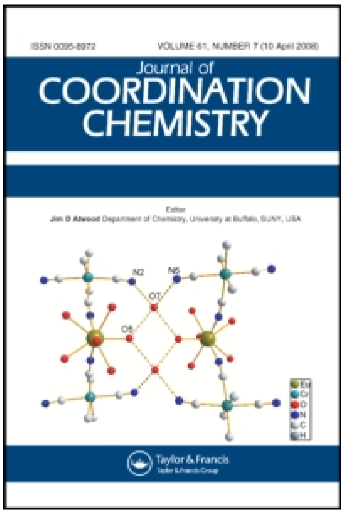

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Jordan, William T. , Lin, Ching-Yü and Douglas, Bodie E.(1973) 'CIRCULAR DICHROISM OF SOME COBALT(III) COMPLEXES WITH 2,2'-DIAMINOBIPHENYL AND R-6,6'-DIMETHYL-2,2'-DIAMINOBIPHENYL', Journal of Coordination Chemistry, 3: 1, 1 — 6
To link to this Article: DOI: 10.1080/00958977308073781
URL: http://dx.doi.org/10.1080/00958977308073781

J. Coord. Chem., 1973, Vol. 3, pp. 1–6

Printed in Woking, England

CIRCULAR DICHROISM OF SOME COBALT(III) COMPLEXES WITH 2,2′-DIAMINOBIPHENYL AND R-6,6′-DIMETHYL-2,2′-DIAMINOBIPHENYL[1]

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(*Received August* 11, 1972; *in final form October* 26, 1972)

The complexes $[Co(en)_2(dabp)]^{3+}$ and α-$[Co(trien)(dabp)]^{3+}$ have been resolved. The β-trien complex was not sufficiently stable to permit resolution. Of the four possible stereoisomers of each complex, only two were isolated. The stereospecificity of these reactions was confirmed since R-dmdabp combined with *cis*-$[Co(en)_2Cl_2]^+$ to form just one of the two possible configurational isomers. The CD spectra were examined to investigate the effect of ligand conformation on the rotatory strengths and to relate the absolute configurations to those of other tris-(diamine)cobalt(III) complexes.

INTRODUCTION

One of the more elusive problems in the study of the rotary power of transition metal complexes is the evaluation of the magnitude of conformational effects due to chelate ring puckering. In order to minimize strain, a five-membered ethylenediamine (en) ring, for example, adopts a dissymmetric conformation, δ or λ.[2,3] In solution at room temperature there is rapid interchange between the δ and λ conformations. However, if an alkyl group is substituted for a methylene proton of the en backbone, the conformation of the ligand with the alkyl group in an equatorial position is stabilized relative to that in which this group is axial. The resulting conformational contribution to the rotatory strength is difficult to evaluate because it is accompanied by a vicinal effect due to the presence of an asymmetric carbon atom. The two contributions occur together for most ligands and are difficult to separate.

2,2′-Diaminobiphenyl (dabp) and its derivatives are exceptional in this respect. The conformation of the ligand becomes fixed on complexation, *without* the presence of a dissymmetric center, because intraligand steric interactions and chelate ring strain are minimized if the benzene rings are twisted from coplanarity. In a metal complex incorporating dabp, therefore, the only rotatory strength contributed by the individual dabp chelate ring is due to the ligand conformation.

The resolution of $[Co(en)_2(dabp)]^{3+}$ together with the ORD spectra were reported by McCullough and Bailar.[4] In the present investigation, the CD data for this complex as well as α-$[Co(trien)(dabp)]^{3+}$ and (−)-$[Co(en)_2(R\text{-}dmdabp)]^{3+}$ were obtained. The latter complex was prepared in order to correlate the circular dichroism of the complex with the known absolute configuration[5] of the ligand and to study stereospecificity in the formation of the complex.

EXPERIMENTAL SECTION

Preparation of 2,2′-Diaminobiphenyl, dabp.

Synthesis was achieved by reduction of 2,2′-dinitrobiphenyl with hydrazine in the presence of Rainey Nickel as described previously.[6]

Preparation and Resolution of 2,2′-Diaminobiphenylbis-(ethylenediamine)cobalt(III) Chloride, $[Co(en)_2(dabp)]Cl_3$.

The complex was prepared by the method of Middleton[4,7] from *trans*-$[Co(en)_2Cl_2]^+$. Resolution was accomplished by the method of Cooley[4,8] using silver *d*-tartrate. *Anal.* Calcd. for $[Co(C_{16}H_{28}N_6)]Cl_3$: C, 40.92; H, 6.01; N, 17.89; Cl, 22.65. Found: C, 40.76; H, 6.11; N, 17.72; Cl, 22.51.

Preparation and Resolution of α-2,2′-Diaminobiphenyl-(triethylenetetraamine)cobalt(III) Chloride Dihydrate, α-[Co(trien)-(dabp)]Cl$_3$·2H$_2$O.

The complex was prepared from α-[Co(trien)Cl$_2$]Cl by a method similar to that of Middleton[4,7] for [Co(en)$_2$(dabp)]Cl$_3$ and resolved with silver *d*-tartrate by a method similar to that of Cooley[4,8] for [Co(en)$_2$(dabp)]$^{3+}$. *Anal.* Calcd. for [Co(C$_{18}$H$_{30}$N$_6$)]Cl$_3$·2H$_2$O: C, 40.66; H, 6.44; N, 15.80; Cl, 20.00. Found: C, 40.03, 40.23; H, 6.46, 6.25; N, 15.67; Cl, 19.74.

Preparation of β-2,2′-Diaminobiphenyl(triethylenetetraamine)-cobalt(III) Chloride, β-Co(trien)(dabp)]-Cl$_3$.

The β-complex was prepared in the same way as the α-isomer only using β-[Co(trien)Cl$_2$]$^+$. The product solution contained the α-isomer as well. Separation was achieved by fractional crystallization. *Anal.* Calcd. for [Co(C$_{18}$H$_{30}$N$_6$)]Cl$_3$: C, 43.47; H, 6.08; N, 16.88; Cl, 21.37. Found: C, 43.38; H, 6.30; N, 16.75; Cl, 21.63.

Preparation and Resolution of 6,6′-Dimethyl-2,2′-diaminobiphenyl, dmdabp.

The starting material, 3-nitro-2-aminotoluene, was converted to 3-nitro-2-iodotuene by means of a diazonium salt as described previously.[9] Condensation of the iodo compound by an Ullman synthesis[10,11] yielded 6,6′-dimethyl-2,2′-dinitrobiphenyl. Reduction of the dinitrobiphenyl was accomplished by the same method used to prepare dabp (see above). Resolution was achieved by the method of Meisenheimer and Höring[12] using *d*-tartaric acid, reproducing their specific rotation.

Preparation of R-6,6′-Dimethyl-2,2′-diaminobiphenylbis(ethylenediamine)cobalt(III) Bromide Trihydrate, [Co(en)$_2$(R-dmdabp)]Br$_3$·3H$_2$O.

The preparation was similar to that for [Co(en)$_2$(dabp)]$^{3+}$. A solution of 0.726 g (0.00347 mole) of R-dmdabp in 25 ml of absolute ethanol was combined with a solution of 0.960 g of *cis*-[Co(en)$_2$Cl$_2$]Cl in 20 ml of water. The resulting solution was covered with a watch glass and stirred at 85° for 2 hours. During this time the solution turned from violet to brown. The solution was concentrated to a volume of *c.* 15 ml in a rotary evaporator and, after cooling to room temperature, filtered to remove unreacted ligand and decomposition products. The filtrate contained a large quantity of unreacted *cis*-[Co(en)$_2$Cl$_2$]$^+$ and the very soluble [Co(en)$_2$(R-dmdabp)]Cl$_3$ could not be removed conveniently by fractional crystallization. The solution was poured onto a column (2.5 × 20 cm) of Rexyn 102H weak acid cation exchange resin in the H$^+$ form and eluted first with 0.5 *M* NaCl to remove *cis*-[Co(en)$_2$Cl$_2$$^+$. A bright yellow band was then eluted with 0.1 *M* HClO$_4$. This eluant was adjusted to a *p*H of *c.* 5.5 with dilute NaOH and then concentrated to near dryness in a rotary evaporator. Very fine orange crystals, removed by filtration, proved to be very soluble in ethanol. The (−)-[Co(en)$_2$(R-dmdabp)](ClO$_4$)$_3$ did not crystallize easily so an attempt was made to convert it to the nitrate salt by dissolving it in a small volume of water and adding a saturated solution of NaNO$_3$ dropwise until fine orange crystals began to form. These were filtered and washed with 95% ethanol and ether. Good crystals were obtained easily, but analyses indicated a mixed perchlorate nitrate salt which retained its identity upon recrystallization. ($\Delta\epsilon_{518} = -3.13$, $\Delta\epsilon_{450} = +0.08$, $\Delta\epsilon_{394} = -0.80$, $\Delta\epsilon_{310} = +27.3$). *Anal.* Calcd. for [Co(C$_{18}$H$_{32}$N$_6$)]$_2$(ClO$_4$)$_5$(NO$_3$): C, 32.22; H, 4.81; N, 13.57. Found: C, 32.04; H, 4.81; N, 13.35.

Conversion to the bromide of the complex ion was accomplished by washing a solution of the mixed perchlorate-nitrate through a column (2.5 × 8 cm) of Dowex 50W–X8 anion exchange resin in the chloride form with water, concentrating the solution in a rotary evaporator, and adding a concentrated solution of sodium bromide dropwise. The orange crystals were filtered and washed with a little 95% ethanol and ether. *Anal.* Calcd. for [Co(C$_{18}$H$_{32}$N$_6$)]Br$_3$·3H$_2$O: C, 31.55; H, 5.59; N, 12.27; Br, 34.98. Found: C, 31.79; H, 4.81; N, 12.47; Br, 34.71

Spectra.

The absorption spectra were recorded on a Cary 14 spectrophotometer at room temperature using a tungsten source. The CD spectra were recorded on Roussel-Jouan Dichograph using a tungsten source in the visible region and a deuterium source in the uv, and on a Jasco ORD–UV–5 spectrophotometer with a Jouan CD attachment using a xenon source. The infrared spectra were measured on a Beckman-8 Spectrophotometer equipped with sodium chloride optics. The samples were prepared as Nujol mulls.

Analyses

Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona, and Alfred Bernhardt, Elbach, West Germany.

RESULTS AND DISCUSSION

Synthesis and Resolutions

The complex ions $[Co(en)_2(dabp)]^{3+}$ and α-[Co(trien)(dabp)]$^{3+}$ were prepared in good yield from the *cis*- and α-*cis*-isomers of the corresponding dichloro- complexes, respectively, with equimolar amounts of dabp. Reaction of β-*cis*-$[Co(trien)Cl_2]^+$ with dabp, however, resulted in a mixture of the α- and β-isomers with the α-isomer predominating. The β-isomer proved to be relatively unstable in aqueous solution and its resolution was, therefore, not attempted.

McCullough and Bailar[4] reported the resolution of $[Co(en)_2(dabp)]^{3+}$ into four optical isomers using silver *d*-tartrate. Preliminary results of this investigation appeared to indicate the presence of four optical isomers of both $[Co(en)_2(dabp)]^{3+}$ and α-[Co(trien)(dabp)]$^{3+}$. In both resolutions, the (+)- and (—)-diastereomers, presumed to be chloride *d*-tartrates, were obtained as gelatinous precipitates. Although (+)- and (—)-fractions were always separable by fractional crystallization, the sequence in which they precipitated was not reproducible over several trials and, therefore, was assumed to depend on small fluctuations in the experimental conditions. The main (+)- and (—)-fractions were recrystallized until the CD intensities were no longer changed by further recrystallization, yielding only one pair of isomers for each complex. The pairs of optical isomers obtained after removal of the resolving agent gave mirror image CD spectra for each complex.

From the filtrate from removal of the less-soluble diastereomers, many fractions of intermediate CD intensity were taken. Repeated recrystallization of these fractions failed to give reproducible CD intensities. However, when a racemic fraction from the filtrate was saturated with silver *d*-tartrate, (+)- and (—)-fractions were obtained which recrystallized to reproducible CD intensities. The optical isomers gave mirror image CD curves (not shown) which were identical in form to those of the isomers isolated previously but of lesser intensity. It would be very unusual for the sum of the vicinal-conformational and the configurational effects[13,14] to have exactly the same form for diastereomers and we feel that these samples giving lower CD intensity were incompletely resolved, and not additional isomers. This is all the more likely since reaction of R-dmdabp, differing from dabp only in the substituents at the 6,6′-positions far from the metal ion, reacted with racemic *cis*-$[Co(en)_2Cl_2]^+$ to give only one configurational isomer of $[Co(en)_2(R\text{-}dmdabp)]^{3+}$. Our results, therefore, as well as those of Fujita, *et al.*[15] indicate that only two optical isomers of $[Co(en)_2(dabp)]^{3+}$ and α-[Co(trien)(dabp)]$^{3+}$ can be obtained due to steric interactions favoring one conformational isomer over the other for a given configuration of chelate rings.

Infrared Spectra

The ir spectra in the region 700 cm^{-1} to 1300 cm^{-1} for the complexes $[Co(en)_2(dabp)]Cl_3$, α-$[Co(trien)(dabp)]Cl_3 \cdot 2H_2O$, and β-$[Co(trien)(dabp)]Cl_3$ are shown in Figure 1. Three regions of the ir spectra may be used to distinguish these three complexes. The region between 700–800 cm^{-1} may be assigned to the aromatic CH-out-of-plane deformation mode. In this region the absorption bands of $[Co(en)_2(dabp)]Cl_3$ and α-[Co(trien)-dabp)]$Cl_3 \cdot 2H_2O$ are very similar and differ from those of β-$[Co(trien)(dabp)]Cl_3$. By examining molecular models or drawings (Figure 2) it can be seen that the two benzene rings are equivalent (C_2 symmetry) for the bis en and α-trien complexes and that the environments are very similar for the two complexes. The benzene rings of the β-trien complex are clearly in different chemical environments (C_1 symmetry).

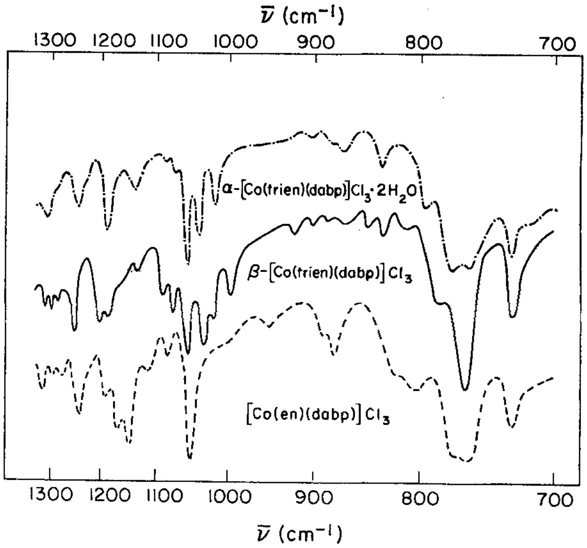

FIGURE 1 The infrared spectra between 700 and 1300 cm^{-1} of α-$[Co(trien)(dabp)]Cl_3 \cdot 2H_2O$, β-$[Co(trien)(dapb)]Cl_3$ and $[Co(en)_2(dabp)]Cl_3$.

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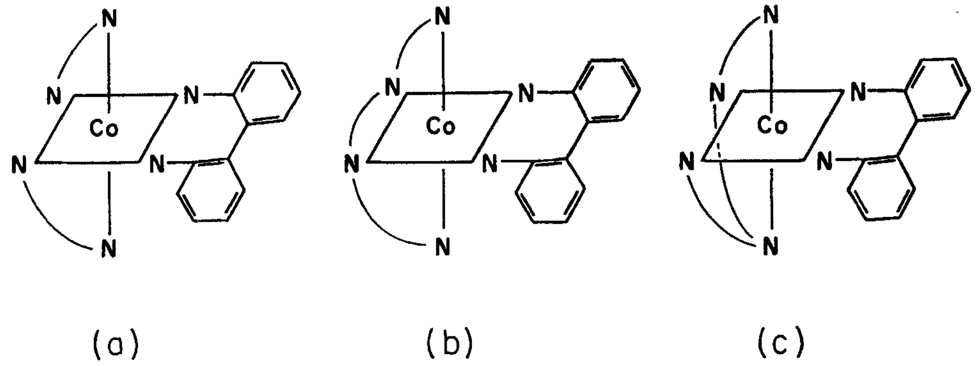

FIGURE 2 The Λ-configurations of (a) $[\mathrm{Co(en)_2(dapb)}]^{3+}$ (b) α-$[\mathrm{Co(trien)(dabp)}]^{3+}$, and (c) β-$[\mathrm{Co(trien)(dabp)}]^{3+}$

In the region between 1100–1300 $\mathrm{cm^{-1}}$, assigned to the phenyl-$\mathrm{NH_2}$ (aniline) stretch, although there are some similarities between the three complexes, the absorption band patterns are distinctly different for the three different complexes. The ir spectra of the bis(en) and α-trien complexes appear to have the lest in common in this region. The aniline donor atoms might be expected to be sensitive to changes in field strengths of other ligand atoms and perhaps less to changes in overall symmetry. It should, therefore, to be noted (Figure 2) that each dabp nitrogen is trans to terminal ethylamine in $[\mathrm{Co(en)_2(dabp)}]^{3+}$, one nitrogen trans to a terminal ethylamine in β-$[\mathrm{Co(trien)_2(dabp)}]^{3+}$, and neither trans to a terminal $-\mathrm{NH_2}$ in α-$[\mathrm{Co(trien)(dabp)}]^{3+}$.

The region (980–1100 $\mathrm{cm^{-1}}$) has been assigned to $\mathrm{NH_2}$ and $\mathrm{CH_2}$ modes by Buckingham and Jones[16] who found it to be the most useful region for distinguishing *α-cis* and *β-cis*-trien complexes. Two strong absorption bands were observed for the α-isomers and four for the β-isomers. As shown in Figure 1, three strong absorptions occur between 980–1100 $\mathrm{cm^{-1}}$ in the spectrum of α-$[\mathrm{Co(trien)(dabp)}]^{3+}$, and five in the spectrum of β-$[\mathrm{Co(trien)(dabp)}]^{3+}$. The additional band in each spectrum may be due to dabp.

Electronic Absorption and Circular Dichroism Spectra.

The absorption and CD spectra of (−)-$[\mathrm{Co(en)_2(dabp)}]^{3+}$, (−)-$[\mathrm{Co(en)_2(R\text{-}dmdabp)}]^{3+}$ and (−)-α-$[\mathrm{Co(trien)(dabp)}]^{3+}$, along with the absorption spectrum of dabp and the CD spectrum of R-dmdabp, are shown in Figure 3. The mirror image CD curves of the (+) dabp complexes are not shown. Only the first ($\mathrm{T_{1g}}$) *d–d* absorption band is observed in the visible region of each spectrum. The band maxima for the three complexes occur at *ca.* 20.5 kK compared to 21.3 kK for $[\mathrm{Co(en)_3}]^{3+}$ [17] and α-$[\mathrm{Co(trien)en}]^{3+}$.[18] The extinction coefficients are also much higher ($\epsilon = 125$–160) for the dabp-type complexes than for the corresponding en complexes ($\epsilon = c.$ 85).[17,18] The second ($\mathrm{T_{2g}}$) absorption band of the Co(III) ion is buried under an intense band which peaks at *c.* 32.5 kK. This intense band is most likely charge transfer in nature since the dabp

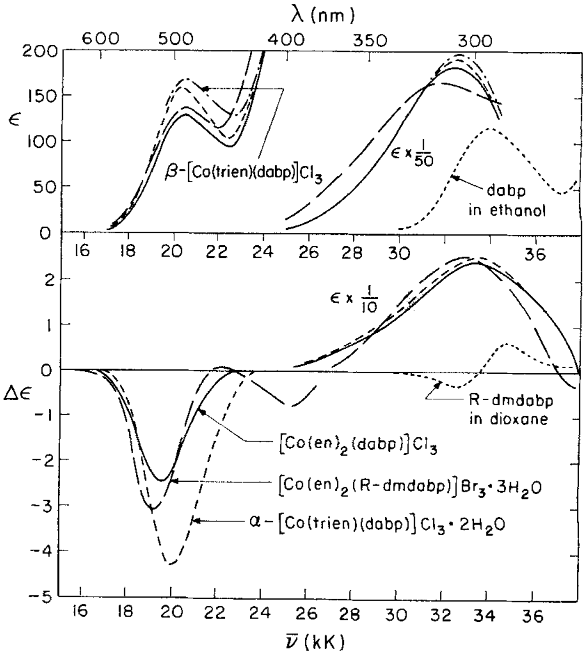

FIGURE 3 The absorption and CD spectra of (−)-$[\mathrm{Co(en)_2(dabp)}]^{3+}$, (−)-$[\mathrm{Co(en)_2(R\text{-}dmdabp)}]^{3+}$, (−)-α-$[\mathrm{Co(trien)(dabp)}]^{3+}$, the CD spectrum of R-dmdabp, and the absorption spectra of β-$[\mathrm{Co(trien)(dabp)}]^{3+}$ and dabp.

"aniline band" in this region is much less intense and occurs at lower energy. It has been observed that the aniline band is quenched in acid solution. An extensive study[19,20] of the absorption spectra of twisted biphenyls has shown that the molar absorptivities decrease as the benzene rings are twisted further from coplanarity, presumably due to the inhibition of resonance. It has been suggested[19] that an amine function adjacent to the biphenyl linking bond can make a resonance contribution by means of the unshared pair of electrons. The lone pair upon protonation is localized and, therefore, unavailable for resonance involving the phenyl ring. Similarly, complexation of dabp to a metal ion through the 2,2′-diamino-functions would also be expected to quench the aniline band.

The actual symmetry of the bis(en) and α-trien complexes with dabp and the dmdabp complex is C_2. The effective symmetry, however, is higher as might be expected since each octahedral site is occupied by a nitrogen donor. The CD spectrum of the reference complex, $[Co(en)_3]^{3+}$, shows trigonal splitting of the T_{1g} transition into an intense peak at 20.3 kK of $E(D_3)$ symmetry and a very weak peak of $A_2(D_3)$ symmetry and opposite sign at 23.4 kK.[17] The CD spectrum of (−)-$[Co(en)_2(R\text{-}dmdabp)]^{3+}$ (Figure 3) exhibits comparable splitting but with both peaks shifted to lower energy by *c.* 1.1 kK. The T_{1g} peaks in the CD spectra of $[Co(en)_2(dabp)]^{3+}$ and α-$[Co(trien)(dabp)]^{3+}$, are unsplit although the displacement of the CD peaks to low energy relative to the corresponding absorption maxima is an indication of trigonal splitting.

The rotatory strengths in the T_{1g} region of the bis(en) complexes with dabp and R-dmdabp are greater than for $[Co(en)_3]^{3+}$. There can be no straightforward interpretation of this result since the relative intensities could depend on several variables including the conformational contribution due to the fixed dabp or R-dmdabp, the chelate ring size, the relative displacements of ligating atoms from octahedral positions, and intensity borrowing from transitions involving ligand states. The T_{1g} rotatory strength for α-$[Co(trien)(dabp)]^{3+}$ is much greater than those for the en complexes in agreement with the general result for α-trien[21] and bis(en)[22] complexes, and indicative of the important influence of the trien backbone chelate ring. The Δ configuration[2] is assigned to the complexes with a negative dominant peak in the T_{1g} region by comparison with $[Co(en)_3]^{3+}$.[22]

The CD spectra of $[Co(en)_2(dabp)]^{3+}$ and α-$[Co(trien)dabp)]^{3+}$ are nearly identical in the near uv region. In each spectrum, a broad peak is observed at *c.* 33.5 kK. The sign of this peak is, presumably, related to the absolute configurations of complex and ligand since it is thought to be charge transfer. The CD spectrum (Figure 3) of R-dmdabp in dioxane has been reported.[23] The absolute configuration of this compound has been established[5] by a sequence of chemical reactions relating back to tartaric acid. Two weak peaks of opposite sign are observed in the CD spectrum of R-dmdabp between 31–37 kK and there is no apparent relationship between these peaks and the single, broad, very intense peak observed at 33 kK in the CD spectrum of $[Co(en)_2(R\text{-}dmdabp)]^{3+}$. This is not surprising since the CD peaks as well as absorption maxima of R-dmdabp in this region are quenched upon protonation. Because of the similarities of the CD spectra of (−)-$[Co(en)_2(dabp)]^{3+}$, (−)-α-$[Co(trien)(dabp)]^{3+}$, and (−)-$[Co(en)_2(R\text{-}dmdabp)]^{3+}$, it is concluded that the former complexes for which the intense charge transfer peak at *c.* 35.5 kK is positive have dabp in the R-configuration (λ conformation, Figure 4). It is, therefore, concluded that dabp coordinates stereoselectively to form Δ(λ)–$[Co(en)_2(R\text{-}dabp)]_3^+$ and Δ(λ)–$[Co(trien)(R\text{-}dabp)]^{3+}$ and the Λ(δ)-S-dabp isomers in preference to the Δ(δ)-S-dabp and Λ(λ)-R-dabp combinations. That these combinations are preferred is reasonable as it can be seen from an examination of models that interactions between hydrogens of R-dabp and the hydrogens of the en or trien rings cam be minimized if the Δ(λ) arrange-

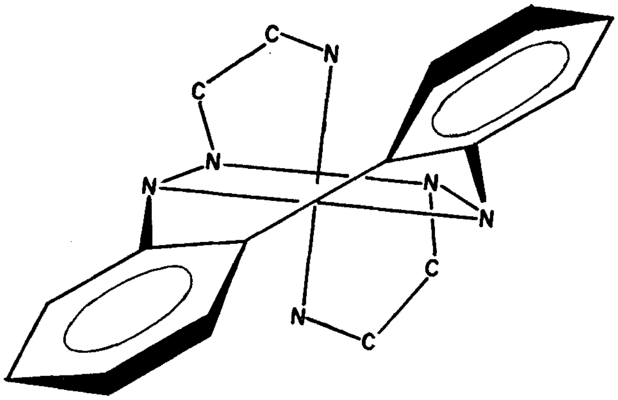

FIGURE 4 Δ(λ)-$[Co(en)_2(R\text{-}dabp)]^{3+}$.

ment (Figure 4) is adopted. In the Δ(λ) and Λ(δ) arrangements the phenyl rings are twisted into the open faces of the octahedron, i.e., faces without an edge spanned by an en chelate ring. If both conformational isomers of these complexes could have been isolated the conformational rotatory strengths in the *d–d* region could then have been calculated.

In summary, our results indicate that dabp coordinates stereoselectively with bis(en) and trien complexes of Co(III), and that the conformation of the complexed ligand can be determined by using dmdabp in its place and comparing the CD spectra of the two complexes. Simple comparison of the CD spectra in the uv region of the dabp complex and of free R-dmdabp does not suffice for determining the ligand conformation since the transitions involving the complexed and free ligand, respectively, are of a different nature. While stereospecificity prevented evaluation of the conformational rotatory strengths of these complexes, it is likely that further studies of other complexes involving dabp-type ligands can provide information of this type.

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