numerical values for K_{eq} indicate that the free energy changes for the reactions are quite small (less than 1 kcal/mol). It has been observed that anion-exchange reactions of this type are a general characteristic of transition metal complexes in nonaqueous solvents.[22]

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Registry No. Co(py)$_2$(NO$_3$)$_2$, 55319-69-2; Co(py)$_2$(NO$_3$)Cl, 55319-70-5; Co(py)$_2$Cl$_2$, 14024-92-1; Co(py)$_2$Br$_2$, 14024-83-0; Co(py)$_2$I$_2$, 14025-00-4.

References and Notes

(1) G. L. McPherson, J. A. Weil, and J. K. Kinnaird, *Inorg. Chem.*, **10**, 1574 (1971).
(2) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).
(3) R. J. H. Clark and C. S. Williams, *J. Chem. Soc. A*, 1425 (1966).
(4) J. D. Dunitz, *Acta Crystallogr.*, **10**, 307 (1957).
(5) G. L. McPherson, H. S. Aldrich, and J. R. Chang, *J. Chem. Phys.*, **60**, 534 (1974).
(6) L. N. Mulay, *Treatise Anal. Chem.* **4**, 1777–1782 (1963).
(7) L. I. Katzin, J. R. Ferraro, and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5471 (1950).
(8) R. H. Nuttall, A. F. Cameron, and D. W. Taylor, *J. Chem. Soc. A*, 3103 (1971).
(9) D. W. Herlocker and M. R. Rosenthal, *Inorg. Chim. Acta*, **4**, 501 (1971).
(10) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963).
(11) A. B. P. Lever, *Inorg. Chem.*, **4**, 1042 (1965).
(12) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **75**, 2830 (1953).
(13) A. F. Cameron, J. McElhatton, and G. L. McPherson, to be submitted for publication.
(14) J. Drew, M. B. Hursthouse, P. Thornton, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 52 (1973).
(15) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965).
(16) A. Earnshaw, P. C. Hewlett, E. A. King, and L. F. Larkworthy, *J. Chem. Soc. A*, 241 (1968).
(17) P. L. Orioli, M. Di Vaira, and L. Sacconi, *Inorg. Chem.*, **5**, 400 (1966).
(18) B. Morosin and E. J. Graebner, *Acta Crystallogr.*, **16**, 1176 (1963).
(19) A. Narath, *Phys. Rev.*, **136**, 766 (1964).
(20) K. Takeda, S. Matsukawa, and T. Haseda, *J. Phys. Soc. Jpn.*, **30**, 1330 (1971).
(21) N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).
(22) L. I. Katzin, *Pure Appl. Chem.*, **20**, 53 (1969).

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A Novel Kind of Configurational Dissymmetry. Preparation, Resolution, and Circular Dichroism of *cis*-Bis(1(a)-methyl-2(a),4(a),6(a)-triaminocyclohexane)cobalt(III) Ion

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The ligand 1-methyl-2,4,6-triaminocyclohexane (Metach) has been prepared by a two-step catalytic reduction of 2,4,6-trinitrotoluene. The isomer isolated has all equatorial substituents on the cyclohexane ring. The bis cobalt(III) complex has been prepared and resolved with *d*-bromocamphorsulfonate. The visible–ultraviolet circular dichroism spectrum of the resolved ion has a single gaussian extremum of low magnitude. The enantiomer isolated is tentatively assigned the Λ absolute configuration on the basis of sector rule arguments.

Introduction

1-Methyl-2,4,6-triaminocyclohexane (Metach) has a total of eight stereoisomers (Figure 1). Two of these have cis,cis amino groups. The other six have cis,trans amines. The compound was prepared for the first time by Middleton[1] in 1938, starting from 2,4,6-triaminotoluene.[2] The method of reduction, which involved high-pressure hydrogenation with Raney nickel catalyst, apparently gave entirely a mixture of the cis,trans isomers. Middleton was in any case unable to prepare any bis metal ion complexes.

The two isomers (cis,cis and cis,trans) of the related, more symmetrical compound 1,3,5-triaminocyclohexane have since both been prepared,[3-6] and stable bis complexes of the cis,cis isomer have been made with several metal ions.[4,6,7] In these complexes the cis,cis amines move into a triaxial conformation and occupy the trigonal face of a coordination octahedron. A similar phenomenon would be expected in the formation of complexes of the cis,cis isomers of 1-methyl-2,4,6-triaminocyclohexane. The bis octahedral complex ion resulting from the coordination of two molecules of a single ligand isomer would itself have three isomers: optically inactive *trans*-M(*cis,cis*-Metach)$_2^{n+}$ and a pair of enantiomers, Δ- and Λ-*cis*-M(*cis,cis*-Metach)$_2^{n+}$ (these enantiomers are shown in Figures 2 and 3).

In this work, 1(e)-methyl-2(e),4(e),6(e)-triaminocyclohexane was prepared, separated, and characterized. Its bis cobalt(III) complex, in which the ligand is "flipped" to the all-axial conformation, was synthesized and the cis isomer of the complex was resolved.

The source of dissymmetry in this ion is remote from the cobalt(III) d → d chromophore. The ion is a novel example of pure configurational dissymmetry. Its circular dichroism (CD) spectrum is thus of some theoretical interest.

Experimental Section

Materials. Commercial 2,4,6-trinitrotoluene was purified by recrystallization from ethyl acetate. Rhodium chloride trihydrate was purchased from Alfa Inorganics and used as received. Ammonium *d*-bromocamphorsulfonate was obtained from Aldrich Chemical Co. and converted to the silver salt by metathetical reaction. Palladium on charcoal catalyst was purchased from Matheson Coleman and Bell. All other chemicals were commercial reagent grade or better.

2,4,6-Triacetaminotoluene. (The preparation of the ligand was based on the method used by Stetter, Theisen, and Steffens[5] to make the related *cis,cis*-1,3,5-triaminocyclohexane.) A 22.7-g amount (0.10 mole) of 2,4,6-trinitrotoluene was dissolved in 200 ml of ethyl acetate. A 60-ml amount of acetic anhydride was added. A 1.4-g sample of 10% palladium on charcoal catalyst was added and hydrogenation was carried out at room temperature and 4 psig pressure for 24 hr in a Paar low-pressure hydrogenation apparatus. The reaction was not complete in this time but longer reaction improved the yield little. The product precipitated during the reaction. It was filtered off and separated from the catalyst by dissolving it in hot 30% ethanol. Crude product precipitated upon cooling this solution. It was recrystallized from 50% methanol. The yield was 14.0 g or 53.2%; mp 296–298° (lit.[8] mp 283°).

***cis*-1(e)-Methyl-2(e),4(e),6(e)-triacetaminocyclohexane.** A 12.7-g quantity (1.05 mol) of the crude 2,4,6-triacetaminotoluene prepared above was suspended in 300 ml of glacial acetic acid. A 1.25-g sample of 7:3 rhodium–platinum catalyst, prepared according to the method of Nishimura,[9] was added, and the mixture was hydrogenated at 40 psig gauge pressure and room temperature for 48 hr. At the end of this time all of the suspended reactant had dissolved and the theoretical

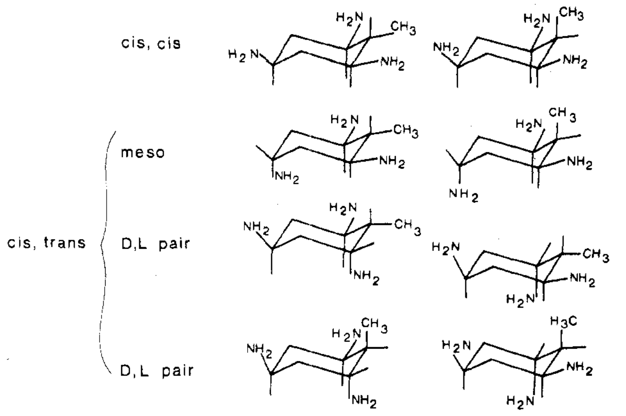

Figure 1. Possible isomers of 1-methyl-2,4,6-triaminocyclohexane.

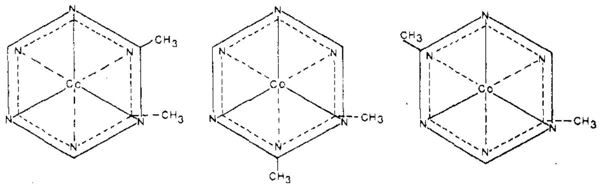

Figure 2. Representation along the pseudo-C_3 axis of the three isomers of Co(*cis,cis*-Metach)$_2^{3+}$ ion. From left to right: (a) Δ-cis; (b) Λ-cis; (c) trans.

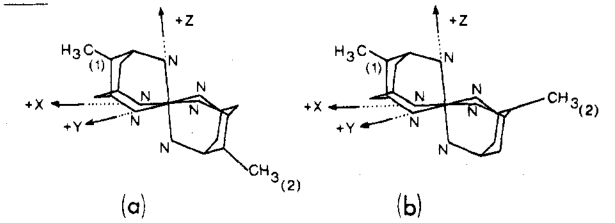

Figure 3. Enantiomeric cis isomers of Co(*cis,cis*-Metach)$_2^{3+}$ ion; H atoms are omitted; the methyl groups are numbered for reference; coordinate system is right handed: (a) Δ-cis; (b) Λ-cis.

quantity of hydrogen had been consumed. A 2.0-g sample of charcoal was added to the resulting solution and, after charcoal and catalyst were removed by filtration, the faintly blue filtrate was concentrated on a rotary evaporator. The resulting blue-green oil was treated with 100 ml of absolute ethanol on the steam bath for 1 hr. After cooling, the white precipitate was filtered and washed with several portions of ethanol. The yield of the alcohol-insoluble material, which proved to be a single cis,cis isomer, was 8.4 g or 65%; mp >360°. Anal. Calcd for $C_{13}H_{23}N_3O_3$: C, 57.97; H, 8.60; N, 15.60. Found: C, 57.24; H, 8.43; N, 15.26. When all of the alcohol washings were combined and evaporated to dryness, 4.5 g of a crude mixture of the cis,trans isomers was obtained. Hence, the total yield of reduced products was better than 95%.

1(e)-Methyl-2(e),4(e),6(e)-triaminocyclohexane Trihydrochloride. Five grams (0.019 mol) of the alcohol-insoluble 1-methyl-2,4,6-triacetaminocyclohexane was refluxed for 3 hr in 25 ml of concentrated HCl. White crystals separated upon cooling and were filtered off. A second crop was obtained upon evaporation in air and addition of ethanol. The product was recrystallized from ethanol–water. The yield was 4.5 g, 96%; mp >360°. Anal. Calcd for $C_7H_{20}N_3Cl_3$: C, 33.28; H, 7.98; N, 16.63. Found: C, 33.23; H, 8.10; N, 16.87. This same hydrolysis procedure was also used on the alcohol-soluble fraction of the 1-methyl-2,4,6-triacetaminocyclohexane.

Bis(1(a)-methyl-2(a),4(a),6(a)-triaminocyclohexane)cobalt(III) Chloride Tetrahydrate. A 0.252-g sample of the ligand was dissolved in 10 ml of water. To this solution was added 0.181 g of freshly prepared $Na_3Co(CO_3)_3·3H_2O$.[10] The solution was warmed gently on the steam bath. Evolution of CO_2 accompanied formation of a red solution which gradually became more orange. After 1 hr the reaction mixture was cooled and thin orange hexagonal plates separated. The product was recrystallized from water. The yield was 0.15 g, 57%. (See next section for the analysis.)

Resolution of Complex Ion. A 0.466-g sample of the Co(Metach)$_2$Cl$_3$·4H$_2$O was dissolved in 30 ml of water. The equivalent amount of silver *d*-bromocamphorsulfonate, 1.115 g, was placed in 30 ml of water. The two solutions were warmed gently on the steam bath and then mixed. After standing of the mixture for 1 hr on the steam bath, the precipitated AgCl was filtered off, washed thoroughly with warm water, and discarded. The filtrate was evaporated to a small volume and allowed to stand. The first crop of about 0.4 g of crystals was filtered and washed with a small portion of cold water. Typically, two to four recrystallizations by slow evaporation brought the specific ellipticity of this material, measured at 490 nm, to a constant value of −8.7. In some instances additional recrystallizations were however needed. The *d*-bromocamphorsulfonate salt was reconverted to the chloride salt by passing a dilute aqueous solution slowly down a 1 × 40 cm column loaded with Dowex 2X-8 anion-exchange resin in the chloride form. The resulting solution was concentrated and showed no CD band at 310 nm (the *d*-bromocamphorsulfonate CD maximum). Further evaporation gave crystals of (−)$_{589}$-*cis*-Co(Metach)$_2$Cl$_3$·4H$_2$O. Anal. Cald for $CoC_{14}H_{34}N_6Cl_3·4H_2O$: C, 32.10; H, 8.08; N, 16.04. Found: C, 31.87; H, 8.18; N, 16.20.

Physical Measurements. Electronic absorption spectra were recorded at room temperature on a Unicam SP800 spectrophotometer. Circular dichroism and optical rotatory dispersion spectra were recorded at room temperature using a Jasco ORD/CD-5 instrument with the SS-21 modification. Proton magnetic resonance spectra were taken at ambient temperature using a Varian A-60A spectrometer.

Analyses. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and by Micro-Tech. Laboratories Inc., Skokie, Ill.

Discussion

Conformation and Geometry of the Ligand. 1-Methyl-2,4,6-triaminocyclohexane has eight isomers (Figure 1). Both of the cis,cis isomers can be expected to be conformationally biased, with the three amines equatorial. The difference between the two cis,cis isomers is thus the situation of the methyl group, axial or equatorial. The isomer isolated in the method of preparation and separation used here proves to be the 1(e)-methyl-2(e),4(e),6(e)-triaminocyclohexane. Only this geometrical isomer was used for preparation of the cobalt(III) complex. Its separation and characterization are discussed as follows.

The second step in the preparation of the ligand is a catalytic reduction carried out in acetic anhydride. It gives the triamide 1-methyl-2,4,6-triacetaminocyclohexane. This precursor, like the ligand itself, has eight possible isomers, two with cis,cis acetamino groups and six with cis,trans acetamino groups. The precursor is readily separated into two fractions by treatment with absolute ethanol. This behavior is analogous to that found for the similar instance of 1,3,5-triacetaminocyclohexane[5] where the insoluble fraction turned out to be the cis,cis isomer. Hydrolysis in this case of the alcohol-insoluble fraction in concentrated HCl leads to the isolation of a 1-methyl-2,4,6-triaminocyclohexane as the trihydrochloride. This material forms the bis cobalt(III) complex under mild conditions and therefore contains the cis,cis geometry. The proton magnetic resonance spectrum of this ligand is given in Figure 4. It has three sets of features: a doublet centered at δ 1.25 ppm, a complex group of peaks centered at δ 2.40 ppm, and an approximate triplet of triplets centered at δ 3.76 ppm. Integrated intensities of the groups are in the ratio of 3:5:3. On this basis, and on the basis of the chemical shifts, the doublet has been assigned to the methyl group. The set of peaks centered at 2.40 ppm has been assigned to the four methylene hydrogens and to the single hydrogen α to the methyl group. The group at δ 3.76 ppm has been assigned to the resonance of the three hydrogens α to the amines.

This spectrum is similar in general features to but less complex than that observed when the alcohol-soluble fraction of the precursor is converted to the triamine–trihydrochloride and the PMR is studied in D_2O solution. The latter PMR spectrum, undoubtedly of a mixture of isomers, includes, for

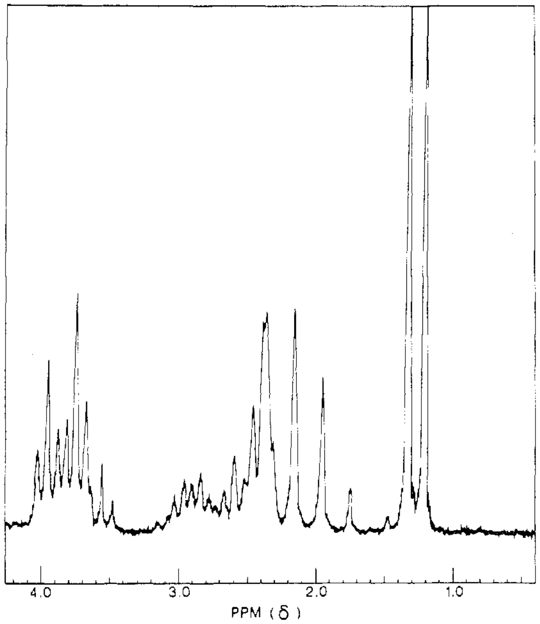

Figure 4. PMR spectrum of 1(e)-methyl-2(e),4(e),6(e)-triaminocyclohexane trihydrochloride in D_2O, vs. TMS external standard.

example, many more peaks in the region centered at δ 2.40, as well as set of six peaks in the methyl region, extending from 1.25 to 1.50 ppm. The comparatively simpler spectrum in Figure 4 tends to confirm that the ligand isolated from the alcohol-insoluble precursor is of a more symmetrical structure, i.e. cis,cis. In particular, the observation of a single kind of methyl resonance in the ligand from the alcohol-insoluble precursor argues strongly that only a single kind of methyl is present. This follows because in other, similar systems (*cis,cis*- and *cis,trans*-1,3,5-trimethylcyclohexane[11]) axial and equatorial methyl groups have distinctly different chemical shifts, with those equatorial resonating at higher field than those axial. Isomers of both the cis,cis and the cis,trans families, which can have their methyl groups in just such varying environments (Figure 1), could, if any significant mixture were present, therefore reasonably be expected to display more than a single methyl doublet resonance. Since several methyl resonances at varying chemical shifts are indeed observed in the triamine–trihydrochloride from the alcohol-soluble precursor (the spectrum described above), the chemical environments of axial and equatorial methyl groups in the isomers of Metach are confirmed to be sufficiently different to cause observable variation in chemical shift. This means that the ligand isolated from the alcohol-insoluble precursor has only one kind of methyl group, and, since the additional methyl peaks are all downfield of δ 1.25 ppm, it is concluded that the δ 1.25 ppm doublet in Figure 4 is due to an equatorial methyl. The latter conclusion of course assumes that an equatorial methyl group will continue to resonate at higher field than an axial even in the presence of vicinal amines.

Although naturally more complicated, the spectrum in Figure 4 is similar in its principal features to that reported for *cis,cis*-tach·3HCl in D_2O.[6] A detailed comparison of the differences between these spectra completes the characterization of the Metach ligand. In *cis,cis*-tach·3HCl, the hydrogens α to the amines give a triplet of triplets centered at δ 4.11 ppm. Substitution of the methyl group shifts this feature upfield—in *cis,cis*-Metach·3HCl, it is centered at δ 3.76 (and distorted by second-order effects). Since the amines are equatorial, their α hydrogens are axial. Substitution of an equatorial methyl has been found to shield vicinal axial hydrogens whereas substitution of an axial methyl has been found to deshield vicinal axial hydrogens.[12] The conclusion is that the methyl group is equatorial in this case.

Another comparison is possible. The equatorial methylene hydrogens in *cis,cis*-tach·3HCl are reported[6] as a doublet of triplets centered at 3.13 ppm. The axial methylene hydrogens are assigned to a quartet centered at 2.23 ppm. The PMR spectrum of *cis,cis*-Metach·3HCl in the region of these resonances retains at least a vague similarity to that of *cis,cis*-tach at the upfield, or axial, end, but it is very much reduced in integrated intensity and more complicated at the downfield, equatorial end. This again suggests that the methyl group has replaced an equatorial hydrogen.

Since the methyl is equatorial and the three amines are cis,cis equatorial, the conformation of the ligand is fully established.

Stereochemistry of the Complex Ion. When it coordinates as a tridentate ligand with cobalt(III), 1(e)-methyl-2(e),4(e),6(e)-triaminocyclohexane forms a cage consisting of three six-membered chelate rings and the cyclohexane ring. Two such cages related by a C_2 symmetry axis passing through the common cobalt(III) comprise the complex ion $Co(Metach)_2^{3+}$. Coordination forces each ligand's three amines into axial positions. The ligands' methyl groups therefore become axial in the complex also. The complex occurs in three isomers. The three, Δ-cis, Λ-cis, and trans, can be regarded as generated at 120° intervals by an imaginary twist of one coordinated ligand relative to the other about the axis passing through the two ligand-occupied triangular faces of the cobalt(III) coordination octahedron. When viewed along this pseudo-C_3 axis, the two enantiomeric cis isomers present chiralities that are, naturally, of equal magnitude but opposite sense. An imaginary line joining the two ligands' axial methyl groups is skewed relative to the pseudo-C_3 axis. Bond vector calculations based on the rigidity and symmetry of the ligand–cobalt(III) cage and using a range of commonly found bond distances and angles put the skew angle between 2.2 and 3.5°. The sense of the chirality thus presented along the pseudo-C_3 axis is right handed in Figure 2a and left handed in Figure 2b. Consistent with the basic principle of current nomenclatural proposals,[13] these are designated Δ and Λ, respectively. The remaining possible isomer, the *trans*-$Co(Metach)_2^{3+}$, belongs to the C_{2h} point group and is of course optically inactive. The enantiomeric cis isomers have C_2 symmetry. In all of its isomers, the stereochemistry of this complex ion is very closely related to that of the $Co(tach)_2^{3+}$ ion, the only difference being the presence of the methyl groups on the ligand's backbone. $Co(tach)_2^{3+}$ has been synthesized and characterized completely.[6]

The relative position of the methyl groups is the only source of dissymmetry in this complex ion. There is no possibility of conformational isomerism; the chelate rings are locked in a rigid cage. There are no asymmetric centers either occupying nonligating positions or serving as donors. With no conformational or vicinal effects present, this complex constitutes a case of pure configurational dissymmetry. The stereochemical situation is thus seen to be in this complex actually simpler than that in commonly encountered complex ions and approaches the kind of idealized system with a single source of dissymmetric perturbation that has been posited in theoretical discussions of rotational strength. Such simplicity is found whether the ligand methyl groups in the complex are both axial or both equatorial—as long as both are the same.

Finally, the geometry of the complex ion is certainly somewhat distorted from that of a perfect octahedron. However, the two components of distortion, ϕ, the twist angle, and s/h (the side:height ratio),[14] are independent of each other in this case insofar as simple geometrical considerations are concerned.

Circular Dichroism of the Complex Ion. The circular dichroism spectrum (Figure 5) of the $(-)_{589}$-*cis*-$Co(Metach)_2^{3+}$

Table I. Circular Dichroism and Visible-Ultraviolet Absorption Spectra of $(-)_{589}$-Co(Metach)$_2$Cl$_3$[a] Compared to Spectra of Co(tach)$_2$Cl$_3$[a] and $(+)_{589}$-[Co(en)$_3$]Cl$_3$[b]

	Co(tach)$_2$Cl$_3$	$(-)_{589}$-*cis*-Co(Metach)$_2$Cl$_3$		$(+)_{589}$-[Co(en)$_3$]Cl$_3$	
	Vis-uv[a,b]	Vis-uv[c,d]	CD[e]	Vis-uv[c,d]	CD[e]
$^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h)	20.90 (75)	20.87 (77)	20.41 (−0.017)	21.28 (84)	20.28 (+1.89)
$^1A_{1g} \rightarrow {}^1T_{2g}$ (O_h)	29.20 (75)	28.95 (74)	None obsd	29.41 (74)	28.49 (+25)
Charge transfer	41.70 (17,900)	40.65 (16,800)			
	~46.00 sh (11,000)	~45.90 sh (10,500)			

[a] tach is 1,3,5-triaminocyclohexane; Metach is 1-methyl-2,4,6-triaminocyclohexane. [b] en is ethylenediamine. [c] Band positions are in kK. Values in parentheses refer to molar absorption coefficients ϵ. [d] Reference 6. [e] Values in parentheses refer to $\epsilon_l - \epsilon_r$.

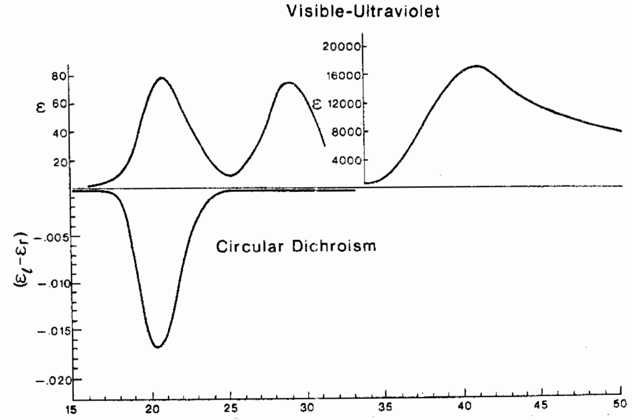

Figure 5. Circular dichroism and electronic absorption spectra of $(-)_{589}$-*cis*-Co(*cis,cis*-Metach)$_2$Cl$_3$ in water. Abscissa gives frequencies in kK.

ion in solution is of quite low magnitude and great simplicity. It consists, in the visible and near-ultraviolet regions, of a single gaussian appearing, negative band centered at 20.41 kK. The symmetrical shape of the CD band suggests that it is the result of a single CD-active electronic transition and not a case of two overlapping bands. The optical rotatory dispersion spectrum is also symmetrically shaped. It shows a single negative Cotton effect, its positive and negative limbs having equal magnitude, centered at 20.37 kK. This latter observation strengthens the conclusion that the observed rotational strength is from a single well-isolated optically active transition. Any rotational strength nearby in the spectrum would certainly be expected to distort the observed symmetrical ORD curve. In ORD, observed rotations are nonzero even at energies remote from the transition energy.[15] Solution CD spectra of the [CoN$_6$] chromophore in dissymmetric environments usually consist in this long-wavelength region of two bands of opposite sign; this case is not typical.

In addition, no rotational strength was observed in the region of the 26.5-kK electronic absorption maximum in this complex ion. The rotational strength of the observed CD band, calculated on the assumption that it is indeed gaussian, is -0.0064×10^{-40} cgsu. This is about 2 orders of magnitude less than the rotational strength in the same part of the spectrum of many other optically active complex ions in solution.

The electronic absorption spectrum (Figure 5) of $(-)_{589}$-*cis*-Co(Metach)$_2^{3+}$ ion in solution is virtually superimposable, especially in the ligand field bands, upon that of the related ion Co(tach)$_2^{3+}$. (Table I is a comparison of the CD and electronic absorption spectra of $(-)_{589}$-*cis*-Co(Metach)$_2^{3+}$ ion with spectra of related ions.) This observation confirms the assignment of the structure of the new cobalt complex. In addition it supports the idea that the *cis*-Co(Metach)$_2^{3+}$ ion, which has C_2 symmetry, is nearly of D_{3d} symmetry. In other words, the [CoN$_6$] chromophore in *cis*-Co(Metach)$_2^{3+}$ is electronically virtually the same as it is in Co(tach)$_2^{3+}$ except for the addition, via the ligand methyl groups, of a small dissymmetric perturbation.

The simplicity of the observed spectrum and the straightforward nature of the dissymmetric influence suggest an easy interpretation of the CD spectrum. According to McCaffery, Mason, and Ballard,[16] the rotatory power of a d–d transition has the same sign as the helicity presented when the complex is viewed along the polarization direction of the transition. In this complex, the pseudo-C_3 axis and the skew line between the methyl groups of the ligands together define a helix (right handed in Figure 2a, left handed in Figure 2b). Therefore, an electronic transition polarized parallel to the pseudo-C_3 axis will have positive rotational strength if the absolute configuration is that of Figure 2a and negative rotational strength if the absolute configuration is that of Figure 2b.

The $^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) electronic transition in the [CoN$_6$] chromophore is split into $^1A_{1g} \rightarrow {}^1A_{2g} + {}^1E_g$ in D_{3d} symmetry. We regard the complex as having "nearly" D_{3d} symmetry, that is, D_{3d} symmetry with a slight dissymmetric perturbation. The transition $^1A_{1g} \rightarrow {}^1A_{2g}$ is polarized parallel to the C_3 axis and thus would have positive rotational strength for the Figure 2a enantiomer. In contrast, $^1A_{1g} \rightarrow {}^1E_g$ is polarized perpendicular to the C_3 axis. The complex presents no helicity along its C_2 axis (Figure 3). Therefore, rotational strength is not predicted for this transition. None is observed. The conclusion is that $(-)_{589}$-*cis*-Co(Metach)$_2^{3+}$ ion is the Λ enantiomer (shown in Figure 2b). Moreover, this conclusion would be the same whether the ligand methyl groups were both axial or both equatorial. The same approach also explains the absence of rotational strength in the other ligand field band, the $^1A_{1g} \rightarrow {}^1T_{2g}$ (O_h). The $^1T_{2g}$ term is split in D_{3d} symmetry into $^1A_{1g} \rightarrow {}^1A_{1g} + {}^1E_g$. The $^1A_{1g} \rightarrow {}^1A_{1g}$ transition is forbidden; the $^1A_{1g} \rightarrow {}^1E_g$ transition is inactive on the basis of the polarization direction argument just given and is predicted to be small in any case since the transition must borrow both electric and magnetic dipole strength. Thus the observed absence of rotational strength in the $^1A_{1g} \rightarrow {}^1T_{2g}$ (O_h) band is rationalized.

Because the CD band occurs at lower frequency than the electronic absorption maximum of the resolved complex (20.41 vs. 20.87 kK), the above assignment of the observed CD band to the $^1A_1 \rightarrow {}^1A_2$ transition implies that the $^1A_2$ term is lower in energy than the ^1E. It seem unlikely that any possible contamination by the *trans*-Co(Metach)$_2^{3+}$ ion would cause a detectable shift in the electric absorption maximum of the resolved *cis*-Co(Metach)$_2^{3+}$ ion since the presence of the methyl groups themselves causes no shift when the spectra of Co(tach)$_2^{3+}$ and *cis*-Co(Metach)$_2^{3+}$ are compared. The direction of the shift implies that the complex is distorted by an elongation along the C_3 axis, that is, that $s/h > 1.22$. The magnitude of the splitting between A$_2$ and E cannot be estimated from available data.

Of all of the sector rules that attempt to correlate the absolute configuration of octahedral complexes with rotatory power, those of Richardson[18] seem most apt for the case of $(-)_{589}$-*cis*-Co(Metach)$_2^{3+}$ ion. Richardson derived rules for determining the net rotatory strength of the triply degenerate cubic $^1A_{1g} \rightarrow T_{1g}$ electronic transition. His model considered to second order the dissymmetric perturbation caused by ligand

Table II. Positional Functions of Perturbing Methyls in Δ-*cis*-Co(*cis,cis*-Metach)$_2^{3+}$ Ion

Function	$CH_3(1)$	$CH_3(2)$
XY	+6.6	+6.6
$X(X^2 - Y^2)$	−9.4	−9.4
XZ	+6.6	+8.4
$X(Z^2 - X^2)$	+9.4	0
YZ	+8.4	+6.6
$X(Y^2 - Z^2)$	0	+9.4

groups outside of the octahedral [ML_6] chromophore. This is exactly the case that *cis*-Co(Metach)$_2^{3+}$ ion represents; the ion has a plane of symmetry except for the skew position of the methyl groups.

Convenient use of Richardson's sector rules requires approximate values for the cartesian positional coordinates of the perturber sites. The estimated coordinates[19] of $CH_3(1)$ on the right-coordinate system defined in Figure 3 are (2.27, 2.90, 2.90). $CH_3(2)$ has coordinates (−2.90, −2.27, −2.90), for the Δ isomer. The signs and approximate magnitudes of the various necessary positional functions are given in Table II.

The sign of the sum of the applicable pair combinations (XY with $Z(X^2 - Y^2)$, XZ with $Y(Z^2 - X^2)$, and YZ with $X(Y^2 - Z^2)$) is positive. This predicts positive net rotatory power in the $^1A_{1g} \rightarrow {}^1T_{1g}$ region for the Δ enantiomer's CD spectrum and, of course, implies that the enantiomer isolated in this study is the Λ-*cis*-Co(*cis,cis*-Metach)$_2^{3+}$ ion.

Along another line, Hawkins'[20,21] octant rule is not really intended for a case of this type and naturally gives a zero octant sign for the sum of the contributions of all atoms except the two methyl groups. However, considering the methyl groups, the octant sign for the Δ enantiomer is negative and the octant sign for the Λ enantiomer is positive. This again predicts positive rotational strength for the Δ enantiomer and negative rotational strength for the Λ enantiomer in the $A_1 \rightarrow A_2$ transition.

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Registry No. 2,4,6-Trinitrotoluene, 118-96-7; 2,4,6-triacetaminotoluene, 55470-90-1; *cis*-1(e)-methyl-2(e),4(e),6(e)-triacetaminocyclohexane, 55470-91-2; *cis*-1(e)-methyl-2(e),4(e),6(e)-triaminocyclohexane trichloride, 55470-92-3; bis(1(a)-methyl-2(a),4-(a),6(a)-triaminocyclohexane)cobalt(III) chloride, 55493-48-6; $(-)_{589}$-*cis*-Co(Metach)$_2Cl_3$, 55528-70-6.

References and Notes

(1) E. B. Middleton, Ph.D. Thesis, University of Illinois at Urbana, 1938.
(2) Fr. Hein and Fr. Wagner, *Ber. Dtsch. Chem. Ges. B*, **68**, 856 (1935).
(3) O. Hassel and K. Lunde, *Research (London)*, **3**, 484 (1950).
(4) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **79**, 1572 (1957).
(5) H. Stetter, D. Theisen, and G. J. Steffens, *Chem. Ber.*, **103** 200 (1970).
(6) R. A. D. Wentworth and J. J. Felten, *J. Am. Chem. Soc.*, **90**, 621 (1968).
(7) R. A. D. Wentworth, *Inorg. Chem.*, **7**, 1030 (1968).
(8) A. McLean, W. Tetlow, and J. Munro, British Patent 589,716; *Chem. Abstr.*, **42**, 217*g*, *h* (1948).
(9) S. Nishimura, *Bull. Chem. Soc. Jpn.*, **34**, 1544 (1961).
(10) H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).
(11) A. Segne and J. I. Musher, *J. Am. Chem. Soc.*, **89**, 709 (1967).
(12) H. Booth, *Prog. Nucl. Magn. Reson. Spectrosc.*, **5**, 242 (1969).
(13) *Inorg. Chem.*, **9**, 1 (1970).
(14) E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, **11**, 434 (1972).
(15) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley-Interscience, New York, N.Y., 1971, p 222.
(16) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).
(17) R. R. Judkins and D. J. Royer, *Inorg. Chem.*, **13**, 945 (1974).
(18) F. S. Richardson, *Inorg. Chem.*, **11**, 2366 (1972).
(19) These coordinates are estimated by bond vector calculations using the following typical values of bond distances and angles: Co–N, 1.95 Å; C–N, 1.47 Å; C–C, 1.54 Å; N–Co–N, 90.0°; Co–N–C, 109.5°; N–C–N, 109.5°; C–C–C, 109.5°.
(20) C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 185 (1965).
(21) C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 1969 (1965).

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Kinetic Isotope Effects in Reductions of Cobalt(III)–Pentaammine Complexes

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Deuterium isotope effects arising in the rates of reduction of $Co^{III}(NH_3)_5L$ complexes have been studied. Only the ammine ligands of the cobalt(III) were deuterated. Ratios of k_H/k_D have been determined for L = OH^-, CN^-, SCN^-, N_3^-, pyridine, nicotinamide, isonicotinamide, 4-pyridinecarboxylic acid, acetate ion, and fumarate ion. Reductions by Cr^{2+} and V^{2+} have been included. Ratios of k_H/k_D near unity are consistent with a chemical mechanism for the Cr^{2+} reductions of the isonicotinamide, 4-pyridinecarboxylic acid, and fumarate complexes. Ratios of k_H/k_D near unity are consistent with substitution-limited reductions for V^{2+} reductions of the azido and isonicotinamide complexes.

Comparisons of the rate of reduction of a pentaamminecobalt(III) complex and the corresponding ammine-deuterated pentaamminecobalt(III) complex are made in this study. Cr^{2+} and V^{2+} are used as reducing agents. It was expected that the k_H/k_D ($k_{Co^{III}(NH_3)_5X}/k_{Co^{III}(ND_3)_5X}$) ratios would be valuable criteria in distinguishing certain types of mechanisms. The mechanisms of several of the present systems were known from previous studies. The results of these can be used to calibrate the k_H/k_D ratios.

It is a well-known consequence of the Franck–Condon principle that the inner coordination shells of both metal centers must undergo a reorganization prior to electron transfer, such that the energy of the system is unchanged in the actual electron-transfer step. For most electron-transfer reactions this adjustment of bond lengths about the metal centers and the accompanying polarization of solvent molecules is the rate-determining process.[2] In such cases, an isotopic change in the inner coordination shell of either reactant would change the energy requirements of activation and thereby give rise to a kinetic isotope effect. Such an isotope effect has been observed in nitrogen[3] and oxygen[4] isotopic fractionation experiments, which make use of the natural isotopic abundances of either nitrogen or oxygen. A comparison of the reduction rates of the ammine-deuterated and undeuterated pentaamminecobalt(III) complexes is a convenient technique because the deuterated complexes are readily prepared from their corresponding undeuterated complexes. A k_H/k_D ratio is expected to be greater than one when reorganization about cobalt(III) is part of the activation process.

Zwickel and Taube[5] have previously examined this k_H/k_D