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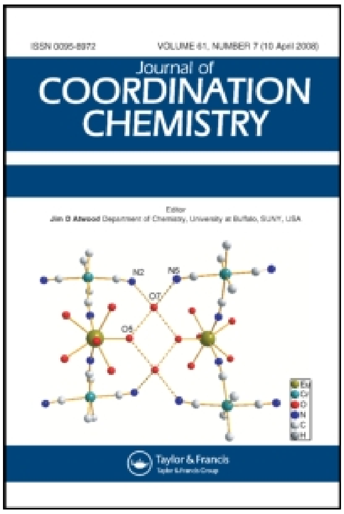

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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To cite this Article Hermer, Robert E. and Douglas, Bodie E.(1977) 'A MODEL FOR THE ION-PAIRS OF TRIS(TRIMETHYLENEDIAMINE)COBALT(III) WITH POLYOXYANIONS. THE ORIGINS OF THE CIRCULAR DICHROISM CHANGES', Journal of Coordination Chemistry, 7: 1, 43 — 52

To link to this Article: DOI: 10.1080/00958977708073037

URL: http://dx.doi.org/10.1080/00958977708073037

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J. Coord. Chem.
1977, Vol. 7, pp. 43–52

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Printed in Great Britain

A MODEL FOR THE ION-PAIRS OF TRIS(TRIMETHYLENEDIAMINE)COBALT(III) WITH POLYOXYANIONS. THE ORIGINS OF THE CIRCULAR DICHROISM CHANGES

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(*Received February 3, 1977*)

Through structural and circular dichroism spectral comparison, 1,1,1-tris(3′-aminopropylaminomethyl)-ethanecobalt(III), $Co(spn)^{3+}$, has been determined to be a model for the oxyanion ion-pairs of $Co(tn)_3^{3+}$. The CD spectral changes of Δ-$Co(spn)^{3+}$ in the presence of oxyanions in conjunction with previous investigations suggest that conformational changes of the six-membered rings cause the intensities of the E_a and A_2 components of the octahedral T_{1g} band to change in a direction opposite to that observed when only asymmetric nitrogens are generated, either by oxyanion hydrogen bonding or by means of an alkyl cap. It appears that when both effects occur together it is the conformational change that dominates the CD spectral changes. In the absence of conformational change the asymmetric nitrogens cause the E_a component to decrease while the A_2 component increases, as was found in previous studies. The nickel(II) and copper(II) complexes of spn are reported also.

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INTRODUCTION

Through the past decade much work has been devoted to the study of the circular dichroism changes that occur in tris(diamine)Co(III) complexes in the presence of various oxyanions. Early workers[2–5] observed that multiply charged oxyanions diminished and enhanced the respective areas of circular dichroism bands due to the E_a and A_2 components of the low energy octahedral T_{1g} transition of the complexes $(+)$-$Co(en)_3^{3+}$ and $(+)$-$Co((+)$-$pn)_3^{3+}$. Mason[5] suggested that these changes resulted from the development of a charge transfer transition which borrows its magnetic moment from the E_a and A_2 transitions in a selective fashion which is dependent on the number of oxyanions participating in the hydrogen bonded outer-sphere complex. By use of a sexidentate hexaamine Co(III) complex, 1,1,1-tris(2′-aminoethylaminomethyl)ethanecobalt(III), $Co(sen)^{3+}$, (a model system which simulates structurally the hydrogen bonding of an oxyanion along the C_3 axis of $(+)$-$Co(en)_3^{3+}$ by means of an alkyl cap) the origins of the CD changes were investigated further by Urbach and Sarneski.[6] Their studies indicated that the observed CD changes are the result of the generation of asymmetric nitrogens by hydrogen bonding of the oxyanion to the tris(diamine)Co(III) complex.

Although most of the work has dealt with complexes of five-membered diamine chelate rings, in the presence of oxyanions similar circular dichroism changes are observed in complexes such as tris(1,3-diaminopropane) cobalt(III), $Co(tn)_3^{3+}$ which has three six-membered chelate rings.[7] It is the purpose of this paper to consider models for oxyanion outer-sphere complexes of $Co(tn)_3^{3+}$ and to study the origins of the CD changes. The model complex 1,1,1-tris(3′-aminopropylaminomethyl)ethanecobalt(III), $Co(spn)^{3+}$ resembles structurally the oxyanion ion-pairs of $Co(tn)_3^{3+}$. The similarity of their CD spectra is consistent with the structural relationship.

EXPERIMENTAL

Preparation of Materials

The starting material for the preparation of spn was 1,1,1-tris(hydroxymethyl)ethane (purchased from Aldrich Chemical Co.), which was converted to 1,1,1-tris(bromomethyl)ethane by the method described in the literature.[8] Elemental analyses were performed by Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

Preparation of 1,1,1-tris(3′-aminopropylaminomethyl)-ethane, spn

1,3-Diaminopropane (1800 ml) stood over KOH for three weeks. After decanting, the diamine was

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refluxed for three days over sodium and then distilled immediately before use. 1,1,1-Tris(bromoethyl)ethane (154 g, 0.498 mol) was added to the distilled amine (1560 ml) under dry N_2 with stirring. The mixture was refluxed for 30 h. The excess amine was distilled and 150 g of NaOH in 250 ml of H_2O was added to the hot residue. The solution was extracted with 2500 ml of pyridine. The pyridine was removed by rotatory evaporation and the residue was filtered. The filtrate was distilled twice at 0.02 torr and the product boiled over a wide range, always greater than 100°. Yield 59.0 g, 40.9%. *Anal.* Calcd for $C_{14}H_{36}N_6$: C, 58.28; H, 12 12.57; N, 29.13. Found: C, 59.51; H, 12.48; N, 28.62.

Preparation of 1,1,1-tris(3′-aminopropylaminomethyl)-ethanecobalt(III) nitrate, [Co(spn)](No$_3$)$_3$

A solution of 2.70 g (0.00935 mol) of spn in 15 ml of methanol was mixed slowly with 2.72 g (0.00935 mol) of $Co(NO_3)_2 \cdot 6H_2O$ and 3 ml of 30% H_2O_2 dissolved in 20 ml of methanol. Vigorous evolution of oxygen gas occurred. The mixture was stirred in an ice bath and a brown precipitate was filtered. The brown material was dissolved in a minimum amount of hot water and filtered while hot, removing the insoluble black material. An equal volume of methanol was added to the filtrate and the solution was cooled. The orange powder which precipitated was recrystallized again in the same way. Yield = 0.85 g, mp = 209°. *Anal.* Calcd for $CoC_{14}H_{36}N_9O_9$: C, 31.52; H, 6.80; N, 23.63. Found: C, 30.73; H, 6.86; N, 23.12.

The $[Co(spn)](NO_3)_3$ was converted to the chloride salt using Dowex 1X8 50–100 mesh anion exchange resin in chloride form. The complex was recrystallized from water–methanol solution. *Anal.* Calcd for $[CoC_{14}H_{36}N_6]Cl_3 \cdot 3H_2O$: C, 33.11; H, 8.34; N, 16.55; Cl, 20.94. Found: C, 33.10; H, 8.46; N, 16.29; Cl, 20.63.

Preparation and resolution of 1,1,1-Tris(3′-aminopropylaminomethyl)ethane cobalt(III) iodide dihydrate, [Co(spn)]I$_3$ · 2H$_2$O

$Co(spn)Cl_3$ (2.5 g, 0.0055 mol) was dissolved in 50 ml of a 50% aqueous solution of methanol. The solution was stirred and heated while 2.07 g (0.0055 mol) of dibenzoyl-*d*-tartaric acid monohydrate was added to the solution. More methanol (10 ml) was added to dissolve all of the dibenzoyl-*d*-tartaric acid. The solution was cooled slowly to room temperature. An orange powder precipitated (0.4 g) and was filtered, $\Delta\epsilon_{19.4} = -0.10$. After a few minutes, more diastereomer precipitated from the filtrate (1.1 g, $\Delta\epsilon_{19.4} = -0.091$). The solution was left overnight at room temperature to evaporate and 0.7 g more of the less soluble diastereomer was filtered, $\Delta\epsilon_{19.4} = -0.05$. Further fractions precipitated were optically inactive. The filtrate obtained after removal of 0.7 g of unresolved complex had a positive $\Delta\epsilon_{19.4}$. This very soluble diastereomer was not isolated optically pure. The first three active fractions of diastereomer were combined and recrystallized twice to a constant $\Delta\epsilon_{19.4} = -0.31$. The optically pure diastereomer was dissolved in water and stirred overnight with Dowex 1X8 50–100 mesh anion exchange resin in iodide form. The water was removed with a rotatory evaporator. The complex was dissolved in a minimum amount of water, methanol was added, and the volume was reduced under an air jet. Orange flakes formed in the solution. Yield = 0.12 g. *Anal.* Calcd for $CoC_{14}H_{40}N_6O_2I_3$: C, 22.00; H, 5.28; N, 11.00; I, 49.82. Found: C, 22.46; H, 5.17; N, 11.06; I, 49.73.

Preparation of 1,1,1-tris(3′-aminopropylaminomethyl)ethanenickel(II) iodide, [Ni(spn)]I$_2$

1,1,1-Tris(3′-aminopropylaminomethyl)ethane (0.9 g, 0.00312 mol) dissolved in 10 ml of methanol was mixed with 0.74 g (0.00312 mol) of $NiCl_2 \cdot 6H_2O$ dissolved in 20 ml of methanol. NaI (3.6 g, 0.0248 mol) was added to the blue solution and, upon cooling, the green material which precipitated was removed by filtration. The filtrate volume was reduced to 5 ml under an air jet and the purple powder which precipitated was filtered, dried and recrystallized from a minimum amount of hot water. The purple crystals were dried at 120°. Yield = 0.51 g, 27%. *Anal.* Calcd for: $NiC_{14}H_{36}N_6I_2$: C, 27.98; H, 6.04; N, 13.98; I, 42.33. Found: C, 27.88; H, 5.95; N, 14.08; I, 42.19.

Preparation of 1,1,1-tris(3′-aminopropylaminomethyl)ethanecopper(II) chloride, Cu$_x$(spn)$_y$Cl$_z$

Copper(II) chloride (0.78 g, 0.00457 mol) dissolved in 20 ml of absolute ethanol was mixed with spn (1.32 g, 0.00457 mol) dissolved in 10 ml of absolute ethanol and the volume was reduced by gentle heating. A large excess of acetone was added which caused a blue complex to precipitate. The precipitate was filtered and washed with anhydrous ether and dried in a vacuum desiccator over $CaCl_2$. The blue powder was recrystallized from a minimum amount

TABLE I

PMR data for spn and its Co(III) complex, $[Co(NH_2\overset{D}{CH_2}\overset{C}{CH_2}\overset{B}{CH_2}NH\overset{A}{CH_2})_3CCH_3]Cl_3$

Proton	Spn[a,b]	$Co(spn)Cl_3$ [d,e]	$Co(spn)(SeO_3)^{+3-x}$ [d,ϵ]
methyl	0.85	1.00	0.99
methylene A	2.50	2.87	2.87
methylene B	2.75[c]	2.44[c]	2.44[c]
methylene C	1.65[c]	2.00	1.98
methylene D	2.75[c]	D,2.72; D′,3.01[c]	D,2.66; D′,3.04[c]
amine	1.20		

[a] Values in ppm relative to TMS in $CDCl_3$ as solvent.
[b] 60 MHz instrument.
[c] Center of multiplet.
[d] 250 MHz instrument locked to H_2O.
[e] Values in ppm relative to DSS in D_2O as solvent.

of methanol in the same manner. *Anal.* Found: C, 36.94; H, 8.33; N, 15.57; Cl, 17.85.

Physical Measurements

Visible and ultraviolet absorption spectra were measured on a Cary Model 14 recording spectrophotometer using tungsten and hydrogen sources. The spectrum of $Co(spn)^{3+}$ was measured on approximately 10^{-3} M solutions in 1-cm quartz cells at room temperature while $Ni(spn)^{2+}$ required saturated solutions in 5-cm quartz cells.

The CD spectra were recorded on a Cary Model 61 spectropolarimeter using a xenon arc source. Spectra were measured for 10^3 M solutions of $[Co(spn)]I_3$ in 1-cm or 2-cm quartz cells at room temperature while saturated solutions of [Co(spn)]-(dibenzoyl-*d*-tartrate)Cl in 5-cm cells were needed. The experimental curves were plotted in units of $\Delta\epsilon$ and wavenumber.

PMR spectra were obtained on a 60 MHz Varian Associates A-60-D Analytical NMR spectrometer using TMS in $CDCl_3$ as an internal reference. For $[Co(spn)]Cl_3$ the PMR spectrum was obtained with a 250 MHz spectrometer at Carnegie-Mellon University. In this case the field frequency was stabilized by locking to internal residual H_2O in D_2O with DSS as the internal reference.

^{13}C NMR spectra were recorded on a JNM FX-60 $^{13}C-^{1}H$ high performance NMR spectrometer operating at 15.030 MHz in the ^{13}C mode. The instrument was used in the broad band random noise ^{1}H decoupling mode so that no splittings of resonances associated with single carbons are observed. The field frequency ratio was stabilized by locking to D_2O. The spectra were obtained using a spectral window of 5000 Hz covered by 4096 addresses in the Fourier transform spectrum. The sample was placed in 8–10-mm coaxial tubes manufactured by Wilmad Spectroscopic Suppliers Inc. Benzene ($\delta = 128.7$ ppm downfield from TMS) was used as the external standard in an outer coaxial tube arrangement.

RESULTS AND DISCUSSION

The ligand 1,1,1-tris(3′-aminopropylaminomethyl)-ethane (abbreviated spn) is very similar to sen in structure and in its coordination. Each hexammine is produced by reaction of the proper diamine with 1,1,1-tris(bromomethyl)ethane. These ligands are sexidentate, coordinating with metal ions octahedrally. In the case of spn, three six-membered chelate rings are formed which give rise to enantiomorphous configurations capable of resolution if the complex is inert. Spn was characterized by its PMR spectrum (Table I) and ^{13}C NMR spectrum (Table II). Both ^{1}H and ^{13}C NMR spectral assignments are based on their proximity to the primary amine group which has a lesser deshielding effect than the secondary amine group.[9]

TABLE II

^{13}C NMR[a,b] data for spn and $Co(spn)^{3+}$,

$[Co(NH_2\overset{D}{CH_2}\overset{C}{CH_2}\overset{B}{CH_2}NH\overset{A}{CH_2})_3CCH_3]^{3+}$

carbon	spn	$Co(spn)^{3+}$
methyl	20.63	21.60
quarternary	37.84	36.38
methylene A	39.31	38.65
methylene B	55.55	55.06
methylene C	31.99	22.74
methylene D	48.24	48.56

[a] Solvent is D_2O with external benzene as reference.
[b] Original data were converted using the factor $\delta_c^{C_6H_6}$ = 128.65 ppm downfield from TMS.

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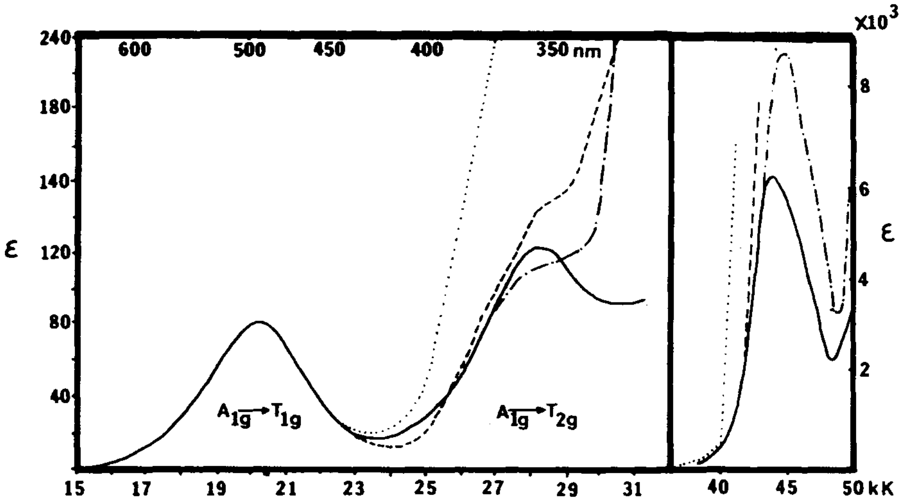

FIGURE 1 The electronic absorption spectrum of $[Co(spn)]I_3$ in water ———, in 0.01 M Na_2SeO_3 – – – –, in 0.01 M Na_3PO_4 – · – · – · –, and in 0.01 M $Na_2S_2O_3$ · · · · .

When free trimethylenediamine is added to $CoCl_2$ in water solution, $[Co(tn)(H_2O)_4]^{2+}$ and $[Co(tn)_2(H_2O)_2]^{2+}$ are formed, but very little $Co(tn)_3^{3+}$ [10] is obtained. Since $Co(spn)^{3+}$ is a derivative of $Co(tn)_3^{3+}$ which contains an alkyl cap bonded to one nitrogen of each trimethylenediamine residue, similar problems occur in its synthesis. Methanol is used as a solvent in the synthesis of $Co(spn)^{3+}$ to prevent coordination of water or hydroxide ion. Resolution was accomplished by using dibenzoyl-*d*-tartaric acid.

The electronic absorption spectrum of $[Co(spn)]I_3$ shown in Figure 1 exhibits a typical tris(diamine)-cobalt(III) absorption spectrum with octahedral transitions $A_{1g} \rightarrow T_{1g}$ (20.2 kK, $\epsilon = 82$) and $A_{1g} \rightarrow T_{2g}$ (28.3 kK, $\epsilon = 124$). In the presence of oxyanions the absorption spectrum shows the beginnings (at about 30.0 kK) of charge transfer bands due to intermolecular charge transfer from the polarizable oxyanions to the cationic metal complex. At much higher energy (44.0 kK) very high intensity absorption bands due to internal transitions of anions appear. At still higher energies (47.6 kK) an intramolecular electron-transfer transition, from the σ bonded nitrogen atom of spn to the cobalt(III) atom e_g level, occurs.[11]

$Co(spn)^{3+}$ as a Model fo9 $Co(tn)_3(oxyanion)^{+3-x}$ Outersphere Complexes

To illustrate the applicability of $Co(spn)^{3+}$ as a model for oxyanion ion-pairs of $Co(tn)_3^{3+}$ it is necessary to compare their structures. Just as $Co(tn)_3^{3+}$ has three possible ring conformations, so does $Co(spn)^{3+}$. Of the three possibilities, the tris-chair (each six-membered ring has the chair conformation), the lel-twist (each ring is skew boat), and the ob-twist form (each ring is a boat), only two have substantial populations. The tris-chair and lel-twist conformations shown in Figures 2 and 3 are the conformations which $Co(spn)^{3+}$ and $Co(tn)_3^{3+}$ adopt.[12] Molecular models show that the ob-twist conformation has large steric strain due to hydrogen interaction which causes this conformation to be of substantially higher energy than the other two. It is obvious from structural comparison that $Co(spn)^{3+}$ is a model for the $Co(tn)_3(oxyanion^{x-})^{+3-x}$ ion-pair just as $Co(sen)^{3+}$ is a model for the $Co(en)_3(oxyanion)^{+3-x}$ ion-pair.[6] The alkyl cap simulates constraint in the 1:1 ion-pair formed by hydrogen bonding between the amine hydrogen *a* of $Co(tn)_3^{3+}$ and the oxyanion along the C_3 axis of the complex.

The similarity between the CD spectra of $Co(spn)^{3+}$ and $Co(tn)_3^{3+}$ in the presence of oxyanions confirms $Co(spn)^{3+}$ as an ion-pair model. Figure 4 shows the CD spectrum of $[Co(spn)]I_3$ derived from the least soluble dibenzoyl-*d*-tartrate diastereomer. From the negative E_a and positive A_2 components (D_3 symmetry) of the octahedral $A_{1g} \rightarrow T_{1g}$ transition, the absolute configuration was determined. The CD spectrum of the least soluble diastereomer of $Co(spn)^{3+}$ shows opposite signs of the E_a and A_2 components in comparison with those of $(+)_{589}$-$[Co(en)_3]^{3+}$ and $(-)_{589}$-$[Co(tn)_3]^{3+}$, whose absolute configurations are known to be Λ from x-ray studies.[13,14] Thus the absolute configuration of the least soluble diastereo-

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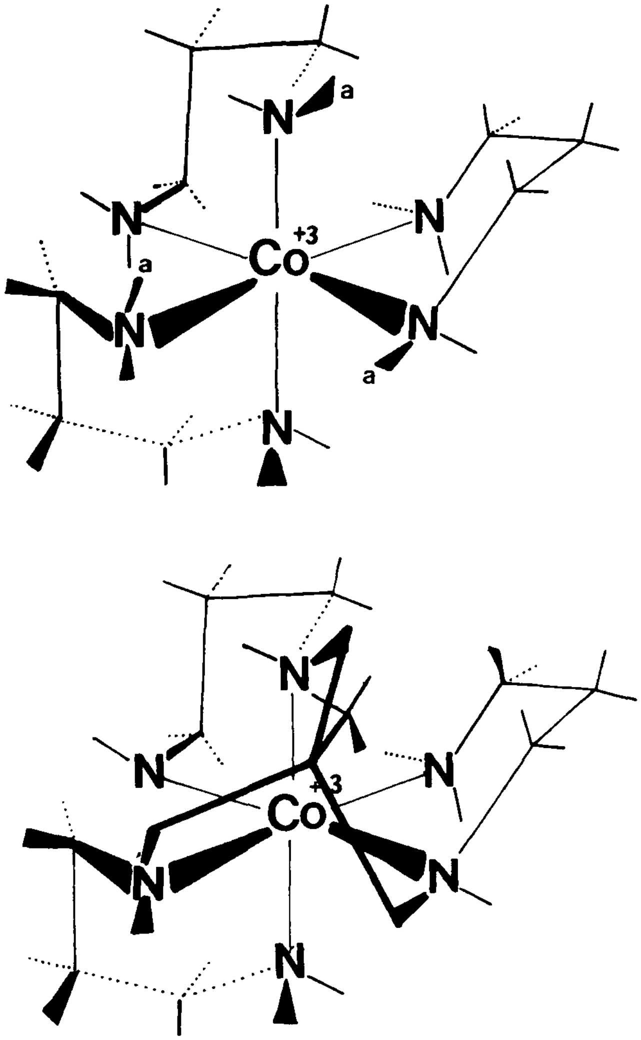

FIGURE 2 The tris-chair conformations of Λ-Co(spn)$^{3+}$ (lower figure) and of Λ-Co(tn)$_3^{3+}$ (upper figure, *a*'s represent potential bonding sites of an alkyl cap or oxyanion).

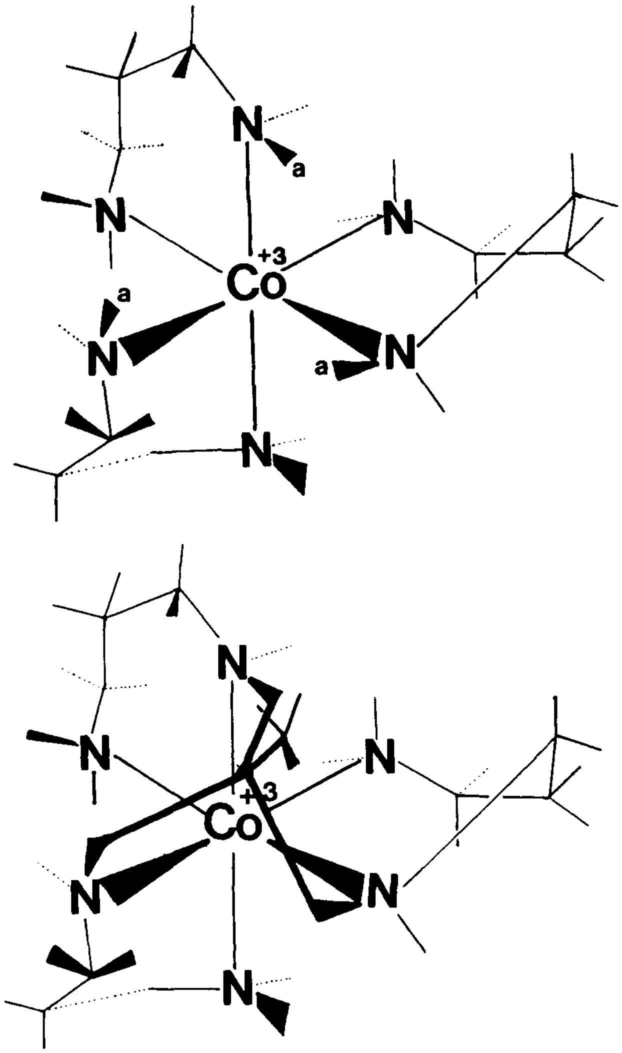

FIGURE 3 The lel-twist conformations of Λ-Con(spn)$^{3+}$ (lower figure) and of Λ-Co(tn)$_3^{3+}$ (upper figure, *a*'s represent potential bonding sites of an alkyl cap or oxyanion).

mer of Co(spn)$^{3+}$ is designated Δ. Comparison of the CD spectra of Δ-(+)-[Co(tn)$_3$]$^{3+}$ [7] and Δ-Co(spn)$^{3+}$ shows both complexes have negative E_a and positive A_2 components at approximately the same energy, as expected for Δ-tris(diamine) complexes.

There has been some controversy about the assignment of the E_a component to the low energy band in the $A_{1g} \rightarrow T_{1g}$ region. Several theoretical treatments[15–18] suggest that changes in the ligand–metal–ligand bond angle, θ, from $\theta < 90°$ to $\theta > 90°$ would reverse the signs and energies of the E_a and A_2 components. Consideration of the CD of Λ-Co(tn)$_3^{3+}$ ($\theta = 94.5$)[14] in the presence of highly charged oxyanions led Mason[19] to assign the low energy band to the E_a component on the basis that the intensity of the A_2 component is increased and the E component is decreased in the presence of oxyanions. This assignment indicates no sign or energy reversal of the T_{1g} band components as compared to Δ-Co(en)$_3^{3+}$ ($\theta < 90°$) and is in direct opposition to the proposal of Judkins and Royer.[20] Their assignment is based on a single crystal CD spectrum of Δ-(+)-[Co(tn)$_3$]Cl$_3$ · 4H$_2$O with light propagated parallel to the three-fold axis of the cation so that only the E component should appear. This spectrum indicates the high energy band is E and not

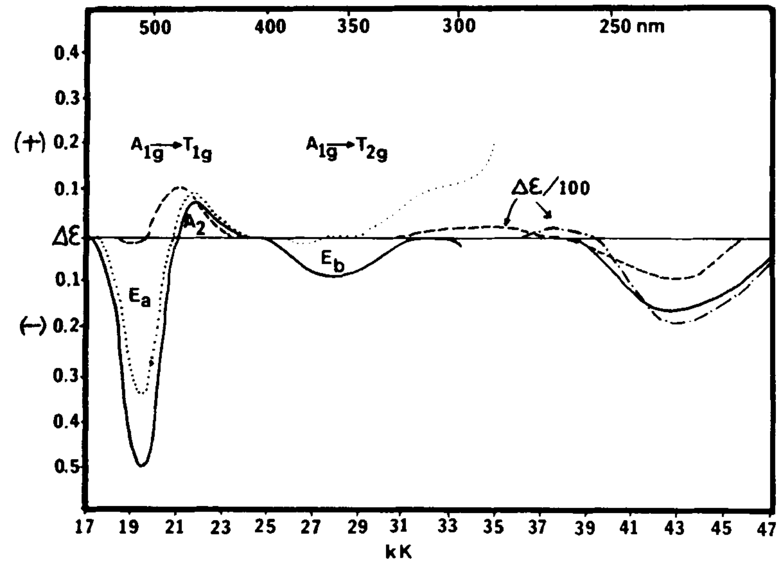

FIGURE 4 The circular dichroism spectrum of Δ-[Co(spn)] I_3 in water ——, in 0.01M Na_2SeO_3 – – – –, in 0.01M Na_3PO_4 – . – . – . –, and in 0.01M $Na_2S_2O_3$ . . . . . .

A_2, as previously assigned. To settle this uncertainty it is necessary to investigate other cases where $\theta > 90°$. Molecular models show that placing an alkyl cap on Co(tn)$_3^{3+}$ to form Co(spn)$^{3+}$ will not affect θ significantly. A single crystal CD spectrum of Δ-Co(spn)$^{3+}$ with light propagated parallel to the three-fold axis of the cation would be of great value here since it is expected that $\theta > 90°$. Butler and Snow[21] suggested that the conflicting results of the crystal and solution CD data might be caused by changes in ring conformation and θ.

The CD data for Δ-Co(tn)$_3^{3+}$ and Δ-Co(spn)$^{3+}$ listed in Table III reveal two striking differences. For Δ-Co(tn)$^{3+}$ and all of its ion-pairs the A_2 band area is greater than the E_a band area, while the reverse is true for Δ-Co(spn)$^{3+}$. Also the intensity of the E_a transition in Δ-Co(spn)$^{3+}$ is more than five times larger than its counterpart in Δ-Co(tn)$_3^{3+}$, while the A_2 component is only half of the intensity of that in Δ-Co(tn)$_3^{3+}$. The overall greater rotational strength of Δ-Co(spn)$^{3+}$ can be explained by the presence of asymmetric nitrogens bonded to the alkyl cap and by the same effect which causes the rotatory strength of Δ-Co(en)$_3^{3+}$ to be larger than that of Δ-Co(tn)$_3^{3+}$ by a factor of ten. In the Co-en chelate rings (Figure 5(a)) and in the chelate rings of Co(spn)$^{3+}$

TABLE III
The variation of the circular dichroism, Δε, of Δ-[Co(spn)] I_3 with various oxyanions in water solution

				E_b		
Δ-Co(tn)$_3^{3+}$		E_a	A_2			
Δ-[Co(spn)] I_3[a]		−0.08(18.69kK)	+0.17(21.0kK)	−0.084	0	−15.91
		−0.50(19.2kK)	+0.076(21.7kK)	(27.0kK)	(35.7kK)	(43.5kK)
Anion	Concentration					
$S_2O_3^{2-}$	0.01M	−0.36	+0.080	−0.013	+0.20[b]	c
SeO_3^{2-}	0.01	−0.0087	+0.114		+2.11	−8.78
SeO_4^{2-}	0.01	−0.41	+0.067	−0.056	0	−6.95
SO_3^{2-}	0.01	−0.40	+0.082	−0.060	0	−5.93
SO_4^{2-}	0.01	−0.40	+0.084	−0.058	0	−4.70
PO_4^{3-}	0.01	0	0	0	+2.17	−17.51
OH^-	0.001M[d]	0	0	0	0	0

[a] Concentration of [Co(spn)] I_3 was 0.001M in all samples.
[b] At 34.5kK.
[c] Dynode voltage too high and optical activity too low to measure.
[d] pH = 11.1 is the same pH as 0.01M solution of Na_3PO_4.

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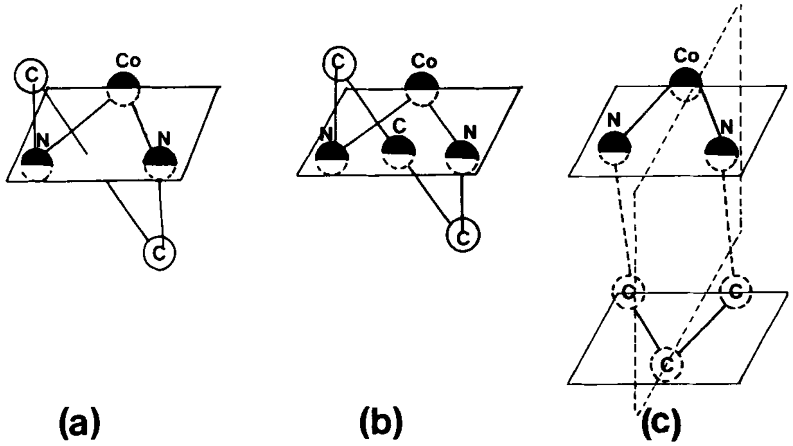

FIGURE 5 (a) Five-membered chelate ring of $Co(en)_3^{3+}$ contains no symmetry plane; (b) six-membered chelate ring of $Co(spn)^{3+}$ in the lel-twist conformation contains no symmetry plane; (c) six-membered chelate ring of $Co(tn)_3^{3+}$ in the tris-chair conformation contains symmetry plane.

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(Figure 5(b)), whose conformation was determined by molecular models, the lel-twist form is favored. Two carbon atoms are arranged above and below the plane formed by the central metal atom and the two nitrogen atoms. In the Co-tn chelate ring, when the complex conformation is tris-chair, the three methylene groups are located on one side of the plane of the cobalt and the two nitrogen atoms (Figure 5(c)). In the tris-chair conformation (70% of the population of $Co(tn)_3^{3+}$ in aqueous solution)[12] each chelate ring has approximately a plane of symmetry which might be expected to decrease the chirality and the rotatory strength. This is part of the reason for the very low rotatory strength of Δ-$Co(tn)_3^{3+}$. (Another reason for the lower rotatory power arises from Moffit's model[22] which states that crowding of the carbon chains of the ligands in space is a source of optical activity. A six-membered ring has less crowding than a five-membered one.) Molecular models indicate a strong preference for the lel-twist conformation of Δ-$Co(spn)^{3+}$ which allows the alkyl groups on the secondary nitrogens to occupy the favored pseudo-equatorial positions.[23] The tris-chair conformation requires one of the alkyl groups to occupy an axial position. On this basis when we compare Δ-$Co(tn)_3^{3+}$ (tris-chair) to Δ-$Co(spn)^{3+}$ (lel-twist) we are going from a conformation in which each ring has a plane of symmetry to one which has no plane of symmetry. From this consideration it is not surprising that Δ-$Co(spn)^{3+}$ has an overall greater rotatory strength.

Since Δ-$Co(spn)^{3+}$ is a model for ion-pairs such as Δ-$Co(tn)_3(PO_4)$, Δ-$Co(tn)_3(SO_4)^+$, and Δ-$Co(tn)_3$-$(SeO_3)^+$, examination of its CD spectrum (Figure 4) in the presence and absence of oxyanions should help elucidate the origin of oxyanion ion-pair induced CD changes. Normally tris(diamine)cobalt(III) complexes exhibit a decrease in the E_a and increase in the A_2 components of the $A_{1g} \rightarrow T_{1g}$ transition accompanying the formation of ion-pairs with oxyanions. A similar change occurs in comparing the CD spectrum of Λ-$Co(en)_3^{3+}$ to that of Λ-$Co(sen)^{3+}$, which is an ion-pair model for tris-(diamine)cobalt(III) complexes with five-membered rings. The alkyl cap of $Co(sen)^{3+}$ locks the conformation into the lel structure, which is already the most stable conformation in the absence of the alkyl cap. Therefore, generation of asymmetric nitrogens either by hydrogen bonding of oxyanions to the coordinated amines or by disposition of an alkyl cap is responsible for the CD changes.[6] When the CD spectrum of Δ-$Co(tn)_3^{3+}$ is compared to that for Δ-$Co(spn)^{3+}$, which is an ion-pair model for tris(diamine)cobalt(III) complexes with six-membered chelate rings, the E_a component increases while the A_2 component decreases. These reverse changes occur because the disposition of an alkyl cap on $Co(tn)_3^{3+}$ not only generates asymmetric nitrogens but also changes the conformation from the most stable tris-chair conformation of $Co(tn)_3^{3+}$ to the lel-twist conformation of $Co(spn)^{3+}$.

Summarized in Figure 6 are the CD changes that occur with oxyanion ion pairing. In each case where the conformation is not changed by the oxyanion or the alkyl cap, the generation of asymmetric nitrogens is the dominant effect, causing the E_a and A_2 components to decrease and increase, respectively. In cases where the conformation is changed by the oxyanion or the alkyl cap, this effect dominates and

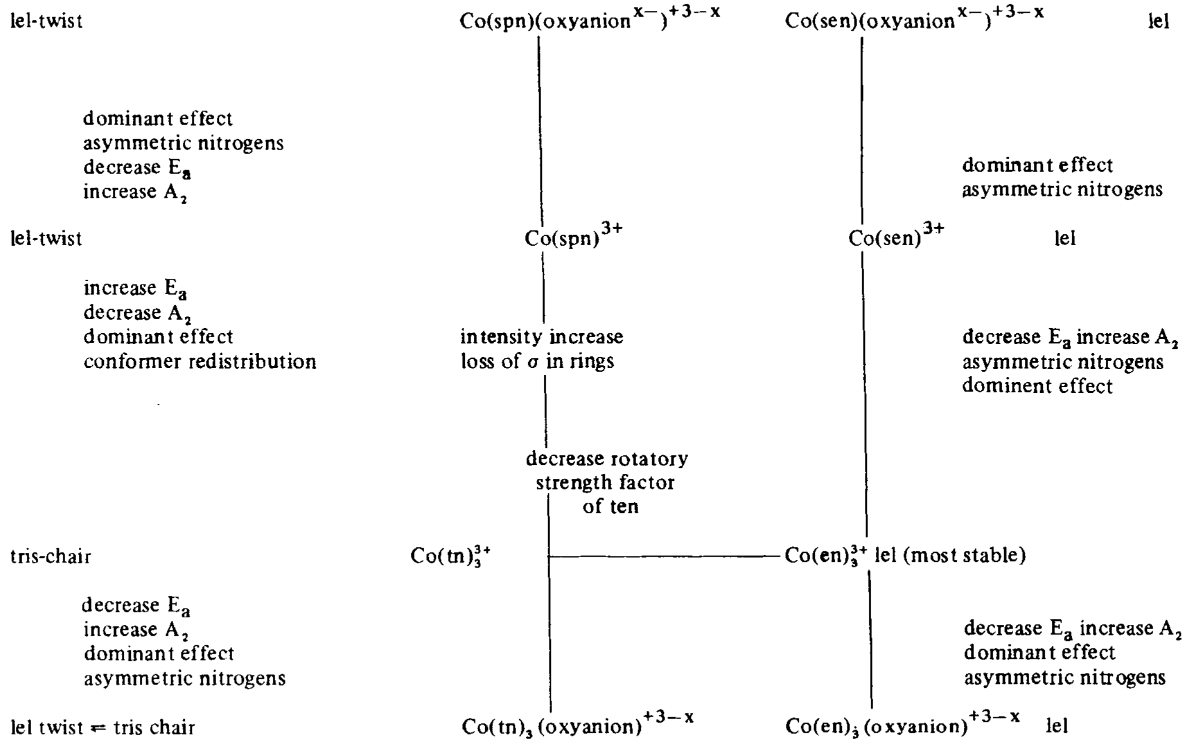

FIGURE 6 Circular dichroism changes and their origins

causes E_a to increase and A_2 to decrease. All of the complexes in Figure 6 fit nicely into this scheme with the exception of Δ-$Co(tn)_3(oxyanion)^{+3-x}$ where a decrease in the E_a and an increase in the A_2 components relative to Δ-$Co(tn)_3^{3+}$ occurs. Strain energy minimizing calculations by Butler and Snow[21] indicate, however, that in the presence of oxyanions, the lel-twist conformation of $Co(tn)_3^{3+}$ is no more favorable than the tris-chair conformation. Therefore, it is likely that substantial fractions of $Co(tn)_3^{3+}$ in the presence of oxyanions will adopt both the lel-twist and tris-chair conformations. Most probably, here the dominant effect arises from the asymmetric nitrogens and not conformational changes.

Further proof of the dominance of the asymmetric nitrogens in the absence of conformational change is evident from the CD changes of Δ-$Co(spn)^{3+}$ in the presence of oxyanions (Table III). In this case the alkyl cap is presumed already to have locked the conformation as lel-twist and the only change that occurs is the generation of new asymmetric nitrogens which decrease the E_a and increase the A_2 components. The 250 MHz PMR spectrum of $Co(spn)^{3+}$ exhibits complex splitting in the methylene region, supporting a single conformation. This is in contrast to the broad, featureless methylene region of $Co(tn)_3^{3+}$[10] expected for rapid conformational change. Figure 7 shows that the presence of oxyanions such as selenite causes only small chemical shifts and minor splitting changes in the PMR spectrum of $Co(spn)^{3+}$. The effect of selenite ion is the generation of asymmetric centers by hydrogen bonding so that the protons affected most are situated on the methylene carbons adjacent to the primary nitrogens. On each of these methylene carbons one proton, labelled D in Table I, is pointed directly toward the primary amine while the other D′, points away in a direction approximately parallel to the C_3 axis. Proton D is assigned to the broad featureless band at 2.72 ppm because of its proximity to the nitrogen, which tends to broaden resonances due to quadrupolar coupling.[24] The other affected multiplet of the proper intensity at 3.04 ppm arises from proton D′. (Other multiplet assignments were based on comparisons to the PMR of spn and $Co(sen)^{3+}$.) From these data it is evident that no significant conformational changes of $Co(spn)^{3+}$ occur in the presence of oxyanions.

The identity of the oxyanion in determining the CD changes of Δ-$Co(spn)^{3+}$ is much more important than with other tris(diamine)cobalt(III) complexes. Surveying the data of Table III for Δ-$Co(spn)^{3+}$ shows that sulfite and sulfate oxyanions cause only minor

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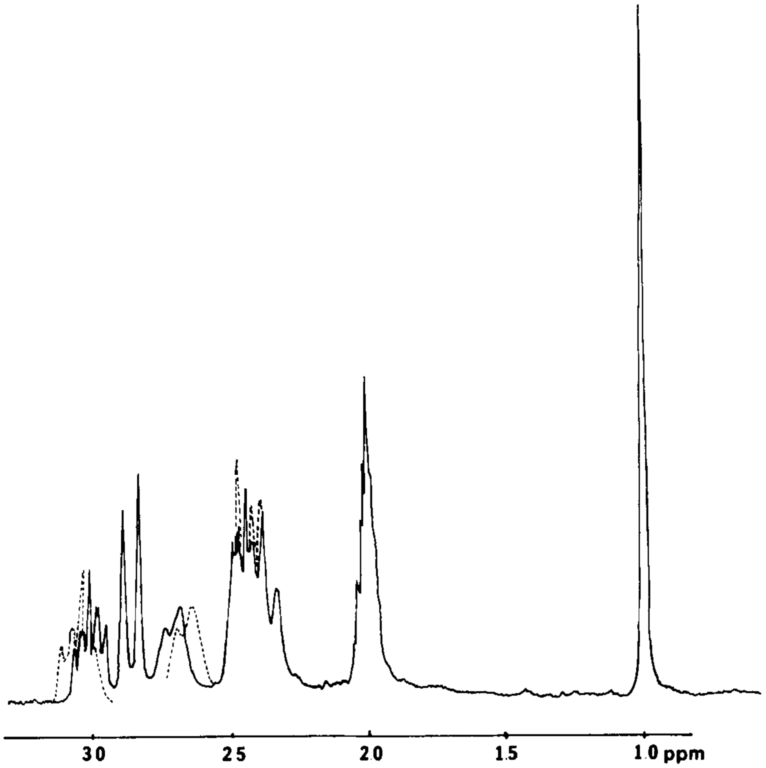

FIGURE 7 The PMR spectrum of $[Co(spn)]Cl_3$ in D_2O ———, and in 0.01M selenite solution (D_2O) – – – –.

CD changes, both in the same fashion. However, selenate ion (tetrahedral) is much less effective in causing CD changes than its trigonal counterpart selenite. This is expected since the oxygen atom charge density which favors hydrogen bonding is greater for trigonal oxyanions than for tetrahedral ones. Since phosphate ion has a minus three charge its oxygen charge density is very high and in other tris(diamine)cobalt(III) complexes it has been the most effective oxyanion for decreasing the E_a and increasing the A_2 components of the octahedral $A_{1g} \rightarrow T_{1g}$ transition. The results with phosphate (0.01 M) in the presence of Δ-$Co(spn)^{3+}$ are very perplexing since atypical CD changes occur. The E_a, A_2, and E_b (component of T_{2g} band) bands are reduced to zero intensity while the charge transfer CD band in the uv increases in intensity. The anamolous results with phosphate are not due to phosphate ion complexation since no changes in the 60 MHz spectrum of $Co(spn)^{3+}$ were observed in the presence of phosphate. A basic solution (NaOH) of the same pH (11.1) causes all optical activity to be lost. From these observations it is assumed that base hydrolysis occurs, causing racemization. While it is thought that phosphate remains in the outer-sphere, it must play a role in stablizing the optically active charge transfer transition of Δ-$Co(spn)^{3+}$ in the presence of hydroxide.

OTHER TRANSITION METAL COMPLEXES OF SPN

The ligand spn was found to coordinate readily with transition metals other than cobalt. In the presence of Ni(II) salts a pink crystalline iodide, $[Ni(C_{14}H_{36}N_6)]I$, was isolated. Its visible region absorption spectrum shows two low intensity bands (18.52 kK, $\epsilon = 7.1$ and 29.24 kK, $\epsilon = 8.4$) typical of an octahedral tris (diamine) nickel(II) complex. The tetraphenylborate and nitrate salts were also isolated. Interaction of spn (1:1 mole ratio and copper(II) chloride, copper(II) nitrate trihydrate, or copper(II) acetate monohydrate in water, methanol or ethanol did not yield an octahedral purple complex as does copper(II) chloride with sen. Instead a blue complex was isolated. This suggests that only four of the six nitrogens function as strong donors to any one copper atom. The other two nitrogens (in one of the trimethylenediamine residues) can coordinate to another copper atom. In this fashion there can be formed square planar copper(II) complexes which are held together in a macromolecular array by the alkyl group connecting the three diamine residues.[25] The analytical data for the blue copper(II) complex do not fit the formulations $Cu_3(spn)_2Cl_6$ or $Cl(spn)_3Cl_8$. The blue product is probably a mixture of these and other macromolecular complexes. Its electronic absorption spectrum showed a very broad band at 15.9 kK.

SUMMARY

The circular dichroism changes that occur with $Co(sen)^{3+}$ and $Co(spn)^{3+}$ in the presence of oxyanions suggest that charge transfer is not essential. It appears that two effects cause opposite changes in the E_a and A_2 components of the octahedral T_{1g} transition. If a conformational redistribution of the chelate rings in the complex occurs, this effect dominates and causes the E_a to increase at the expense of the A_2 component. When the conformation does not change, the generation of asymmetric centers via hydrogen bonding of the complex with the oxyanion causes the E_a component to decrease as the A_2 component increases. When these complex molecules change conformation and at the same time asymmetric nitrogens are generated, the conformational effect is dominant over the vicinal effect.

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