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Studies of the Circular Dichroism of Bisdiamine Complexes of Cobalt(III).

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Circular dichroism spectra are reported for cis-*bisdiamine d^6 metal complexes with C_{4v} symmetry, of the type* cis-*$[Co(en)_2(NH_3)(X)]^{n+}$. An empirical molecular orbital treatment is used to predict and assign the circular dichroism transitions associated with the d→d absorption bands. The theory is extended to the* trans-*bisdiamine and* cis-*bisdiamine metal complexes with D_{4h} and C_2 symmetry, respectively. The band splittings of the d→d transitions of the* trans-*bisdiamine complexes are twice those of the cis-bisdiamine complexes with C_{4v} symmetry. Linear relationships are found experimentally between the frequencies of the circular dichroism components of the visible absorption bands and δΔ, the empirical molecular orbital parameter, which has sigma and pi components, and is the digonal perturbation due to the ligands.*

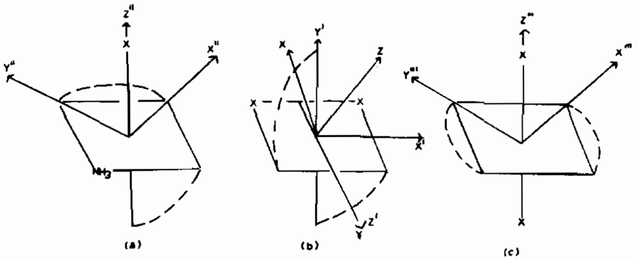

Figure 1. The coordinate frame for the bisdiamine complexes of cobalt(III) with (a) C_{4v}, (b) C_{2v}, (c) D_{4h} symmetry. The zero single, double, and triple primes refer to the coordinate axes of the D_3, C_{2v}, C_{4v}, and D_{4h} metal complexes, respectively.

Introduction

The present work is a continuation of previous studies[1] of the spectroscopic assignments for bisdiamine complexes of cobalt(III). The electronic absorption and circular dichroism spectra of the complexes investigated are given in Table I. Consider first the series of complexes, *cis*-$[Co(en)_2(NH_3)(X)]^{n+}$, with X = Br^-, Cl^-, OH^-, H_2O, CNS^-, and NO_2^-, which approximate to C_{4v} symmetry, if the perturbation due to the ligand, X, is stronger than that due to chelation. The octahedral $^1T_{1g}$ transition breaks down in these C_{4v} complexes (Figure 1) into components with $^1A_2$ and ^1E symmetry, and the octahedral $^1T_{2g}$ transition breaks down into components with $^1B_2$ and ^1E symmetry. The circular dichroism spectra of these complexes with X = Br^-, Cl^-, OH^-, and H_2O in the visible wavelength region consist of two bands associated with the octahedral $^1T_{1g}$ transition, (Table I, Figures 2-7), and these have the same sign of rotatory power, and an approximate band area ratio of 2: 1. The minor band at higher energy and the major band at lower energy are due respectively to the $^1A_2$ and ^1E components of the octahedral $^1T_{1g}$ transition, since the former occurs at approximately the mean frequency of the $^1A_2$ and ^1E_a bands of $Co(en)_3^{3+}$, and the position of the latter is displaced from that frequency by an amount depending on the separation between the ligand X and the amines in the spectrochemical series (Table II). Since both the minor and the major long-wavelength circular dichroism bands of the complexes under consideration have negative rotatory powers for the negative isomer, they must have the same absolute configuration[2] as $(-)Co(en)_3^{3+}$. The unpolarised absorption spectra of the complexes with X = Br^-, and Cl^- are split in the region of the octahedral $^1T_{1g}$ transition (Figures 2-3), and must be due to the $^1A_2$ and the ^1E components. In the wavelength region of the octahedral $^1T_{2g}$ transition, two negative circular dichroism bands are observed in the spectra of the complexes, *cis*-(-)-$[Co(en)_2(NH_3)(X)]^{n+}$, with X = Br^-, Cl^-, OH^-, and H_2O. These are due to the $^1B_2$ and the unresolved ^1E components of the octahedral $^1T_{2g}$ transition. Only one circular dichroism band of negative rotatory power is associated with the $^1T_{2g}$ absorption for the negative isomers of the complexes with X = CNS^- and NO_2^-. The major long-wavelength negative circular dichroism band of *cis*-(-)-$[Co(en)_2(NH_3)(NO_2)]^{2+}$ extends for some two-thirds of the $^1T_{1g}$ absorption band and is due to the ^1E component; the small positive band is assigned to the $^1A_2$ transition. Only one negative circular dichroism band could be distinguished in the spectrum of *cis*-(-)-$[Co(en)_2(NH_3)(CNS)]^{2+}$, under the long-wavelength absorption band.

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[1] A. J. McCaffery, S. F. Mason and Miss B. J. Norman, *J.*, 5094 (1966).

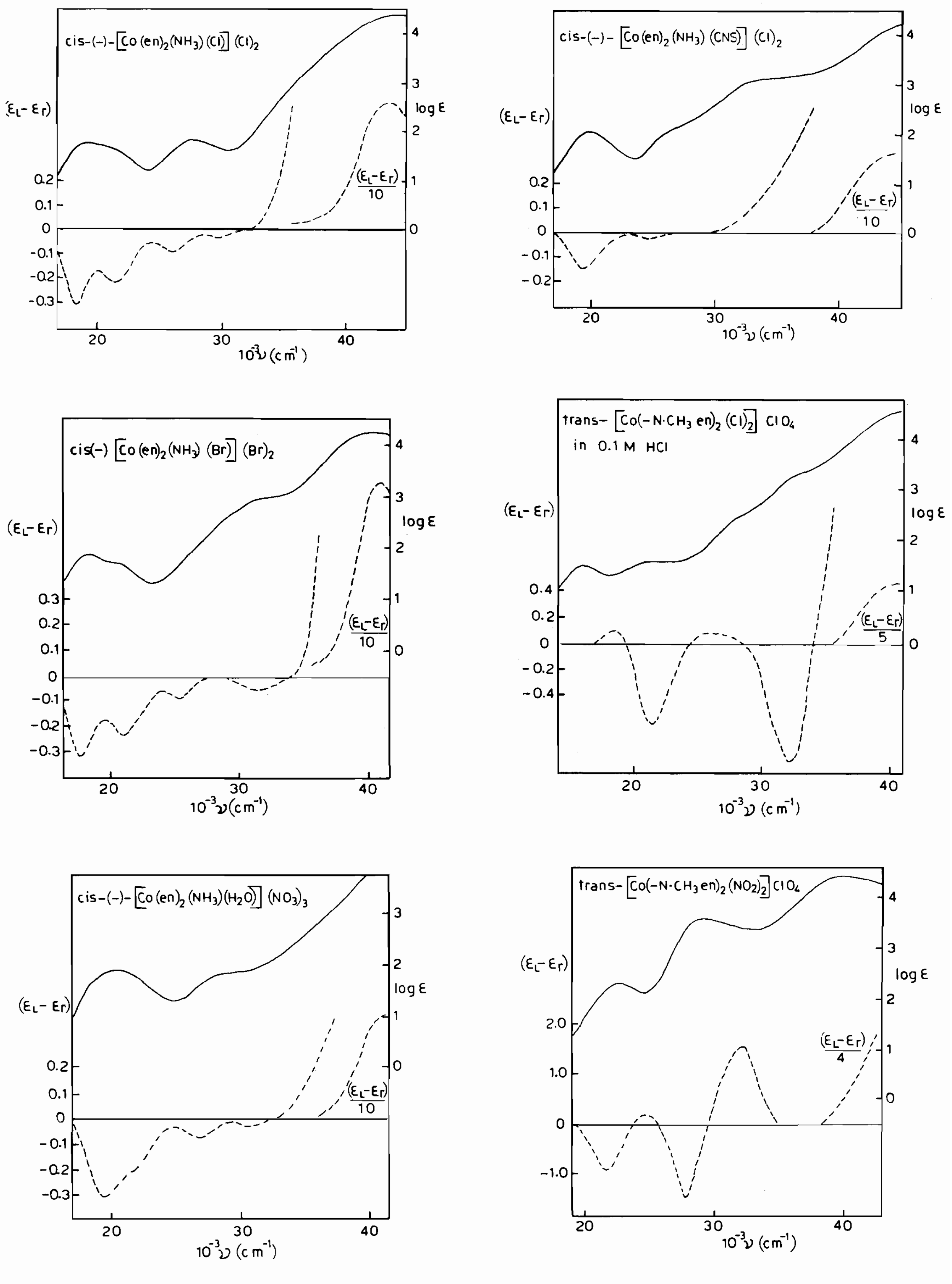
[2] A. J. McCaffery, S. F. Mason and R. E. Ballard, *J.*, 2883 (1965).

Table I. The electronic absorption and the calculated and experimental circular dichroism frequencies of the *cis*- and *trans*-bis-diamine complexes of cobalt(III), due to the spin-allowed d→d electronic transitions. Shoulders are given in italics. The octahedral field strength, Dq, and the digonal perturbation δΔ, due to the ligands, given in parentheses, and the sum of the digonal perturbation ΣδΔ, for a particular transition, are indicated. The assignements of the transitions are described.

Complex and ref.	Absorption		Circular Dichroism			Transition	Dq[3] cm^{-1}	δΔ[b] cm$^{-1}\times 10^{-3}$	ΣδΔ cm$^{-1}\times 10^{-3}$
			exp.		calc.				
	ν_{max} cm$^{-1}\times 10^{-3}$	ε_{max}	ν_{max} cm$^{-1}\times 10^{-3}$	$(\varepsilon_l-\varepsilon_r)_{max}$	ν_{max} cm$^{-1}\times 10^{-3}$				
cis(+)Co(en)$_2$(NH$_3$)$_2^{3+}$	21.30	73	20.3	+0.42		^1E_a	2490		
(1)			23.26	—0.04		$^1A_2$	(NH$_3$)		
	29.30	62	28.1	+0.056		^1E_b			
C_{4v} Complexes									
cis(-)Co(en)$_2$(NH$_3$)(Br)$^{2+}$	18.20	71	17.70	—0.315	17.8	^1E	1090	—14	—3.5
[a]	21.00	42	21.05	—0.232	21.3	$^1A_2$	(Br)[c]	(Br)	0
	31.50	775	25.25	—0.094	24.64	$^1B_2$			—4.66
			31.25	—0.06	28.13	^1E			—1.07
cis(-)Co(en)$_2$(NH$_3$)(Cl)$^{2+}$	19.00	58	18.28	—0.30	18.98	^1E	1559	—9.3	—2.32
[a]	21.50	41	21.41	—0.22	21.3	$^1A_2$	(Cl)	(Cl)	0
	27.50	66	26.11	—0.09	26.20	$^1B_2$			—3.1
			29.85	—0.03	28.40	^1E			—0.88
cis(-)Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$	20.60	65	19.42	—0.31	19.8	^1E	1888	—6.02	—1.5
[a]			*22.22*	*—0.18*	21.3	$^1A_2$	(H$_2$O)	(H$_2$O)	0
	28.50	72	26.67	—0.09	27.3	$^1B_2$			—2.0
			30.77	—0.03	28.8	^1E			—0.5
cis(-)Co(en)$_2$(NH$_3$)(OH)$^{2+}$	20.20	73.7	19.15	—0.29	19.3	^1E	1690	—8.0	—2.0
[a]			*22.0*	*—0.17*	21.3	$^1A_2$	(OH)	(OH)	0
cis(-)Co(en)$_2$(NH$_3$)(CNS)$^{2+}$	19.8	119	19.42	—0.142	20.60	^1E	2210	—2.8	—0.7
[a]					21.3	$^1A_2$	(CNS)	(CNS)	0
cis(-)Co(en)$_2$(NH$_3$)(NO$_2$)$^{2+}$	21.8	109	21.05	—0.57	21.3	$^1A_2$	3152	+6.62	0
[a]			24.10	+0.08	22.87	^1E	(NO$_2$)	(NO$_2$)	+1.57
D_{4h} Complexes									
trans-Co(-pn)$_2$(Cl)$_2^+$	16.45		16.57		16.16	^1E_g	1460	—10	—5.0
(8) [a]	22.00		21.5		21.3	$^1A_{2g}$	(Cl)	(Cl)	0
trans-Co(-pn)$_2$(Br)$_2^+$	15.37		15.50		15.24	^1E_g	1277	—12.13	—6.06
(8)	21.50		22.10		21.3	$^1A_{2g}$	(Br)	(Br)	0
trans-Co(-pn)$_2$(CNS)$_2^+$	19.61		19.95		19.9	^1E_g	2210	—2.8	—1.4
(8) [a]			23.15		21.3	$^1A_{2g}$	(CNS)	(CNS)	0
trans-Co(-pn)$_2$(NO$_2$)$_2^+$	23.10		21.74		21.3	$^1A_{2g}$	3152	+6.62	0
(3)			24.39		24.61	^1E_g	(NO$_2$)	(NO$_2$)	+3.31
trans-Co(-N.CH$_3$en)$_2$(Cl)$_2^+$	15.8		18.35		16.3	^1E_g	1460	—10	—5.0
[a]	21.3		21.50		21.3	$^1A_{2g}$	(Cl)	(Cl)	0
	27.0		25.64		22.7	$^1B_{2g}$			—6.66
			32.26		27.6	^1E_g			—1.66
trans-Co(-N.CH$_3$en)$_2$(NO$_2$)$_2^+$	22.4		21.60		21.3	$^1A_{2g}$	3152	+6.62	0
[a]			24.39		24.4	^1E_g	(NO$_2$)	(NO$_2$)	+3.31
	28.5		27.78		30.40	^1E_g			+1.1
			32.26		33.7	$^1B_{2g}$			+4.4
C_2 Complexes[d]									
cis(+)Co(en)$_2$(Cl)$_2^+$	*16.1*		16.26		16.3	$^1B_1$	1460	—10	—5.0
(1)	18.69		18.59		18.8	$^1A_2+{}^1B_2$	(Cl)	(Cl)	—2.5
	25.77		23.81		25.14	$^1A_2+{}^1B_2$			—4.16
			33.3		27.6	$^1A_1$			—1.7
cis(+)Co(en)$_2$(H$_2$O)$_2^{3+}$	20.20		17.86		17.29	$^1B_1$	1888	—6.02	—3.01
(1)			20.62		19.8	$^1A_2+{}^1B_2$	(H$_2$O)	(H$_2$O)	—1.5
	27.70		26.45		26.8	$^1A_2+{}^1B_2$			—2.5
			29.41		28.3	$^1A_1$			—1.0
cis(+)Co(en)$_2$(NO$_2$)$_2^+$	22.73		21.74		22.95	$^1A_2+{}^1B_2$	3152	+6.62	+1.65
(1)			25.0		24.61	$^1B_1$	(NO$_2$)	(NO$_2$)	+3.31
	30.80		29.8		30.40	$^1A_1$			+1.10
			34.7		32.05	$^1A_2+{}^1B_2$			+2.75
cis(+)Co(en)$_2$(CN)$_2^+$	25.00		22.68		23.8	$^1A_2+{}^1B_2$	3500	+10	+2.5
(1)			27.25		26.3	$^1B_1$	(CN)	(CN)	+5.0
	32.47		30.03		30.97	$^1A_1$			+1.67
			32.79		32.46	$^1A_2+{}^1B_2$			+4.16

[a] Present work. [b] $\delta\Delta = 10(Dq^N—Dq^X)$. [c] δΔ was obtained from the splittings of the $^1T_{1g}$ band of Co(NH$_3$)$_5$(Br)$^{2+}$, $\delta\Delta = 4[E(^1E)—E(^1A_2)]$. [d] The d→d transitions are described in terms of the $^1A_2$, $^1B_1$, and $^1B_2$ transitions of the corresponding C_{2v} complex.

In order to analyse the spectra obtained experimentally, splitting of both the $^1T_{1g}$ and $^1T_{2g}$ absorption bands would be necessary to evaluate the parameters involved, using either crystal field or molecular orbital theory. Since, in general, only the $^1T_{1g}$ absorption band is split, an empirical method was devised by Piper and Wentworth[3] to account for the band splittings caused by different ligands. They successfully explained the



Figures 2-7. The electronic absorption spectra (————), and the circular dichroism (— — —), in aqueous solution.

Table II. Predicted shifts of the $^1T_{1g}$ and $^1T_{2g}$ bands due to the replacement of the ligands

Electronic Transition		Predicted Shift and Symmetry					
		C_{4v}		D_{4h}		C_{2v}	
$^1T_{1g}$	$d_{xy}\rightarrow d_{x^2-y^2}$	O	$(^1A_2)$	O	$(^1A_{2g})$	$(1/2)\delta\Delta$	$(^1B_1)$
	$d_{yz}\rightarrow d_{y^2-z^2}$	$(1/4)\delta\Delta$	(^1E_a)	$(1/2)\delta\Delta$	(^1E_g)	$(1/4)\delta\Delta$	$(^1A_2, {}^1B_2)$
	$d_{zx}\rightarrow d_{z^2-x^2}$						
$^1T_{2g}$	$d_{xy}\rightarrow d_{z^2}$	$(1/3)\delta\Delta+(1/3)\delta\pi$	$(^1B_2)$	$(2/3)\delta\Delta+(2/3)\delta\pi$	$(^1B_{2g})$	$(1/6)\delta\Delta-(1/3)\delta\pi$	$(^1A_1)$
	$d_{yz}\rightarrow d_{x^2}$	$(1/12)\delta\Delta-(1/6)\delta\pi$	(^1E_b)	$(1/6)\delta\Delta-(2/3)\delta\pi$	(^1E_g)	$(5/12)\delta\Delta+(1/6)\delta\pi$	$(^1A_2, {}^1B_2)$
	$d_{zx}\rightarrow d_{y^2}$						

splitting of the $^1T_{1g}$ state of monoacidopentaammine, CoN_5X, and diacidotetraammine, CoN_4X_2, complexes of C_{4v} and D_{4h} symmetry, respectively, using a crystal field model in which the crystal field radial parameters are empirical,[3] and an empirical molecular orbital treatment.[3] Their molecular orbital method, which is a modification of Yamatera's[4] and McClure's,[5] is used to analyse the circular dichroism spectra of the complexes considered here. A comparable study has recently been carried out by Treptow[6] on the pseudotetragonal 1-cyclohexanediamine complexes of cobalt(III). Their[4,5] results lead to the expressions given in Table II for the predicted shifts of the components of the $^1T_{1g}$ and $^1T_{2g}$ transitions due to the replacement of the ligands for complexes approximating to C_{4v}, D_{4h}, and C_{2v} symmetry.

In Table II,

$$\delta\Delta = 10(Dq^X - Dq^N) = \Delta^X - \Delta^N = \delta\sigma - \delta\pi \quad (1)$$

and is the difference between the octahedral field strengths of the axial and in-plane ligands. The sigma and pi components are given[3] by the following equations:

$$\delta\sigma = E(e_g, CoX_6) - E(e_g, CoN_6) \quad (2)$$

$$\delta\pi = E(t_{2g}, CoX_6) - E(t_{2g}, CoN_6)$$

Values of $\delta\Delta$ were calculated from equation (1) using the octahedral field strengths, Dq, of the various ligands, obtained by Piper and Wentworth[3] using an empirical crystal-field model for the monoacidopentaammine and *trans*-diacidotetraammine complexes of cobalt(III). The pi-contribution, $\delta\pi$, to the perturbation is almost zero.

Theoretical values of the energies of the ^1E_a and $^1A_2$ components of the $^1T_{1g}$ band, and the ^1E_b and $^1B_2$ componets of the $^1T_{2g}$ band were calculated from the values of the predicted shifts (Table II) and the energies of the $^1T_{1g}$ and $^1T_{2g}$ of the parent hexamine compound, and these are compared with the corresponding circular dichroism frequencies ($\nu_{C.D.}$) obtained for the analogous C_{4v} complexes, *cis*-$[Co(en)_2(NH_3)(X)]^{n+}$, (Table I). The agreement between the experimental and theoretical frequencies is good for the complexes with X = Br^-, Cl^-, OH^- and H_2O. Table II shows that the frequencies of the $^1A_2$ and ^1E_a components of the $^1T_{1g}$ band are respectively undisplaced and displaced by (1/4) $\delta\Delta$ from the parent hexammine transition. In the calculations, the values of the energies of the $^1T_{1g}$ and $^1T_{2g}$ states of the parent compound *cis*-$[Co(en)_2(NH_3)_2]^{2+}$ for the series *cis*-$[Co(en)_2(NH_3)(X)]^{n+}$ are 21,300 cm^{-1} and 29,300 cm^{-1} respectively.[1]

An analogous treatment was carried out for the D_{4h} complexes *trans*-$[Co(\text{-}pn)_2(X)_2]^{n+}$, with X = Br^-, Cl^-, CNS^-, NO_2^-, and *trans*-$[Co(\text{-}N.CH_3en)_2(X)_2]^+$, with X = Cl^- and NO_2^-. The methyl group is attached to the nitrogen atom in the latter ligand, N-methylethylenediamine, and to the carbon atom in the former ligand, propylenediamine. Since the methyl group is constrained in the equatorial position[7] in both complexes, the conformation of the rings is fixed. The predicted shifts of the $^1T_{1g}$ and $^1T_{2g}$ components for the complexes belonging to the point group, D_{4h}, are given in Table II. On comparing the values for the complexes with D_{4h} and C_{4v} symmetry, it can be seen that the energy splittings of the former are twice those of the latter components. The frequencies of the complexes, *trans*-$[Co(\text{-}pn)_2(X)_2]^{n+}$, and *trans*-$[Co(\text{-}N.CH_3en)_2(X)_2]^{n+}$ mentioned above, were calculated from the predicted shifts (Table II) and the energies of the $^1T_{1g}$ and $^1T_{2g}$ transitions of the parent hexammine compound, i.e. *trans*-$[Co(\text{-}pn)_2(NH_3)_2]^{2+}$, and are 21,500 cm^{-1} and 29,770 cm^{-1}, respectively.[8] The values obtained were compared with the frequencies of the circular dichroism components (Table I). The Dq values used to compute $\delta\Delta$ were those obtained by Piper[3] for the analogous *trans*-diacidotetraammine complexes of cobalt(III). The agreement between the experimental and the theoretical frequencies is good for all of the *trans*-complexes with the exception of the ^1E_g ($^1T_{1g}$) component of *trans*-$[Co(\text{-}N.CH_3en)_2(Cl)_2]^+$.

Finally, similar calculations were also carried out on some complexes with C_2 symmetry,[1] notably *cis*-$[Co(en)_2(X)_2]^{n+}$, with X = Cl^-, H_2O, NO_2^-, and CN^-, which give a suitable range over the spectrochemical series. The frequencies were calculated by the same method as for the other complexes considered here. The results obtained for the C_2 complexes are included in Table I, and again the experimental results agree with theoretical predictions.

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Now it is possible to find linear relationships between the frequencies of the circular dichroism components of the $^1T_{1g}$ and $^1T_{2g}$ absorption bands with octahedral parentage O_h, and the digonal perturbation due to the ligands, for a particular transition. For example, from the energies of the singlet states of the C_{4v}, D_{4h}, and C_2 complexes, (Table II), it can be seen that if a graph is plotted of the frequencies, $\nu_{C.D.}$; of the circular dichroism components of the $^1T_{1g}$ and $^1T_{2g}$ transitions against the sum of the δΔ components, ΣδΔ, for the corresponding transition, then all the points belonging to the $^1T_{1g}$ state will lie on a straight line of slope unity, and those associated with the $^1T_{2g}$ absorption band will be on another line also of slope unity. The results using the experimental circular dichroism frequencies are plotted in Figure 8, yielding two lines each of slope unity. The ΣδΔ values ore given in Table I.

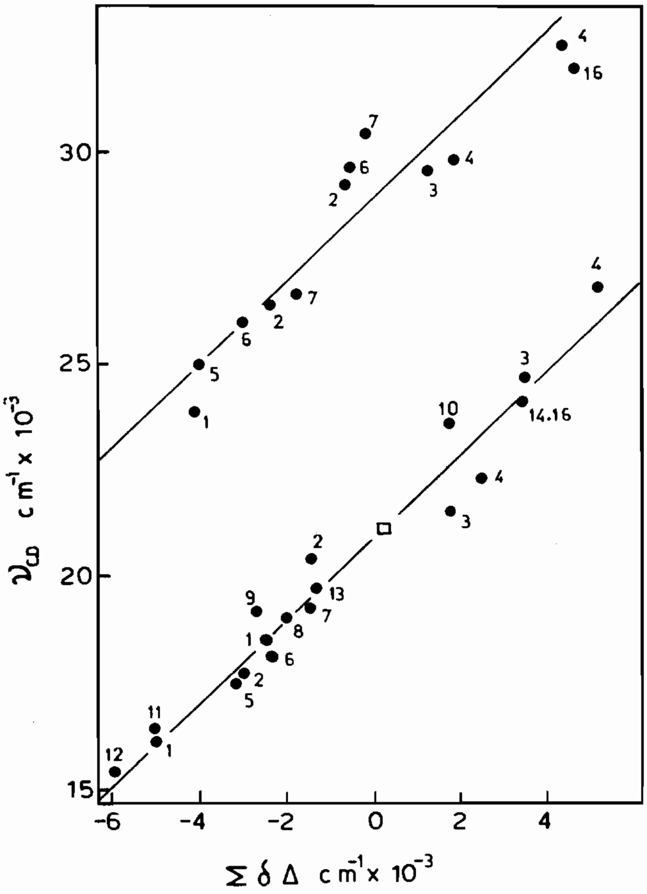

Figure 8. The frequencies of the circular dichroism bands of the d→d transitions against ΣδΔ, the sum of the digonal perturbations of the ligands, for the corresponding transition. Corresponds to the mean experimental circular dichroism frequency $\nu_{C.D.}$ of the transition for which δΣΔ = 0, for the C_{4v} and D_{4h} complexes.

1. *cis*-(+)-Co(en)$_2$(Cl)$_2^+$
2. *cis*-(+)-Co(en)$_2$(H$_2$O)$^{3+}$
3. *cis*-(+)-Co(en)$_2$(NO$_2$)$_2^+$
4. *cis*-(+)-Co(en)$_2$(CN)$_2^+$
5. *cis*-(-)-Co(en)$_2$(NH$_3$)(Br)$^{2+}$
6. *cis*-(-)-Co(en)$_2$(NH$_3$)(Cl)$^{2+}$
7. *cis*-(-)-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$
8. *cis*-(-)-Co(en)$_2$(NH$_3$)(OH)$^{2+}$
9. *cis*-(-)-Co(en)$_2$(NH$_3$)(CNS)$^{2+}$
10. *cis*-(-)-Co(en)$_2$(NH$_3$)(NO$_2$)$^{2+}$
11. *trans*-Co(-pn)$_2$(Cl)$_2^+$
12. *trans*-Co(-pn)$_2$(Br)$_2^+$
13. *trans*-Co(-pn)$_2$(CNS)$_2^+$
14. *trans*-Co(-pn)$_2$(NO$_2$)$_2^+$
15. *trans*-Co(-N.CH$_3$en)$_2$(Cl)$_2^+$
16. *trans*-Co(-N.CH$_3$en)$_2$(NO$_2$)$_2^+$

Experimental Section

The following complexes were prepared according to the methods of Werner^9 and Mathieu,^{10} and they were resolved into their optical isomers with ammonium (+)-α-bromocamphor-π-sulphonate. The molecular rotation at the sodium-D-line, [M]$_D$, of the optical isomers are given; -*cis*-(-)-[Co(en)$_2$(NH$_3$)(Cl)](Cl)$_2$, [M]$_D$ = —600°; *cis*-(-)-[Co(en)$_2$(NH$_3$)(Br)](Cl)$_2$, [M]$_D$ = —500°; *cis*-(-)-[Co(en)$_2$(NH$_3$)(NO$_2$)](NO$_3$)$_2$, [M]$_D$ = —200°; *cis*-(-)-[Co(en)$_2$(NH$_3$)(CNS)](Cl)$_2$, [M]$_D$ = —190°; *cis*-(-)-[Co(en)$_2$(NH$_3$)(H$_2$O)](NO$_3$)$_3$, [M]$_D$ = —450°.

Cis-(-)-[Co(en)$_2$(NH$_3$)(OH)]$^{2+}$ was prepared from the corresponding aquo complex by hydrolysis with sodium hydroxide to pH = 8.

Trans-[Co(-pn)$_2$(CNS)$_2$]$^+$ and *trans*-[Co(-pn)$_2$(NO$_2$)$_2$]$^+$ were kindly provided by Dr. E. Larsen, and *trans*-[Co(-N.CH$_3$en)$_2$(Cl)$_2$]$^+$ and *trans*-[Co(-N.CH$_3$en)$_2$(NO$_2$)$_2$]$^+$ by Dr. A. M. Sargeson.

Circular dichroism spectra were measured with a Jouan Dichrograph, and the absorption spectra with a Unicam SP 700 visible and ultraviolet spectrophotometer. Optical rotations were measured with a Bellingham and Stanley spectropolarimeter. The unpolarised and the circularly polarised light absorption indices are the decadic molar extinction coefficient [$\varepsilon = (1/cl)\log(I_o/I)$] in units of l. mole^{-1} cm^{-1}.

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