A Model for the Circular Dichroism Perturbations Which Arise upon Ion Pairing between Tris(diamine)–Metal Chelates and Certain Polyoxyanions[1]

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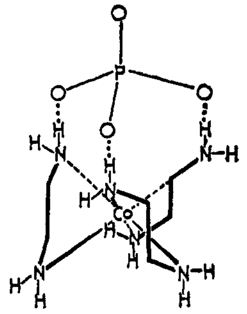
Abstract: A complete resolution of the cobalt(III) complex of the sexadentate ligand $CH_3C(CH_2NHCH_2CH_2NH_2)_3$, sen, has been effected. The circular dichroism (CD) spectrum of this complex is very similar to the CD spectrum obtained for $[Co(en)_3]^{3+}$ in the presence of phosphate ion. The inherent structural likeness of $[Co(sen)]^{3+}$ and the suggested model for the $[Co(en)_3]^{3+}$–PO_4^{3-} ion pair, combined with their CD spectral similarities, support the proposed mode of outer-sphere complexation and indicate that the sexadentate chelate may serve as a useful model to elucidate the nature of CD perturbations by inactive anions. From a consideration of the origins of optical activity in $[Co(sen)]^{3+}$ and $[Co(en)_3]^{3+}$, the major source of changes in rotatory strength in the d → d chromophores of tris(diamine) complexes upon polyoxyanion interaction is proposed to be a vicinal effect from the stereospecific production of new asymmetric centers at the primary amine donors. Support for this vicinal mechanism of CD alterations in tris(diamine) chelates is derived from the CD perturbations of phosphate ion on the conformationally locked (Δ)-[Co-(–)-(chxn)$_3$]$^{3+}$.

Recent observations have led to an empirical method for the assignment of the trigonal d–d transitions in the circular dichroism (CD) spectra of tris(diamine) complexes of d^3 and d^6 metal ions. In general, the addition of a tetrahedral or trigonal oxyanion, such as PO_4^{3-} or SeO_3^{2-}, to a solution of an active tris(diamine) complex produces selective changes in the rotatory strength of the transitions attributed to the trigonal components associated with the lowest energy octahedral transition.[2–5] In the presence of a suitable oxyanion, the rotatory strength of the A component is enhanced while that of the E component is diminished. Employing this gegenion technique, recent workers[6,7] correctly predicted the chirality of $(-)_{589}$-$[Co(tn)_3]^{3+}$,[8] which was determined by X-ray diffraction.[9]

Two proposals have been put forth in an attempt to rationalize the CD effects. It has been suggested[4] that CD variations in the d–d region are indirectly caused by the generation of a new interionic charge-transfer transition which appears upon ion aggregation. Alternatively, stereospecific outer-sphere complexation, **1**, has been considered[10] to perturb the equilibrium distribution[11] of ring conformers in solution producing the observed CD alterations. The structural similarity of $[Co(sen)]^{3+}$, **2**, to the proposed mode[3,10] of ion pairing between $[Co(en)_3]^{3+}$ and phosphate ion suggests that the sexadentate complex may provide a useful model for understanding the mechanism by which CD changes are induced by optically inactive ions.



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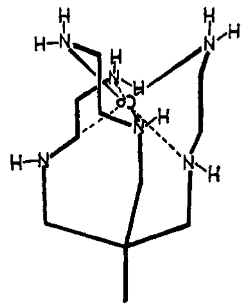

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Experimental Section

1,1,1-Tris(2′-aminoethylaminomethyl)ethane (sen). The procedure outlined by Green, *et al.*,[12] was used to prepare this ligand. The hexamine distilled as a colorless, viscous liquid at 176–177° (0.05 mm). The amine was characterized by its pmr in D_2O which showed singlets at δ 0.91 and 2.46 and a multiplet at 2.64 ppm, in the integration 1:2.1:3.7, respectively.

[Co(sen)]Cl$_3$. Several methods of preparation of this complex were used; however, the procedure employed by the previous workers[12] using $Na_3[Co(CO_3)_3]\cdot 3H_2O$ was found to be most convenient. [Co(sen)]Cl$_3$ was obtained as large orange crystals when

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[8] Abbreviations used: sen = 1,1,1-tris(2′-aminoethylaminomethyl)ethane; en = ethylenediamine; pn = propylenediamine; chxn = cyclohexane-1,2-diamine; tn = trimethylenediamine; meen = *N*-methylethylenediamine.

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Table I. Circular Dichroism Data for the Sexadentate Chelate

	$[\theta]_{502}$[a]	$[\theta]_{450}$	$[\theta]_{340}$
(Δ)-[Co(sen)]Cl-*d*-tart $\cdot H_2O$[b]	−1390	+3990	*c*
(Λ)-[Co(sen)]Cl-*d*-tart $\cdot H_2O$	+1300	−4200	*c*
(Δ)-[Co(sen)]Cl_3	−1370	+3450	−400
(Λ)-[Co(sen)]Cl_3	+1410	−3420	+410

[a] Molar ellipticities at indicated maxima measured in water. [b] Less soluble diastereomer. [c] Not measured.

Table II. The Effect of Phosphate Ion on the CD of Various Cobalt(III) Chelates[a]

	$^1A \rightarrow {}^1E_a$			$^1A \rightarrow {}^1A$			$^1A \rightarrow {}^1E_b$		
		$\Delta\epsilon_{max}$			$\Delta\epsilon_{max}$			$\Delta\epsilon_{max}$	
	λ_{max}[b]	Pure	With PO_4^{3-}	λ_{max}	Pure	With PO_4^{3-}	λ_{max}	Pure	With PO_4^{3-}
(Λ)-$(+)_{589}$-$[Co(en)_3]^{3+}$[c]	490	+1.89	+1.53	430	−0.17	−1.26			*d*
(Λ)-$(+)_{589}$-$[Co(sen)]^{3+}$[e]	502	+0.42	+0.31[f]	450	−1.05	−1.94[f]	340	+0.13	+0.22[f]
(Λ)-$(+)_{589}$-$[Co\{(+)pn\}_3]^{3+}$[c]	490	+1.96	+1.32	437	−0.58	−1.67			*d*
(Λ)-$(+)_{589}$-$[Co\{(+)chxn\}_3]^{3+}$[e]	500	+2.15	+1.41[f]	443	−0.65	−1.81[f]	350	+0.17	+0.39[f]

[a] All spectra measured in aqueous solution as chloride salts. [b] Wavelength in mμ. [c] Data obtained from ref 5. [d] Available graphical data indicate that the $^1A \rightarrow {}^1E_b$ transition also increases in $\Delta\epsilon$ in the presence of phosphate; see ref 3 and 4. [e] Data measured for Δ isomers and transposed for tabular presentation. [f] 3.5×10^{-3} *M* in complex and 0.1 *M* in phosphate ion.

recrystallized from aqueous ethanol. *Anal.* Calcd for $C_{11}H_{30}N_6Cl_3Co$: C, 32.09; H, 7.35; N, 20.41. Found: C, 31.93; H, 7.40; N, 20.60.

Resolution of [Co(sen)]Cl_3. The sexadentate complex, 18.6 g (0.045 mol), was dissolved in 100 ml of hot water and this solution was triturated for 15 min with 16.3 g (0.045 mol) of freshly prepared silver *d*-tartrate. The silver chloride precipitate was then carefully filtered off and washed several times with hot water (approximately 200 ml total) until the washings were colorless. Cooling the solution slowly to room temperature yielded fine golden needles of the less soluble diastereomer, which were filtered off, washed with absolute ethanol and ether, and air dried. The yield was 3.5 g. The filtrate was reduced in volume to 250 ml on a steam bath. Upon cooling and seeding with a crystal of the above material, a second crop of needles (1.0 g) was isolated. The first fraction was recrystallized from water five times, with no observable change in CD after the third recrystallization (Table I). For analysis, the purified diastereomer was dried *in vacuo* at 80° for 2 hr. *Anal.* Calcd for $C_{15}H_{36}N_6O_7ClCo$: C, 35.54; H, 7.16; N, 16.58. Found: C, 35.34; H, 7.52; N, 16.50. The electronic spectrum of this diastereomer was obtained, 467 mμ (ϵ 112) and 340 (99).

After collection of the second fraction of less soluble diastereomer, the filtrate was allowed to evaporate over a period of several days to a volume of ~30 ml. The resulting large, orange crystals of the more soluble diastereomer (1.7 g) were easily separated mechanically from the fine needles of the less soluble diastereomer and were recrystallized to constant CD (Table I). A pulverized sample of this solid was dried for 2 hr *in vacuo* at 100° and gave an electronic spectrum identical with that of the less soluble salt. From these data, the more soluble chloro-*d*-tartrate salt was formulated as a monohydrate also.

The purified diastereomers were converted to the enantiomeric iodides *via* metathesis in water. After two recrystallizations, a solution of the iodide salt was triturated with freshly prepared silver chloride to yield the active trichloride salt. The purity of these compounds was established using extinction coefficients in the visible spectrum. The CD data for the enantiomeric trichlorides are presented in Table I.

Tris((*RR*)-(−)-cyclohexane-1,2-diamine)cobalt(III) Trichloride Dihydrate, (Δ)$(-)_{589}$-[Co-[(*RR*)(−)chxn]$_3$]$Cl_3 \cdot 2H_2O$. Instead of the original synthetic procedure[13] used to prepare this compound, an alternate route was chosen. (*RR*)-(−)-Cyclohexane-1,2-diamine (0.38 g, 3.3 mmol), $[\alpha]^{21}D$ +42.6° (benzene), was dissolved in 20 ml of water. $Na_3[Co(CO_3)_3] \cdot 3H_2O$ (0.36 g, 1.0 mmol) was suspended in solution and 11.9 ml of 0.505 *N* HCl slowly added to the suspension while heating on a steam bath. When the evolution of carbon dioxide was complete, the red solution was filtered and, upon cooling, 0.1 g of complex was isolated. *Anal.* Calcd for $C_{18}H_{46}N_6O_2Cl_3Co$: C, 39.75; H, 8.53. Found: C, 40.31; H, 8.06. This compound exhibited transitions in the visible spectrum at 466 mμ (ϵ 130) and 340 (230). The circular dichroism spectrum (see Table II) is in good agreement with that previously reported.[11] The authors wish to thank Dr. Roger S. Downing for his resolution of the cyclohexane-1,2-diamine.

Measurements. Absorption spectra were obtained with a Cary Model 14 recording spectrophotometer. Circular dichroism measurements were made using a Cary Model 60 recording spectropolarimeter equipped with a Model 6001 circular dichroism attachment. The ^1H nmr studies were carried out using Varian HA-100 and HR-220 high-resolution spectrometers. These spectra were recorded with sodium trimethylsilylpropanesulfonate as the internal "lock" reference in D_2O. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

The ability of 1,1,1-tris(2′-aminoethylaminomethyl)-ethane, sen, to function as a sexadentate ligand may be inferred from the ligand-field spectrum of its cobalt(III) complex. The complex $[Co(sen)]^{3+}$ displays electronic transitions at 467 mμ (ϵ 113), $^1A_{1g} \rightarrow {}^1T_{1g}$, and 340 (103), $^1A_{1g} \rightarrow {}^1T_{2g}$, yielding crystal-field parameters[14] (Dq = 2510 cm^{-1}, B = 450 cm^{-1}) identical with those obtained for $[Co(en)_3]^{3+}$.

The pseudooctahedral geometry of $[Co(sen)]^{3+}$ is confirmed by a complete resolution into its enantiomeric forms *via* the chloro-*d*-tartrate diastereomers (Table I). The circular dichroism spectrum of $[Co(sen)]^{3+}$ (Figure 1) exhibits two bands of opposite sign in the region of the lowest energy electronic transition. These two CD bands are attributed to magnetic-dipole-allowed transitions to the two trigonal components of the parent $^1T_{1g}$ octahedral term. The $^1A \rightarrow {}^1E$ transition is assigned to the lower energy band and the $^1A \rightarrow {}^1A$ to the band at higher energy based on the ordering of the trigonal components found[15] for $[Co(en)_3]^{3+}$ and other tris(diamine)–cobalt(III) complexes. The predominant intensity of the Cotton effect ascribed to the higher energy $^1A \rightarrow {}^1A$ component (Figure 1) is in apparent contradiction with the intensity relationship in the first two CD bands for all other tris(diamine)–cobalt(III) complexes, but will be reconciled when the effect of the capping device is discussed. The above assignment is supported by the effect of phosphate ion on the CD spectrum of $[Co(sen)]^{3+}$ (Table II). The significant enhancement of the Cotton effect assigned to the ^1A component together with a decrease in intensity for the ^1E band in the presence of phosphate ion are in agreement with the CD behavior of other tris(diamine)–cobalt(III) complexes. The CD in the region of the higher energy $^1A_{1g} \rightarrow {}^1T_{2g}$ octahedral band is consid-

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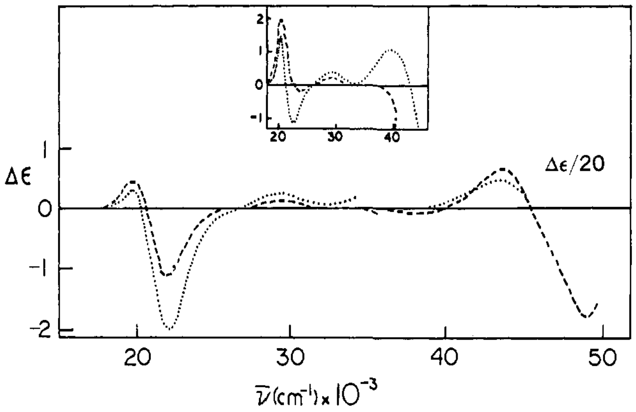

Figure 1. Circular dichroism spectrum of [Co(sen)]Cl$_3$ in water (– – –) and in 0.1 *M* phosphate ion (· · ·). Insert shows the CD of [Co(en)$_3$]$^{3+}$ and its behavior with phosphate ion using same legend above (ref 3).

erably weaker than in the low-energy transitions and suggests that the selection rules for the parent octahedral transitions dominate the allowedness of these transitions. In the molecular symmetry of the complex, C$_3$, all transitions are magnetic dipole allowed, and a significant increase in rotatory strength of the higher energy band would have been expected compared to D$_3$ complexes,[16] where the $^1A_1 \rightarrow {}^1A_1$ component of the second octahedral transition remains magnetic dipole forbidden.

From the signs of the low-energy CD couplet of [Co(sen)]$^{3+}$, the Δ[17] or P(C$_3$)[18] absolute configuration is assigned to the cation of the less soluble diastereomer by comparison with the CD of (+)$_{589}$-[Co(en)$_3$]$^{3+}$ whose absolute configuration has been established by X-ray diffraction.[19] This assignment contradicts the observation[20] that tris(diamine) complexes with Λ[17] or M(C$_3$)[18] absolute configuration form the less soluble halo-*d*-tartrate salt. It has been pointed out, however, that such a correlation of absolute configuration should only be applied in cases where the complexes are isomorphous.[21]

[Co(sen)]$^{3+}$ as a Model for Tris(diamine)cobalt(III)–Polyoxyanion Ion-Pairing Interactions. The changes in the circular dichroism spectrum upon going from [Co(en)$_3$]$^{3+}$ to [Co(sen)]$^{3+}$ are remarkably similar to the CD changes which occur when phosphate ion is added to a solution of [Co(en)$_3$]$^{3+}$. This similarity suggests that [Co(sen)]$^{3+}$ is an appropriate model for these ion-pairing effects and that a comparison of the sources of optical activity in [Co(sen)]$^{3+}$ and [Co(en)$_3$]$^{3+}$ may help to elucidate the origins of the CD changes for [Co(en)$_3$]$^{3+}$ upon interaction with phosphate ion.

For both the sexadentate complex and the tris(diamine) complex, the helical disposition of the ligands about the metal ion (configurational effect) contributes to the rotational strength in the d → d transitions. In this discussion it is assumed that the capping device does not alter the gross helicity of the five-membered chelate rings and therefore changes in the configurational contribution are not responsible for the observed CD changes. Molecular models indicate that the alkyl cap in [Co(sen)]$^{3+}$ may also possess some chirality; however, this contribution will be neglected since it appears to be slight compared to the helicity of the side rings and may be effectively cancelled by a simple twisting motion in the capping group which would produce essentially equal populations of the two chiral forms.

The enantiomeric conformations of the chelate rings provide an additional contribution to the optical activity of both [Co(en)$_3$]$^{3+}$ and [Co(sen)]$^{3+}$. For [Co(en)$_3$]$^{3+}$, an equilibrium distribution of four possible conformers is present in solution, with each conformer making a weighted average contribution of its individual absolute magnitude to the observed circular dichroism.[11] Sargeson has proposed that the formation of the [Co(en)$_3$]$^{3+}$–PO$_4^{3-}$ ion pair perturbs the conformational equilibrium of [Co(en)$_3$]$^{3+}$ in solution and alters the conformational contribution to the CD. The structural similarity of [Co(sen)]$^{3+}$, **2**, and the proposed ion-pair adduct, **1**, in which the phosphate ion stabilizes the lel[22] conformation, is readily apparent. The fact that both of these species exhibit similar CD spectral changes compared to [Co(en)$_3$]$^{3+}$ strongly suggests that the proposed structure for a stereospecific ion-pair interaction is correct.

The application of an alkyl apical constraint to [Co(en)$_3$]$^{3+}$ will undoubtedly alter the conformer distribution of the five-membered chelate rings. Although unsubstituted chelate rings of tris(diamine) complexes favor the lel conformer in solution, carbon-substituted chelate rings, such as pn, exhibit a considerable preference for the conformations[23] where the substituent occupies a pseudoequatorial position. Evidence from magnetic resonance studies[24] indicates that a similar conformational preference exists for the alkyl substituent located on the coordinated secondary nitrogen donor of [Ni(H$_2$O)$_4$(meen)]$^{2+}$. Similarly [Co(sen)]$^{3+}$, in which the nitrogen substituents are constrained to occupy the favored pseudoequatorial position, should exhibit an even greater preference for one conformer; molecular models favor the lel conformer as proposed[4] for the stereospecific [Co(en)$_3$)]$^{3+}$–PO$_4^{3-}$ interaction.

Evidence for a conformational preference in [Co(sen)]$^{3+}$ is obtained from the pmr data summarized in Table III. Even though an analysis of this spectrum may not be proposed at the present time, considerable information can be derived from these data. The observed complexity of the methylene proton resonances of [Co(sen)]$^{3+}$, while those in [Co(en)$_3$]$^{3+}$ produce a single broad resonance,[25] lends support to the proposed conformational preference in the sexadentate system. A center of asymmetry in a molecule, such as the coordinated secondary amine groups in [Co(sen)]$^{3+}$, allows the possibility of magnetic nonequivalence of protons in a nearby methylene group.[26] For substan-

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Table III. Chemical Shift[a] and Coupling Constant[b] Data for $[Co(sen)]^{3+}$ in D_2O[c]

δ	Multiplet pattern[d]	J	Integration[e]
0.95	Singlet		1
2.70[f]	Doublet	9	2
2.42	$^1/_2$ AB pair	14[g]	1
3.02	$^1/_2$ AB pair	14[g]	2
3.0	$^1/_2$ AB pair[h]	~8	
3.2	$^1/_2$ AB pair	~8	1

[a] Values in ppm relative to DSS. [b] Values in Hz. [c] only slight temperature dependence observed over the range 20–100°. [d] Established from behavior of resonances at 100 and 220 MHz. [e] From 220-MHz spectrum. [f] Additional weak resonances at 2.55 and 2.85 ppm attributed to combination bands. [g] Further splitting of 1–2 Hz observed. [h] Detected by slight shift with increasing temperature.

tial nonequivalence of such protons to be manifested, it is generally considered necessary to have a pronounced conformational preference in a molecule so that the protons of interest may reside in quite different magnetic environments.[27] The fact that the individual protons of a methylene group in $[Co(sen)]^{3+}$ exhibit significant chemical shift differences and give rise to multiplet patterns indicates a substantial difference in their magnetic environments. Such a difference in magnetic environment may result from these individual protons residing in axial or equatorial positions of a favored conformer. Rapid intramolecular exchange of proton environments between two unequally populated conformations produces proton chemical shifts and coupling constants which are a weighted average of the chemical shifts and coupling constants of the individual protons in each of the discrete conformers.[28]

The pmr data for $[Co(sen)]^{3+}$ indicate, therefore, that the presence of the alkyl cap residue confers a pronounced conformational preference and imply that a similar effect would be expected for the $[Co(en)_3]^{3+}$ ion pair with phosphate ion. Since the ion-pairing interaction would probably be rapid on the nmr time scale, it would not be expected to produce similar splittings in the nmr spectrum, although recent workers[29] have described the effect of phosphate ion on the pmr of $[Co(en)_3]^{3+}$ and interpreted line-width results in terms of a perturbation of the conformational equilibrium present. It is likely, therefore, that the capping device alters the conformer population of the tris-chelate rings, and a portion of the CD perturbations may be attributed to this effect.

Mason[3] has suggested that the observed CD changes in the low-energy d → d bands of $[Co(en)_3]^{3+}$ are indirectly brought about by interaction with a new interionic charge-transfer transition which appears in the near-ultraviolet region of the spectrum upon ion-pair formation. This charge-transfer band is suggested to be magnetic dipole forbidden and interacts with the allowed d → d band of the same symmetry from which it borrows some magnetic moment to gain finite intensity. Since the CD spectrum of $[Co(sen)]^{3+}$ is similar to the spectrum obtained for the $[Co(en)_3]^{3+}$–PO_4^{3-} interaction and since there is no interionic charge transfer transition in the sexadentate species, it may be concluded that the charge transfer transition is not essential to the production of CD changes. It is more likely that structural effects are responsible for the systematic CD changes which occur upon ion-pair formation.

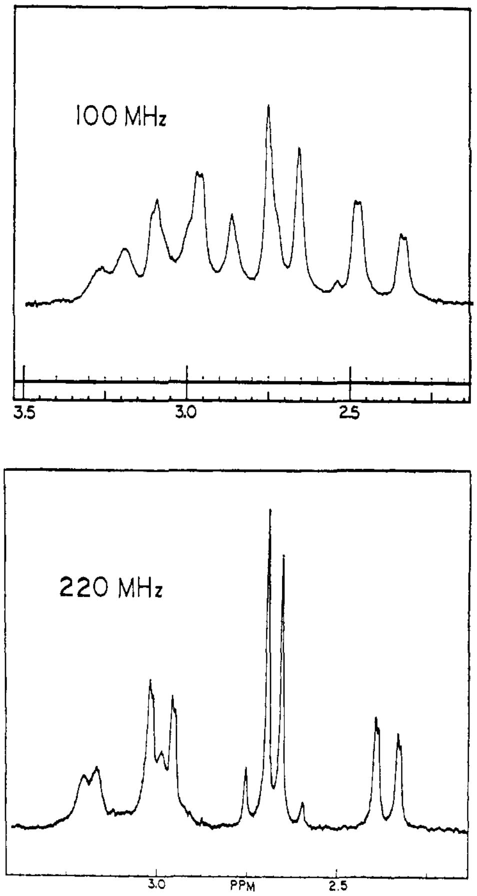

Figure 2. The pmr spectra of the methylene protons of $[Co(sen)]Cl_3$ in D_2O at 100 and 220 MHz.

A further source of optical activity in $[Co(sen)]^{3+}$ is represented by the vicinal effect of the three coordinated secondary amine functions. Molecular models indicate that these secondary amine groups stereospecifically adopt the *S* configuration[18] in the Δ complex to avoid severe interactions between the secondary amine protons and the neighboring chelate rings. The vicinal contribution of asymmetric carbon atoms to observed d → d activity has been the subject of several studies[30–32] and was found to be small in comparison with the conformational effect in dihalobisdiamine complexes. Recently, however, several complexes have been resolved[33] where asymmetry due to the coordinated secondary nitrogen atom of meen combines with the conformational contribution of the gauche chelate ring to produce optical activity. In contrast to the apparent minor contribution from carbon asymmetric centers, Hawkins has

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suggested[34] that vicinal contributions from the asymmetric nitrogen donors in *trans*-dihalobisdiamine complexes dominate the contribution to the observed activity and apparently have an oppositely signed contribution compared to the conformational effect. Certainly this is not surprising since the asymmetric donor atom is attached to the metal ion and therefore should provide a greater effect on the environment of the d → d chromophore. Thus a significant portion of the CD activity observed for $[Co(sen)]^{3+}$ must be attributed to the vicinal effect of the three asymmetric secondary amines.

A similar vicinal contribution may be postulated for the phosphate ion pair with tris(diamine) complexes. The selective interaction of the phosphate ion with the three amine protons aligned with the C_3 axis in the lel conformer will render these protons distinct from the remaining protons and stereospecifically generate three asymmetric centers as in $[Co(sen)]^{3+}$. *The configurations of these temporarily asymmetric amines will be dictated only by the configuration of the chelate rings about the metal ion (S for Δ, R for Λ) and hence the CD changes upon ion-pair formation reflect the absolute configuration of the tris(diamine) species.* Although the ion pair may be short lived, the proposed species should exist long enough to allow the contribution of the generated asymmetric centers to influence the rotatory strength of the metal-ion chromophore.

Evidence from several sources allows an estimate of the relative magnitude of the vicinal *vs.* the conformational contribution to be made. The first line of evidence regarding the importance of these two contributions comes from the CD changes which occur when $[Co(sen)]^{3+}$ itself interacts with phosphate ion (Figure 1). Molecular models indicate that the configuration induced at the primary amine groups of $[Co(sen)]^{3+}$ by ion pair formation is identical with that found at the secondary nitrogen atoms and hence the effect would be expected to be additive, as is observed. Since phosphate interacts with $[Co(sen)]^{3+}$ to produce substantial CD changes, and since the pmr data for $[Co(sen)]^{3+}$ suggests that the alkyl cap has already produced a strong conformational preference in the side rings, it is concluded that these changes are more likely to be attributable to the vicinal effect than to a conformational change.

Further support for the dominance of the vicinal contribution through asymmetric induction in these systems is gained by considering the magnitude of gegenion effects in other situations where strong conformational preference exists prior to ion-pair formation. In Table II, the effect of phosphate ion on the CD spectrum of $(+)_{589}$-$[Co(+)\text{-}(pn)_3]^{3+}$ [5] is cited. In this complex, the chelate rings are constrained to adopt a conformation which places the methyl groups in a pseudoequatorial position.[23] Thus the effect of phosphate ion cannot be attributed to any large degree to conformer redistribution and must arise from the vicinal contribution at induced asymmetric centers.

To further test this hypothesis, the effect of phosphate ion interaction with $(-)_{589}$-$[Co(-)\text{-}(chxn)_3]^{3+}$ was examined. When this conformationally locked chelate is exposed to phosphate ion, CD changes occur (see Table II) which are of the same magnitude and in the same direction as all the other CD perturbations reported. This result strongly supports the contention that stereospecific induction of asymmetric centers at the primary amine donors provides the predominant effect upon the interaction of phosphate ion with diamine complexes.

Summary

The following conclusions have been drawn from this study. (1) The proposed stereospecific mode of interaction between phosphate ion and $[Co(en)_3]^{3+}$, **1**, is substantiated by CD studies of a structurally similar sexadentate chelate. (2) The major source of CD spectral alterations in the d–d region upon interaction with phosphate ion is due to the production of asymmetry at the stereospecifically capped primary amine groups. The configuration at these induced asymmetric centers is dictated solely by the configuration of the chelate rings about the metal ion and hence the CD changes reflect the absolute configuration of the complex. (3) Although the redistribution of chelate conformers will produce CD spectral variations, this contribution appears to be smaller than the vicinal effect since the chelates (Λ)-$[Co(+)\text{-}(pn)_3]^{3+}$ and (Δ)-$[Co(-)\text{-}(chxn)_3]^{3+}$ which are conformationally rigid exhibit similar, large CD changes in the presence of phosphate ion.

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