted in eq 2. Here sensitization results from the bimolecular

$$Cu(PPh_3)_2BH_4 \xrightarrow{h\nu} Cu(PPh_3)_2BH_4^* \xrightarrow{NBD} Cu(PPh_3)_2BH_4^*,NBD \rightarrow Cu(PPh_3)_2BH_4 + Q \quad (2)$$

interaction of the photoexcited copper(I) compound with ground-state NBD.

A combination of structural and electronic factors will determine which of the two sensitization mechanisms predominates for a particular Cu(I) compound.[6] The ready availability of a vacant coordination site about copper clearly favors the first pathway. Conversely, sensitization via the second mechanism will become more prominent among coordinatively saturated Cu(I) compounds whose ligands are not

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