erizes to the chelated glycinato complex in aqueous solution.

Attempts to open the glycinato chelate ring by heating the complex in concentrated hydrochloric acid were unsuccessful. This method has been used to open one of the chelate rings (an $NRR'CH_2CO_2^-$ chelate ring) in ethylenediaminetetraacetatocobaltate-(III) ion to yield chloro(ethylenediaminetriacetato-acetic acid)cobaltate(III) ion.[13]

(13) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1958).

The chelate ring can be opened, however, if the glycinato complex is refluxed in ethanolic HCl for several hours. In this case esterification of the glycine occurs without rupture of any amine–cobalt(III) bonds to yield the glycine ester complex, *cis*-[Co(en)$_2$(NH$_2$-CH$_2$CO$_2$C$_2$H$_5$)Cl]Cl$_2$.

Optical Activity and Electronic Spectra. Pseudo-tetragonal *l*-Cyclohexanediamine Complexes of Cobalt(III)

BY R. S. TREPTOW[1]

A series of pseudo-tetragonal complexes of *l-trans*-1,2-diaminocyclohexane (*l*-chn) have been prepared. The ions studied are *trans*-[Co(*l*-chn)$_2$X$_2$]$^+$ (where X$^-$ = F$^-$, Cl$^-$, Br$^-$, and NO$_2^-$), *trans*-[Co(*l*-chn)$_2$(NH$_3$)$_2$]$^{3+}$, and *trans*-[Co(*l*-chn)$_2$-(NH$_3$)Cl]$^{2+}$. Absorption, circular dichroism, and optical rotatory dispersion spectra are reported in the region 220–700 mμ. Assignments of the ligand field and charge-transfer transitions are made using selection rules applicable to circular dichroism curves. Rotational strengths and absorption intensities are discussed.

Introduction

The correlation of circular dichroism, optical rotatory dispersion, and electronic absorption spectra of optically active coordination compounds provides a valuable tool in the study of electronic and molecular structure. This is largely due to the unique selection rules and resolving power of circular dichroism. Two recent reviews underline the principles involved.[2,3]

Most of the complexes investigated to date have been of trigonal symmetry, such as tris(ethylenediamine)cobalt(III) of the D$_3$ point group. Another optically active geometry, that of D$_2$ symmetry, presents a new opportunity for investigation. These "digonal dihedral" compounds have been considered in a recent theoretical treatment by Liehr.[4] Experimental results have been reported on *trans*-diacidobis(*l*-propylenediamine)cobalt(III) complexes, which approximate D$_2$ symmetry.[5]

We now report some complex ions of exact D$_2$ or C$_2$ symmetry. They are *trans*-[Co(*l*-chn)$_2$X$_2$]$^+$ (where X$^-$ = F$^-$, Cl$^-$Br$^-$, and NO$_2^-$), *trans*-[Co(*l*-chn)$_2$(NH$_3$)$_2$]$^{3+}$, and *trans*-[Co(*l*-chn)$_2$NH$_3$Cl]$^{2+}$. The optically active chelate *l*-chn (*l-trans*-1,2-diaminocyclohexane) was first

synthesized and resolved by Jaeger and co-workers.[6] Only *trans*-[Co(*l*-chn)$_2$Cl$_2$]$^+$ has been previously reported.[5b,6c,7] A series of various X ligands has been used in the present work to provide a more extensive study. They were chosen to represent a variety of bonding types and positions in the spectrochemical series. Another purpose in changing the *trans* ligands was to determine their influence on optical activity.

Experimental Section

Resolution of the Ligand.—*trans*-1,2-Diaminocyclohexane sulfate, purchased from Aldrich Chemical Co., was dissolved in boiling water with the calculated amount of Ba(OH)$_2$·8H$_2$O. After cooling, the thick BaSO$_4$ precipitate was removed by centrifugation. Resolution[6b] was accomplished by precipitation as the *d*-tartrate salt from hot aqueous solution. The less soluble diastereoisomer, *l*-chn *d*-tartrate, was recrystallized to a constant optical rotation, [α]D +12.0° (lit.[6b] +11°). *Anal.* Calcd for C$_{10}$H$_{20}$N$_2$O$_6$: C, 45.44; H, 7.63; N, 10.60. Found: C, 45.54; H, 7.68; N, 10.61.

For preparative purposes a stock solution of *l*-chn was conveniently made by addition of the calculated amount of Ba-(OH)$_2$·8H$_2$O to a hot suspension of *l*-chn *d*-tartrate. After cooling overnight in an ice bath, the precipitated barium tartrate was removed.

Preparation of the Coordination Compounds.—The syntheses described here are generally modifications of those used to prepare the well-known ethylenediamine analogs. The chemical properties and spectra of complexes formed by the two chelates are very similar. This fact facilitated the characterization of

(1) This research was begun under the direction of the late Professor T. S. Piper. Because of his untimely death, the results and discussions are entirely those of R. S. Treptow. Address correspondence to Miami Valley Laboratories, Procter and Gamble Company, Cincinnati, Ohio.

(2) S. F. Mason, *Quart. Rev.* (London), **17**, 20 (1963).

(3) F. Woldbye, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **24**, 197 (1963).

(4) A. D. Liehr, *J. Phys. Chem.*, **68**, 3629 (1964).

(5) (a) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202 (1965); (b) C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

(6) (a) F. M. Jaeger and J. A. van Dijk, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **B39**, 384 (1936); (b) F. M. Jaeger and L. Bijkerk, *ibid.*, **40**, 12 (1937); (c) F. M. Jaeger and L. Bijkerk, *ibid.*, **40**, 246 (1937).

(7) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1492 (1965).

products. One notable difference is that cyclohexanediamine complexes are more soluble, especially with small anions.

trans-[Co(*l*-**chn**)₂F₂]ClO₄·H₂O.—A method[8] for the preparation of *trans*-difluorobis(ethylenediamine)cobalt(III) nitrate from cobalt(II) carbonate was used with some modification. The crude product, obtained after addition of organic solvents to the aqueous extract, was converted to the perchlorate by adding a lithium perchlorate solution to the dissolved crude product. The *trans*-[Co(*l*-chn)₂F₂]ClO₄·H₂O was dissolved in an aqueous slurry with Dowex Cl⁻ exchange resin and reprecipitated by addition of lithium perchlorate. This purification procedure was repeated. The final product was a pale green-gray powder. *Anal.* Calcd for CoC₁₂H₃₀N₄F₂ClO₅: C, 32.55; H, 6.82; N, 12.66. Found: C, 32.84; H, 6.87; N, 12.77.

trans-[Co(*l*-**chn**)₂Cl₂]ClO₄.—The early preparation[6c] of this complex ion has recently been questioned.[7] We also were unable to obtain an acceptable product by the oxidation of cobalt(II) chloride with hydrogen peroxide. The method, however, was successfully modified using air oxidation.

Cobalt(II) chloride (0.048 mole) and *l*-chn (0.072 mole) were combined in 250 ml of water. Air was bubbled into the solution for 3 hr after which 40 ml of concentrated hydrochloric acid was added and the volume was reduced over steam to 70 ml. The reaction mixture was cooled overnight and filtered. The product was found to be a mixture of *cis*- and *trans*-[Co(*l*-chn)₂-Cl₂]Cl·*n*H₂O. This solid was refluxed in 200 ml of methanol for 1 hr. A small amount of [Co(*l*-chn)₃]Cl₃ present is largely insoluble under these conditions, while the [Co(*l*-chn)₂Cl₂]⁺ undergoes a *cis* to *trans* isomerization. The hot methanolic solution was filtered; on cooling, green *trans*-[Co(*l*-chn)₂Cl₂]·¹/₂H₂O precipitated. When slightly more water was present, the product obtained from methanol was in the form of green needles containing 1 mole of water of crystallization. The complex was converted to the perchlorate by slow addition of a methanolic solution of lithium perchlorate to the complex, also dissolved in methanol. *Anal.* Calcd for CoC₁₂H₂₈N₄Cl₃O₄: C, 31.49; H, 6.17; N, 12.24. Found: C, 31.50; H, 6.23; N, 12.32.

trans-[Co(*l*-**chn**)₂Br₂]Br.—A hot methanolic solution of *trans*-[Co(*l*-chn)₂Cl₂]Cl was three times evaporated to dryness with excess hydrobromic acid. The final product was recrystallized from hot methanol. Emerald-green needles were obtained. *Anal.* Calcd for CoC₁₂H₂₈N₄Br₃: C, 27.34; H, 5.35; N, 10.63. Found: C, 27.37; H, 5.63; N, 10.64.

trans-[Co(*l*-**chn**)₂(**NO₂**)₂]NO₃.—Cobalt(II) nitrate (0.011 mole), sodium nitrite (0.024 mole), and *l*-chn (0.019 mole) were combined in 50 ml of water containing 1 ml of concentrated nitric acid. Air was bubbled through the solution for 1 hr. The volume was reduced to 25 ml by boiling. After cooling the solution, the precipitate was collected and recrystallized from hot water. Small orange needles were obtained. *Anal.* Calcd for CoC₁₂H₂₈N₇O₇: C, 32.65; H, 6.39; N, 22.22. Found: C, 32.32; H, 6.34; N, 22.30.

trans-[Co(*l*-**chn**)₂(**NH₃**)₂]Cl₃·H₂O.—Ammonia gas was bubbled into a solution of 1 g of *trans*-[Co(*l*-chn)₂Cl₂]Cl·H₂O in 20 ml of methanol. After 15 min the bubbling was stopped and a yellow precipitate began to form. This product was collected 8 hr later and recrystallized from aqueous ethanol. *Anal.* Calcd for CoC₁₂H₃₆N₆Cl₃O: C, 32.33; H, 8.14; N, 18.86. Found: C, 32.16; H, 8.09; N, 18.79.

To demonstrate that the pure *trans* isomer had been isolated, the product was again recrystallized. The CD spectrum was unchanged. It is very similar to that reported[5b] for *trans*-[Co(*l*-pn)₂(NH₃)₂]³⁺.

trans-[Co(*l*-**chn**)₂**NH₃Cl**]Cl₂·³/₂H₂O.—*trans*-[Co(*l*-chn)₂Cl₂]-Cl·¹/₂H₂O (0.6 g) was dried at 100° *in vacuo* and placed in a 125-ml flask. The container was purged with ammonia gas and placed in a Dry Ice–acetone bath to condense about 2 ml of ammonia over the complex. When the color of the reaction mixture began to change, the ammonia was evaporated by a stream

of dry nitrogen. The product obtained was dark red. After drying to remove excess ammonia, it was recrystallized from water. *Anal.* Calcd for CoC₁₂H₃₄N₅Cl₃O₃/₂: C, 39.92; H, 7.83; N, 15.99. Found: C, 33.12; H, 7.91; N, 15.85.

The CD curve of the product was invariant under further recrystallization. As would be expected, it is quite similar to the CD spectrum of other *trans* *l*-chn complexes, but different[9] from that of *cis*-[Co(en)₂NH₃Cl]²⁺. These facts establish the *trans*-[Co(*l*-chn)₂NH₃Cl]²⁺ configuration.

Spectral Measurements.—Absorption spectra were measured on a Cary Model 14 spectrophotometer. The decadic molar extinction coefficient, ϵ, has units of M^{-1} cm⁻¹. Circular dichroism curves were determined with a Roussel-Jouan Dichrograph; $\epsilon_l - \epsilon_d$ is reported as $\Delta\epsilon$. A Jasco ORD/UV-5 spectropolarimeter was used for measuring the optical rotatory dispersion. The molecular rotation, $[M]$, is given in circular deg M^{-1} m⁻¹.

All spectra were determined in the region 220–700 mμ. The concentrations employed ranged from 5×10^{-3} to 10^{-4} M with path lengths from 5 cm to 1 mm. In the case of the halo complexes, where aquation can occur, the spectra were obtained in anhydrous methanol. The intense absorptions of the compounds in the ultraviolet region made CD and ORD measurements difficult. Results in this region are not so accurate as in the visible.

Results

The three spectra obtained for each complex are shown in Figures 1–6. The data are summarized in Table I. Dipole strengths were calculated from the integrated intensities of the absorption bands by use of the formula[2]

$$D = \frac{3hc(10^3)}{8\pi^3N \log e} \int \frac{\epsilon}{\nu} d\nu$$

Similarly the rotational strengths were obtained by the areas under the CD curves

$$R = \frac{3hc(10^3)}{32\pi^3N \log e} \int \frac{\Delta\epsilon}{\nu} d\nu$$

Overlapping bands were resolved visually into their components to obtain areas. Meaningful quantitative values were difficult to obtain for severely overlapping bands. Also in these overlapping cases ν_{max} values of Table I will not indicate the true band centers.

When a single Cotton effect is well isolated, it is possible to obtain R from the ORD spectrum. The formulas[2,3] employed are

$$\Delta\epsilon_{max} = ([M]_{peak} - [M]_{trough})/4028$$

$$\Delta\nu_{1/2} = 0.925(\nu_{peak} - \nu_{trough})$$

$$R = 2.45 \times 10^{-39}\Delta\epsilon_{max}\Delta\nu_{1/2}/\nu_{max}$$

The quantities $\Delta\epsilon_{max}$ and $\Delta\nu_{1/2}$ are the height and band width of the hypothetical CD band corresponding to the Cotton effect. As is usually the case, ORD in these compounds does not reveal as many transitions as CD. In the discussions to follow, attention is centered on CD spectra.

Discussion

Stereochemistry and Selection Rules.—Figure 7 shows the geometry of the complexes prepared. The

(8) W. R. Matousch and F. Basolo, *J. Am. Chem. Soc.*, **78**, 3972 (1956).

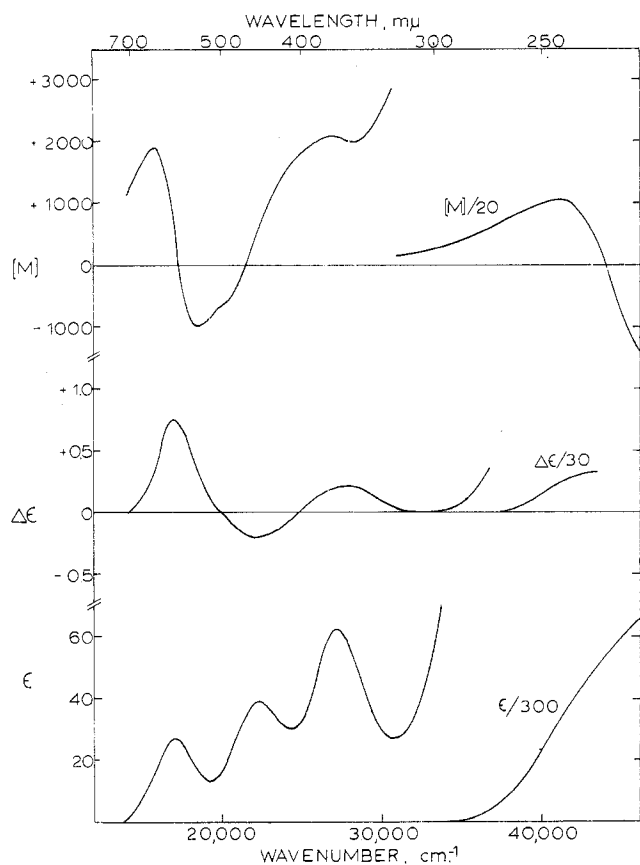(9) J. P. Mathieu, *Bull. Soc. Chim. France*, [5] **3**, 476 (1936).

Figure 1.—ORD, CD, and absorption spectra of *trans*-[Co-(*l*-chn)$_2$F$_2$]$^+$ in methanol.
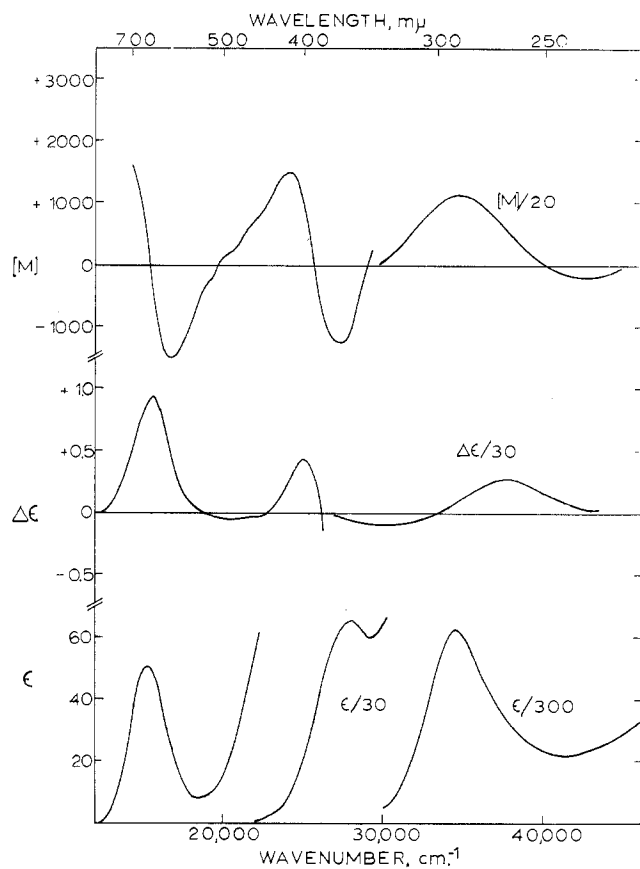

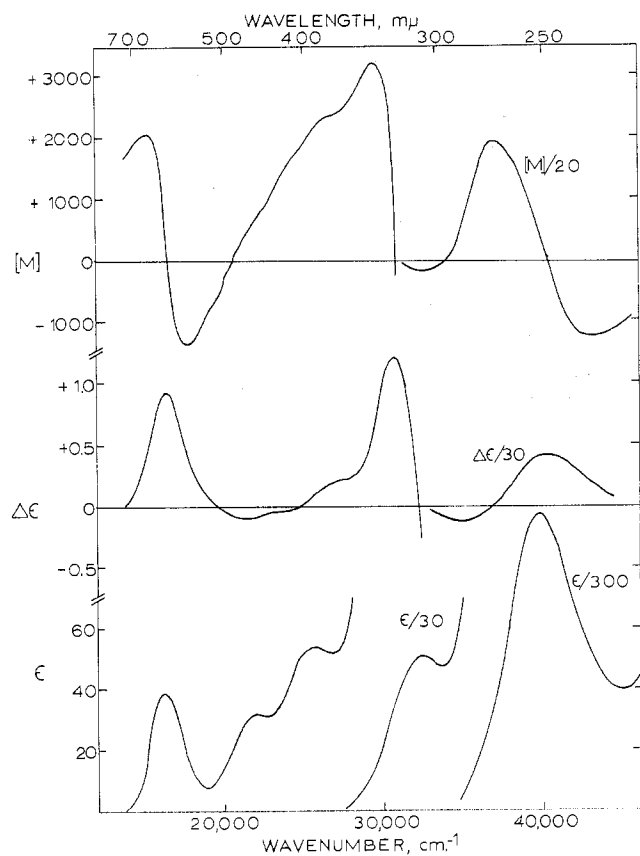Figure 3.—ORD, CD, and absorption spectra of *trans*-[Co-(*l*-chn)$_2$Br$_2$]$^+$ in methanol.

Figure 2.—ORD, CD, and absorption spectra of *trans*-[Co-(*l*-chn)$_2$Cl$_2$]$^+$ in methanol.

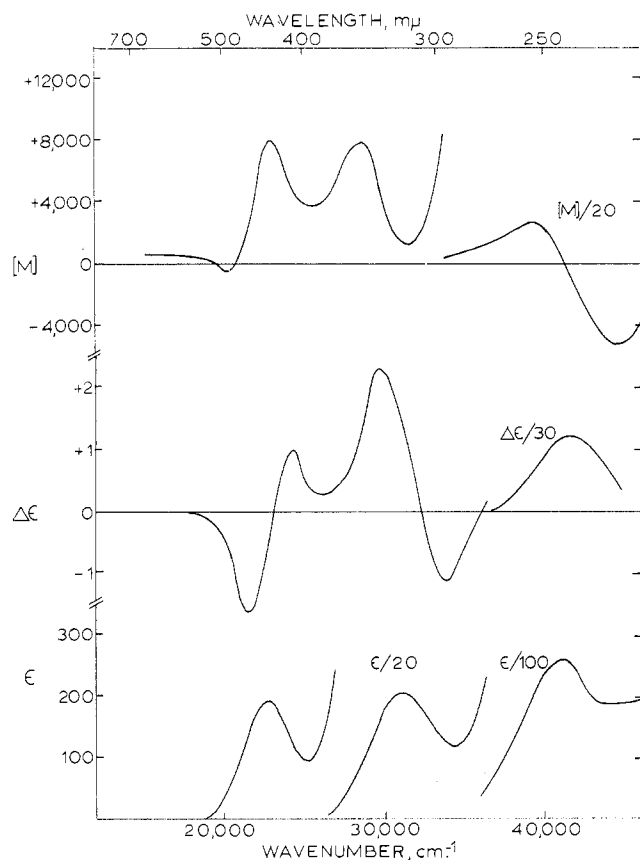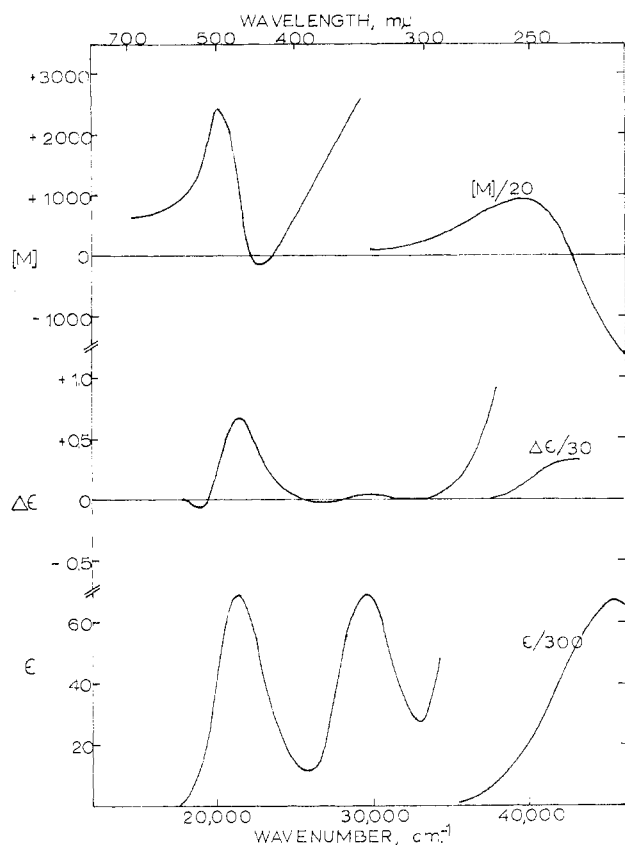Figure 4.—ORD, CD, and absorption spectra of *trans*-[Co-(*l*-chn)$_2$(NO$_2$)$_2$]$^+$ in water.

Figure 5.—ORD, CD, and absorption spectra of *trans*-[Co-(*l*-chn)$_2$(NH$_3$)$_2$]$^{3+}$ in water.
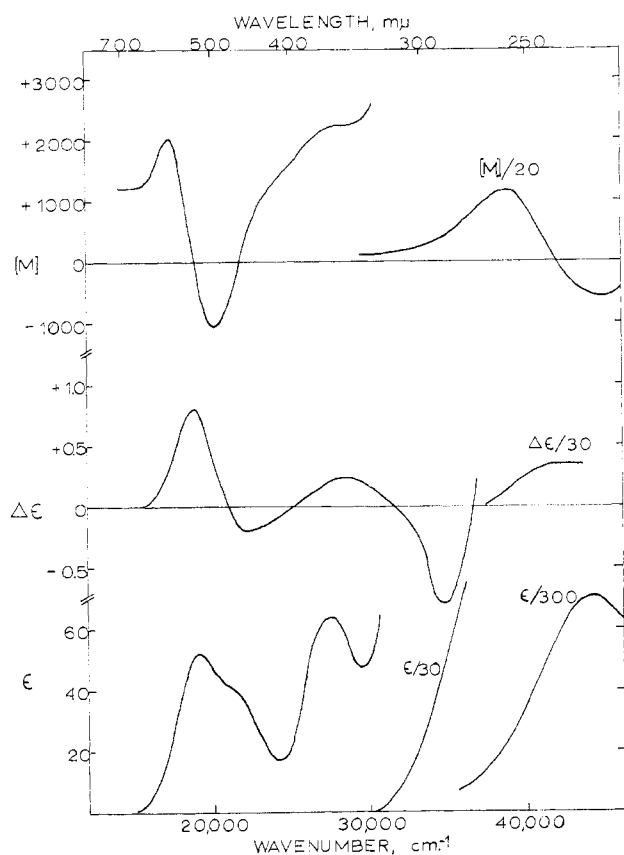
Figure 6.—ORD, CD, and absorption spectra of *trans*-[Co-(*l*-chn)$_2$NH$_3$Cl]$^{2+}$ in methanol.
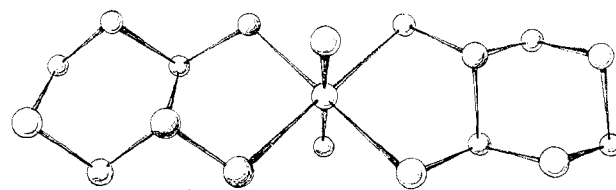

Figure 7.—Absolute configuration of the *trans*-[Co(*l*-chn)$_2$X$_2$]$^-$ ions. Hydrogen atoms are not shown. The puckering of the rings is responsible for the D$_2$ symmetry.

absolute configuration of the *l*-chn chelate was deduced[3] by a comparison of the ORD curves of [Co(en)$_3$]$^{3+}$ and [Co(*l*-chn)$_3$]$^{3+}$ and assuming the latter to have the preferred "lel" configuration. The same result is obtained by associating *l*-chn with *l*-pn, for which the absolute configuration is known by the X-ray determination of *trans*-[Co(*l*-pn)$_2$Cl$_2$]Cl·HCl·2H$_2$O.[10] This association is substantiated by analogies in the solubility of *d*-tartrate diastereoisomers and by comparison of ORD curves.

The rotational strength of an electronic transition results from the scalar product of the electric and magnetic dipole transition moments. In an optically inactive species this product is zero either because one or both of the transition moments are zero or because they are orthogonal to each other. The complexes under study are approximately symmetrical with only a slight perturbation causing the optical activity. As suggested by Moffitt,[11] in these cases an estimate of the rotational strength can be made by reverting to selection rules from the approximate, optically inactive point group. A transition must be magnetically allowed, electrically allowed, or both in this symmetry in order to have a large rotational strength when the slight perturbation induces activity. Selection rules have been obtained for the various complexes by ascending symmetry as indicated in Table II.

Ligand Field Transitions.—The spin-allowed transitions predicted by ligand field theory for these strong-field d^6 case complexes are listed in Table II. Magnetic selection rules indicate those transitions which will have large magnetic dipole transition moments. If D$_2$ or C$_2$ symmetry is considered, they all become slightly electric dipole allowed. Three transitions having strong rotational strengths are expected for D$_{4h}$ and C$_{4v}$; one is expected for O$_h$. The CD curves in the d–d region are in accord with these predictions (see Figures 1–3, 5, and 6). The assignments of Table I are thus made. For the halo complexes it has been assumed that the two ^1E_g states will have the same sign of rotation. These assignments are generally consistent with those based on energy level shifting in a tetragonal field[12a,b] and polarized crystal spectra.[12c,d]

In several cases the CD spectra show more d–d bands than predicted by the approximate symmetries.

(10) Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

(11) W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).

(12) (a) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958); (b) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709, 1524 (1965); (c) C. J. Ballhausen and W. Moffitt, *J. Inorg. Nucl. Chem.*, **3**, 178 (1956); (d) R. A. D. Wentworth, *Inorg. Chem.*, **5**, 496 (1966).

TABLE I
SPECTRAL DATA AND ASSIGNMENTS

Complex ion	Excited state	Absorption $\nu_{max}{}^a$	ϵ_{max}	D^b	Circular dichroism ν_{max}	$\Delta\epsilon_{max}$	R^c	ORD ν	R
trans-[Co(*l*-chn)$_2$F$_2$]$^+$	$E_g{}^a$ (D$_{4h}$)	17.3	27.3	4.56	17.1	+0.77	+2.66	17.1	+2.6
	A$_{2g}$	22.4	39.4	6.20	22.2	−0.21	−0.60		
	B$_{2g}$ }27.3		62.2	9.03					
	E$_g{}^b$				27.8	+0.22	+0.70		
	CT				43.5	+11	+40	44.8	+49
trans-[Co(*l*-chn)$_2$Cl$_2$]$^+$	$E_g{}^a$	16.3	39.2	5.70	16.4	+0.93	+3.08	16.4	+2.8
	A$_{2g}$	21.9	31.6	5.19	21.4	−0.10	−0.31		
	B$_{2g}$ }25.6		53.7	5.46	23.7	−0.05	−0.05		
	E$_g{}^b$				27.3	+0.21	+0.55		
	$\pi_u \rightarrow d_{z^2}$	32.4	1,530	200	30.5	+1.12	+2.4		
	$\pi_g \rightarrow d_{z^2}$				35.0	−3.9	−7.0		
	$\sigma_u \rightarrow d_{z^2}$	39.8	29,000	3700	40.0	+12	+40	40.2	+53
trans-[Co(*l*-chn)$_2$Br$_2$]$^+$	$E_g{}^a$	15.3	51.4	8.40	15.4	+0.94	+3.36		
	A$_{2g}$				20.4	−0.04	−0.11		
	B$_{2g}$				22.2	−0.02	−0.03		
	E$_g{}^b$				}25.0	+0.43	+0.64		
	$\pi_u \rightarrow d_{z^2}$	27.9	1,970	290					
	$\pi_g \rightarrow d_{z^2}$				30.8	−2.4	−7.1		
	$\sigma_u \rightarrow d_{z^2}$	34.4	18,800	2400	37.1	+9	+30	37.6	+30
trans-[Co(*l*-chn)$_2$(NO$_2$)$_2$]$^+$	A$_{2g}$ }22.8		193	30	21.5	−1.61	−5.0	21.7	−5.9
	E$_g{}^a$				24.4	+0.98	+4.0		
	E$_g{}^b$				29.6	+2.3	+5.6		
	B$_{2g}$ }31.1		4,100	570	33.8	−1.1	−2.0		
	CT	41.2	26,000	3400	41.7	+31	+80	41.7	+104
trans-[Co(*l*-chn)$_2$(NH$_3$)$_2$]$^{3+}$	T$_{1g}$ (O$_h$)	21.3	69.8	11.5	18.9	−0.07	−0.29		
					21.5	+0.67	+2.14	21.4	+1.77
					27.0	−0.02	−0.02		
	T$_{2g}$	29.7	69.4	10.3	30.1	+0.05	+0.10		
	CT	45.7	20,000	4100	43.8	+9	+50	44.5	+57
trans-[Co(*l*-chn)$_2$NH$_3$Cl]$^{2+}$	E^a (C$_{4v}$)	19.0	53.1	9.3	18.6	+0.79	+2.65	18.7	+2.6
	A$_2$	22.0	(sh)	3.2	22.0	−0.18	−0.63		
	B$_2$ }27.6		64.0	10.7					
	E^b				28.2	+0.24	+0.78		
	$\pi \rightarrow d_{z^2}$				34.7	−0.80	−1.7		
	$\sigma \rightarrow d_{z^2}$	44.0	21,000	4500	41.7	+10	+40	41.3	+30

^{a} Frequency in cm^{-1}, ×10^{-3}. ^{b} Dipole strength in cgs units, ×10^{38}. ^{c} Rotational strength in cgs units, ×10^{40}.

TABLE II
LIGAND FIELD TRANSITIONS AND MAGNETIC SELECTION RULES

Complex ion and point group	Approx symmetry	Spin-allowed transitions	Magnetic selection rule
trans-[Co(*l*-chn)$_2$X$_2$]$^+$ (D$_2$)	D$_{4h}$	^{1}A$_{1g} \rightarrow {}^1$E$_g{}^a$ (T$_{1g}$)	Allowed ⊥
		→ ^{1}A$_{2g}$ (T$_{1g}$)	Allowed ||
		→ ^{1}B$_{2g}$ (T$_{2g}$)	Forbidden
		→ ^{1}E$_g{}^b$ (T$_{2g}$)	Allowed ⊥
trans-[Co(*l*-chn)$_2$(NH$_3$)$_2$]$^{3+}$ (D$_2$)	O$_h$	^{1}A$_{1g} \rightarrow {}^1$T$_{1g}$	Allowed ||, ⊥
		→ ^{1}T$_{2g}$	Forbidden
trans-[Co(*l*-chn)$_2$NH$_3$Cl]$^{2+}$ (C$_2$)	C$_{4v}$	^{1}A$_1 \rightarrow {}^1$E^a (T$_{1g}$)	Allowed ⊥
		→ ^{1}A$_2$ (T$_{1g}$)	Allowed ||
		→ ^{1}B$_2$ (T$_{2g}$)	Forbidden
		→ ^{1}E^b (T$_{2g}$)	Allowed ⊥

A slight shoulder appears at about 23,000 cm^{-1} in *trans*-[Co(*l*-chn)$_2$Cl$_2$]$^+$ and *trans*-[Co(*l*-chn)$_2$Br$_2$]$^+$. It is assigned to the ^{1}A$_{1g} \rightarrow {}^1$B$_{2g}$ transition, which is forbidden even under D$_2$ symmetry. Spin–orbit coupling must be invoked to provide the rotational strength. In the dichloro complex all four ligand field transitions have now been found. Four CD bands also appear in *trans*-[Co(*l*-chn)$_2$(NO$_2$)$_2$]$^+$. They are in the energy ordering expected for the strong field NO$_2^-$ ligand.

However, the high ϵ and $\Delta\epsilon$ values indicate some charge-transfer character so that it is somewhat of an over-simplification to label them in Table II as d–d transitions. The CD spectrum of *trans*-[Co(*l*-chn)$_2$(NH$_3$)$_2$]$^{3+}$ shows slight activity in the ^{1}T$_{2g}$ region. This indicates the extent of deviation from O$_h$ symmetry in which this band is magnetic dipole forbidden. The splitting of the ^{1}T$_{1g}$ band has also been observed in *trans*-[Co-(*l*-pn)$_2$(NH$_3$)$_2$]$^{3+}$ and explained by resorting to D$_2$ symmetry.[5b]

With the detection of the individual components of the ^{1}T$_{2g}$ band of the dihalo complexes it is now possible to calculate the bonding parameters of Yamatera[12a] and Wentworth and Piper.[12b] In the molecular orbital model the halides are found to exert less σ-antibonding but more π-antibonding interaction on the metal d orbitals than does cyclohexanediamine. The $\delta\sigma$ parameters for F$^-$, Cl$^-$, and Br$^-$ are -7500, -8100, and $-11,100$ cm^{-1}, respectively. In all three cases $\delta\pi$ is about 1000 cm^{-1}. Alternately, the
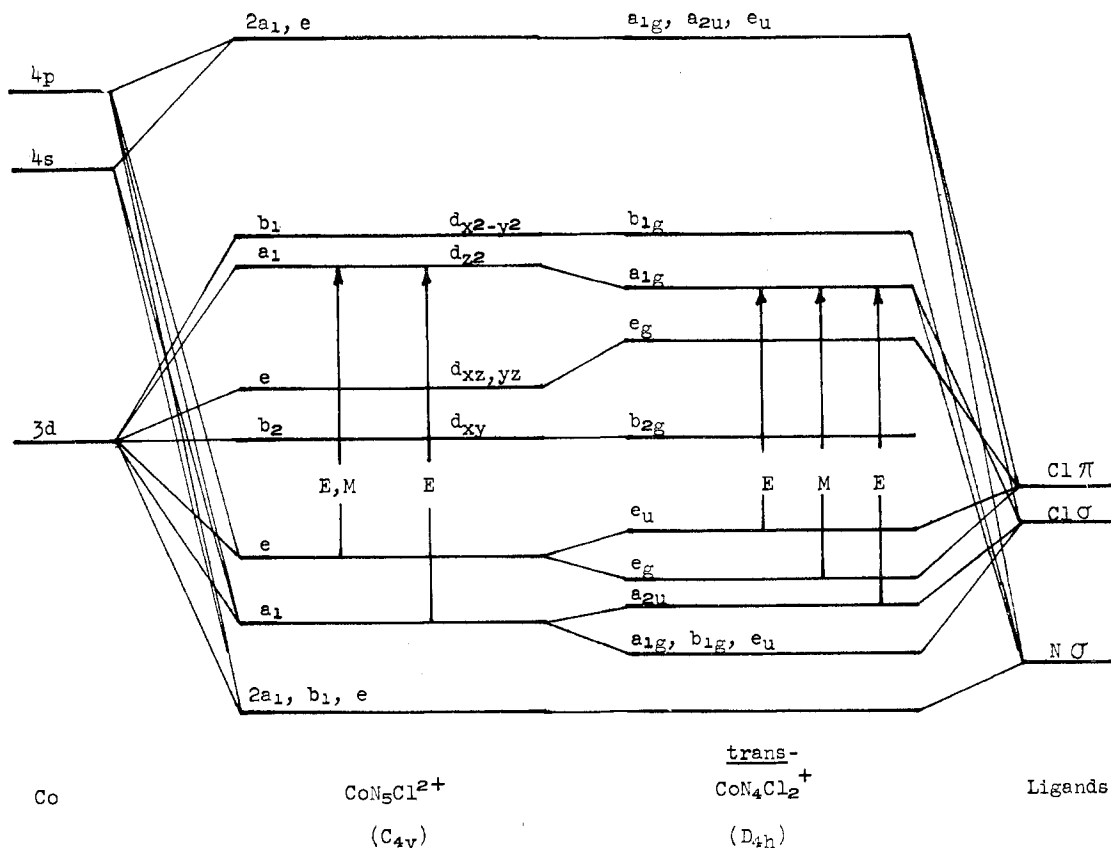
Figure 8.—Molecular orbitals and charge-transfer transitions for chloroamminecobalt(III) complexes. Only excitations of the type Cl → d_{z^2} are considered. Electrically and magnetically allowed transitions are labeled E and M, respectively.

crystal field approach may be taken. Ds and Dt for the difluoro, dichloro, and dibromo complex are 650, 490; 720, 570; and 1000, 690 cm^{-1}, respectively. These values give a relationship $Ds \approx 1.3Dt$. The ordering of d orbitals as determined by the empirical parameters is independent of the model and found to be $d_{xy} < d_{xz} = d_{yz} < d_{z^2} < d_{x^2-y^2}$.

Charge-Transfer Transitions.—Various assignments have been made of the two intense absorption bands generally found in haloamminecobalt(III) complexes.[13] Authors agree that the excited states result from the transfer of an electron of the halogen to an empty cobalt 3d orbital. The intensity calculations of Yamatera for [Co(NH$_3$)$_5$Cl]$^{2+}$ indicate that the acceptor orbital is the d_{z^2} on the metal. With this restriction Figure 8 shows the molecular orbitals and selection rules for the chloro and dichloro complexes. More complete MO energy level diagrams have been constructed by Nakamoto and co-workers.[14] An intense absorption band normally arises only from an electrically allowed transition. According to the principles stated earlier, a CD band may result from a transition labeled in Figure 8 as either electrically or magnetically allowed.

For *trans*-[Co(*l*-chn)$_2$NH$_3$Cl]$^{2+}$, considered again in C$_{4v}$ pseudo-symmetry, the two high-energy CD transitions are assigned to Clπ → d_{z^2} and Clσ → d_{z^2}

transitions. Both are expected to have intensity in the absorption spectrum. Probably the intense Cl σ → d_{z^2} obscures the Clπ → d_{z^2} band. This latter transition is seen[15] as a shoulder in *trans*-[Co(en)$_2$-NH$_3$Cl]$^+$ at about 36,000 cm^{-1}. These assignments are essentially those of Yamatera.[13] However, as with absorption spectra, CD does not detect his anticipated splitting of the first band into singlet and triplet states.

In the case of *trans*-[Co(*l*-chn)$_2$Cl$_2$]$^+$ the D$_{4h}$ MO diagram indicates three transitions having a rotational strength, two of which also have dipole strength. The CD bands are assigned Clπ_u → d_{z^2}, Clπ_g → d_{z^2}, and Clσ_u → d_{z^2}. The first and last of these correlate with the two absorption bands. For *trans*-[Co(*l*-chn)$_2$-Br$_2$]$^+$ three and two bands are found in the CD and absorption spectra, respectively. This close similarity to the dichloro complex dictates the same assignments. The dibromo bands are shifted to lower energies because Br$^-$ is less electronegative than Cl$^-$.

In the remainder of the complexes, the *trans* ligands are F$^-$, NH$_3$, and NO$_2^-$, which are more electronegative than Cl$^-$. All bands are shifted to above 40,000 cm^{-1}. At this high energy, additional types of charge transfer become possible; the assignments are simply listed as CT in Table I.

Rotational and Dipole Strengths.—The linear X–Co–X fragment in these complexes is in no way asymmetric. It is not unexpected that, to a first approxima-

(13) H. Yamatera, *J. Inorg. Nucl. Chem.*, **15**, 50 (1960).
(14) K. Nakamoto, J. Fujita, M. Kobayashi, and R. Tsuchida, *J. Chem. Phys.*, **27**, 439 (1957).
(15) A. V. Ablov and M. P. Filippov, *Zh. Neorgan. Khim.*, **2**, 42 (1957).

tion, the optical activity of the *trans*-[Co(*l*-chn)$_2$X$_2$]$^+$ ions is independent of X. However, a closer examination of the rotational strengths reveals some trends. In the series X$^-$ = F$^-$, Cl$^-$, and Br$^-$ for the transition $^1A_{1g} \rightarrow {}^1E_g{}^a$ there is an increase and for $^1A_{1g} \rightarrow {}^1A_{2g}$ a decrease in *R*. Of the theoretical treatments proposed to date, neither the crystal field[5a] nor the molecular orbital[4] model explicitly provides for the effect of the *trans* ligands. A more complete molecular orbital model mixing halogen and metal orbitals would be necessary.

While it is interesting that the trends noted above for the rotational strength are also found for the dipole strength, nothing more than a qualitative correlation exists. This is because the absorption band intensity results from odd vibrational states[5a, 12c, d] whereas the CD band involves even vibrations.[16]

(16) W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).

Complexes of Trivalent Lanthanide Ions. III. Bidentate Chelates[1]

BY GREGORY R. CHOPPIN AND H. GEORGE FRIEDMAN, JR.

The enthalpy and entropy of complexation are reported in an ionic strength of 2.00 *M* (NaClO$_4$) for lanthanide ions with glycolate, lactate, and α-hydroxyisobutyrate ligands. The complexes are found to be stabilized by both the enthalpy (exothermic) and the entropy (positive). Interpretations of these thermodynamic values are offered in terms of (a) the increasing basicity of the α-hydroxyl group and (b) the inclusion of a water molecule in the chelate ring between the metal ion and the α-hydroxyl group.

The two previous publications of this series[2,3] have reported the thermodynamic parameters for the formation of complexes of lanthanide ions with inorganic anions and with monodentate organic anions. In this paper, we report the extension of this study to bidentate anions. We also describe the calorimetric apparatus used both in this study and in the previous one.[3]

Experimental Section

Reagents.—A carbonate-free solution of NaOH was made up and standardized against potassium hydrogen phthalate, primary standard grade.

A stock solution of HClO$_4$ was diluted from the 9 *M* reagent grade solution obtained from G. F. Smith Co. and standardized by titration against the standard NaOH. The solution for the standard cell was prepared by diluting this stock solution. Anhydrous reagent grade NaClO$_4$ from G. F. Smith Co. was used to make the final ionic strength 2.00 *M*.

Stock solutions of lanthanide perchlorates were made and standardized as described previously.[4] Final solutions were made by diluting the stock solution to ~25 m*M*. If necessary, stock HClO$_4$ solution was added to maintain a maximum pH of ~3.5, which was considered necessary to prevent hydrolysis of the trivalent lanthanide ions. Solid NaClO$_4$ was used to make the final ionic strength 2.00 *M*.

Glycolate, lactate, and α-hydroxyisobutyrate buffer solutions were made and standardized as described previously.[4]

Quinhydrone of potentiometric quality was used as obtained from Fisher Scientific Co.

Calorimeter.[5]—The calorimeter used in these studies was similar to that described by Schlyter.[6] The calorimeter initially contained 50.00 ml of lanthanide perchlorate solution at 25.00°. Ligand solution at the same temperature was added from a thermostated buret. This arrangement requires far less work per experimental point than the conventional ampoule-breaking method, with only a slight decrease in accuracy.[6] The calorimeter was provided with a heater and a cooler for adjusting its internal temperature prior to adding an increment of titrant. The sensitivity of the calorimeter was approximately 10^{-4}°.

The calorimeter heater was a length of no. 32 nichrome wire wound into a spiral on a glass rod. Copper leads were silver-soldered to the ends of the nichrome wire, which was then given a thin coating of epoxy resin. The resistance of the wire was measured using a potentiometer with a constant current source and standard resistor (each accurate to ±0.01%).

The titrant solution was delivered by a buret system consisting of a fine buret tip, a 50-ml reservoir, and a piston buret. The reservoir was immersed in the water bath. Its purpose was to ensure that the titrant delivered was at the temperature of the water bath.[6]

The temperature was measured by a Sargent S-81620 thermistor, rated at 0–90°. The thermistor formed one arm of a Wheatstone bridge. The unbalance voltage of the bridge was amplified and used to indicate temperature change. The output of the linear amplifier was recorded on a strip-chart recorder.

The pH in the calorimeter was measured in one of two ways. In the earlier experiments, the calorimeter solution was saturated

(1) Abstracted from a Ph.D. dissertation by H. G. F., Florida State University, 1966.

(2) G. R. Choppin and W. F. Strazik, *Inorg. Chem.*, **4**, 1250 (1965).

(3) G. R. Choppin and A. J. Graffeo, *ibid.*, **4**, 1254 (1965).

(4) G. R. Choppin and J. A. Chopoorian, *J. Inorg. Nucl. Chem.*, **22**, 97 (1961).

(5) A detailed description of the calorimeter and its use may be found in the dissertation of H. G. F., which may be obtained from University Microfilms, Inc.

(6) K. Schlyter, *Trans. Roy. Inst. Technol., Stockholm*, **132**, 1 (1959).