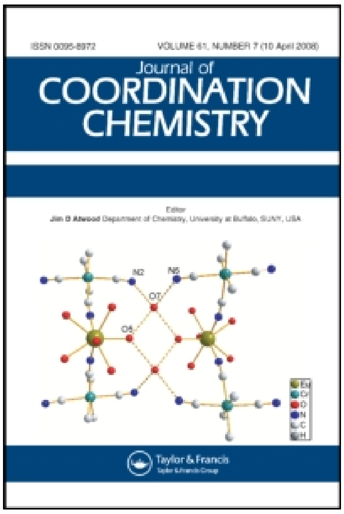

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ISOMERS OF TRIS(2-METHYL-1,3-PROPANEDIAMINE)COBALT(III)—A COMPLEX OF A PROCHIRAL SINAMBIC LIGAND

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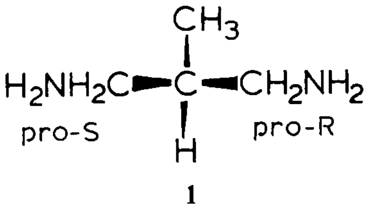
The complex ion $[Co(metn)_3]^{3+}$ (metn = 2-methyl-1,3-propanediamine) has been synthesized and the facial and meridional isomers have been separated by column chromatography and identified by ^{13}C and ^{1}H NMR spectroscopy. This is the first reported separation of isomers of a tris complex where the isomerism is due to the presence of prochiral ligands with enantiotopic donor atoms (prochiral "sinambic" ligands). The ^{13}C and visible spectra indicate a large contribution from conformers containing skew-boat chelate rings in solution. An incomplete (owing to disorder) crystal structure shows a tris-(skew-boat) conformer for the cationic complex present in *fac*-$[Co(metn)_3]Cl_3$.

INTRODUCTION

In recent articles[1,2] we have discussed isomerism in complexes owing to the presence of bidentate ligands with enantiotopic donor atoms ("ligators"). Since such ligands have rotationally nonequivalent and, therefore, distinguishable ligators, they can give rise to isomerism in metal ion complexes in the same way as unsymmetrical (AB) bidentates. The term "sinambic" (*L. sine ambito*: "without rotation") has been proposed[1] to designate bidentates with rotationally nonequivalent ligators whether or not the ligands possess non-trivial symmetry – as do those with enantiotopic donor atoms.

Octrahedral tris chelates containing three identical sinambic ligands can exist in two isomeric forms – facial, having idealized C_3 symmetry, and meridional, having C_1 symmetry.[2] Such isomers are well-known for tris chelates of unsymmetrical bidentates. In recent years, these isomers have been separated for tris chelates of meso bidentates where enantiotopic donor atoms are in oppositely chiral portions of the molecule.[3–6] Such isomers have not, however, been separated for a third type of sinambic ligand – prochiral bidentates where the enantiotopic ligators are in oppositely prochiral portions of the molecule and may, therefore, be uniquely labeled *pro-R* ("pR") and *pro-S* ("pS")[7] as shown for 2-methyl-1,3-propanediamine (**1**), the ligand which has been used in our studies. With this and other prochiral sinambic ligands, facial and meridional isomers are also possible (Figure 1).



$H_2NH_2C-C(CH_3)(H)-CH_2NH_2$

1

In this paper, we report the synthesis of tris-(2-methyl-1,3-propanediamine)cobalt(III) chloride, $[Co(metn)_3]Cl_3$, the separation of the facial and meridional geometrical isomers, and their characterization. The Δ and Λ enantiomers of the isolated

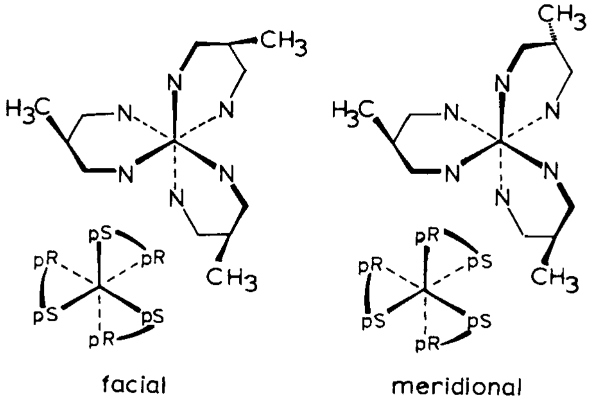


FIGURE 1 Facial (C_3 symmetry) and meridional (C_1 symmetry) isomers of $[Co(metn)_3]^{3+}$.

geometrical isomers have not been separated. In the only previously reported study on tris prochiral diamine complexes, facial/meridional isomerism was not discussed.[8]

EXPERIMENTAL

Preparation of 2-Methyl-1,3-propanediamine Dihydrochloride

The ligand was prepared by a procedure similar to that employed by Mann.[9] A slurry of potassium phthalimide (100 g, 0.53 mol) and commercially available (Chemical Samples Co.) 1-bromo-3-chloro-2-methylpropane (45 g, 0.26 mol) in N,N-dimethylformamide was refluxed for 4 h with stirring, cooled, and KCl and KBr were removed by filtration. Addition of the filtrate to rapidly stirred water caused the precipitation of 75 g (82% yield) of water-insoluble 1,3-diphthalimido-2-methylpropane, $C_6H_4(CO)_2NCH_2CH(CH_3)CH_2N(CO)_2C_6H_4$. *Anal.* Calcd. for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N 8.04; Found: C, 68.83; H, 4.44; N, 8.13.

The diphthalimide was hydrolyzed by heating it with con hydrochloric acid (4 g of the diphthalimide in 15 ml con HCl) for 18 h at 170°C in a sealed Pyrex tube (caution). The cooled mixture was filtered, the filtrate was evaporated to near dryness, 10 ml of absolute methanol were added, and evaporation was continued to give about 2 ml of liquid. Addition of 100 ml of ethyl ether caused the precipitation of 0.64 g (35% yield) of 2-methyl-1,3-propanediamine dihydrochloride as a fine white powder. *Anal.* Calcd. for $C_4H_{12}N_2 \cdot 2HCl$: C, 29.83; H, 8.76; N, 17.39. Found: C, 30.15; H, 8.63; N, 17.23.

Synthesis of Tris(2-methyl-1,3-propanediamine)-cobalt(III) Chloride

The dihydrochloride salt of the ligand (1.1 g, 7 mmol) was dissolved in 1 ml of H_2O and approximately 95% of the theoretical amount of 6 M NaOH necessary to give the free diamine was added. Upon addition of 95% ethanol to bring the volume to 10 ml, NaCl precipitated and was removed by filtration. The filtrate was added to a solution of $CoCl_2 \cdot 6H_2O$ (0.5 g, 21 mmol) in 100 ml ethanol to give a brownish orange solution which was neutralized with glacial acetic acid, stirred for 1–2 h, and oxidized by bubbling with oxygen overnight. The solution was reduced in volume to 25 ml and the solid complex removed by filtration, washed with 5 ml methanol and air-dried to give 0.8 g (80% yield) of product *Anal.* Calcd. for $Co(C_4H_{12}N_2)_3Cl_3$: C, 33.54; H, 8.44; N, 19.56. Found: C, 33.81; H, 8.20; N, 19.77.

Isomer Separation

Aqueous solutions of the chloride salt of the complex were chromatographed on a 2.6 cm x 200 cm column packed with SP Sephadex C-25 cation exchange resin employing 0.2 M Na_2SO_4 as the eluant and a flow rate of about 0.7 ml/min. Two well-defined orangish yellow bands, the first corresponding to the facial isomer and the second to the meridional (*vide infra*) in a ratio of 1:3:1, were eluted. The relative abundances were determined for combined fractions from several chromatographic separations using the absorbances at the maxima of the longest wavelength d-d bands and the extinction coefficients determined by us (*vide infra*).

Solid chloride salts of the two isomeric complexes were prepared by evaporating the eluted fractions to 50 ml, filtering to remove Na_2SO_4, precipitating the remaining sulfate ion by careful addition of $BaCl_2$ solution, centrifuging, and allowing the decanted supernatant liquid to evaporate to dryness. The complex was dissolved in a minimum amount of con hydrochloric acid, the solution was filtered to remove the less soluble $BaCl_2$ and NaCl salts, and the filtrate was allowed to evaporate to yield well-defined orange crystals. *Anal*: Calcd. for $Co(C_4H_{12}N_2)_3Cl_3$: C, 33.54; H, 8.44; N, 19.56. Found (facial): C, 33.31; H, 8.20, N, 19.37. Found (meridional): C, 33.47; H, 8.37; N, 19.36.

Physical Measurements

Visible spectra of the chloride salts of the isomeric complexes were determined for approximately 0.003 M aqueous solutions on a Cary Model 15 RI spectrophotometer. Proton and natural abundance ^{13}C NMR spectra were recorded at approximately 35°C on a Varian FT-80 NMR spectrometer. All NMR spectra were determined in D_2O solution with external TMS as the reference. The ^{13}C NMR spectra were collected with a 0.4 s acquisition time, a 4 μs pulse width (equivalent to a 40° pulse), a 4000 Hz sweep width, a 0.1-s pulse delay, and noise-modulated proton decoupling. The ^1H NMR spectra were collected with an 8-s acquisition time, a 20 μs pulse width (43° pulse), a 1000 Hz sweep width, and no pulse delay. An accuracy better than ±0.05 ppm is estimated for all reported chemical shifts.

X-ray Diffraction

Preliminary oscillation and Weissenberg photographs of a single crystal of *fac*-[Co(metn)$_3$]Cl$_3$ grown from aqueous solution were consistent with the space group $P6_322$ ($00l$ absent for $l = 2n + 1$ and Laue symmetry of $6/mmm$). The dimensions of the hexagonal unit cell were $a = b = 11.80$ Å, $c = 8.066$ Å. Intensity data were collected on an automated Picker diffractometer.

Attempts to solve the structure were only partially successful. The Co atom was located at 1/3, 2/3, 1/4 by Patterson methods and subsequent Fourier syntheses revealed the positions of the remaining nonhydrogen atoms except for the methyl carbon atoms. The structure was found to be disordered with a crystallographic twofold axis passing through each of the methine carbon atoms (the molecular ion lies at a site of D_3 symmetry). This disorder required that the methyl groups be half-weighted; however, even with half-weighting, the methyl carbon atom thermal parameters were unacceptably large, bond lengths involving the methine carbon atoms were anomalous, and the R factor failed to drop to a reasonable value. Least-squares refinement of the nonhydrogen atoms with anisotropic temperature factors for cobalt and chlorine, with calculated positions for hydrogen atoms, and with half-weighted methyl carbon atoms converged to an unweighted R factor of $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.138$. Attempts to refine the structure further were unsuccessful.

RESULTS AND DISCUSSION

Isomer Separation

A number of observations on the use of Sephadex ion exchange resins in the separation of isomeric complexes indicate that symmetry has little effect on the elution order of facial/meridional tris chelates.[10] In our system, the facial isomer elutes first. That the ratio of facial to meridional abundances of 0.32 is very near to the value of 0.33 expected from statistical factors alone,[2] indicates that there may be little difference in enthalpy (and, therefore, strain as a result of steric constraints) between the two isomers. The agreement may, however, be fortuitous. Experimental isomer distributions in cobalt(III) complexes are known to be highly dependent on synthetic conditions.[11]

Nuclear Magnetic Resonance

The ^{13}C and ^{1}H NMR spectra (Table I) clearly distinguish between the facial and meridional isomers (Figure 1). *Fac*-[Co(metn)$_3$]$^{3+}$ exhibits the ^{13}C NMR spectrum expected for a C_3-symmetry species (Figure 2). The ^{13}C NMR spectrum of *mer*-[Co(metn)$_3$]$^{3+}$, though not containing the theoretical maximum number of peaks owing to accidental overlap, exhibits additional resonances as expected for a C_1-symmetry molecular ion. As a result of ^{1}H-^{1}H, ^{1}H-^{59}Co, and ^{1}H-^{14}N coupling and quadrupolar interactions from nitrogen,[12] only the methyl proton resonances (Figure 3) in the ^{1}H NMR spectra are sufficiently well resolved to permit the two isomers to be distinguished. NMR spectral differences have previously been used to identify facial and meridional isomers in the tris meso complexes [Co(*ms*-bn)$_3$]$^{3+}$ ("bn" = 2,3-butanediamine),[3,13] [Co(*ms*-ptn)$_3$]$^{3+}$ ("ptn" = 2,4-pentanediamine),[4] and [Co(*cis*-chn)$_3$]$^{3+}$ ("chn" = 1,2-cyclohexanediamine).[5]

The six-membered chelate rings formed by bidentate 2-methyl-1,3-propanediamine can exist as four conformers – two chair forms (one with an axial methyl group, the other with an equatorial

TABLE I
NMR chemical shifts and coupling constants

		^{13}C(δ, ppm)			^{1}H(δ, ppm[$^3J_{HH}$, Hz])
Compound	Conc., M	$\overset{\vert}{\underset{\vert}{\text{CH}_2}}$	$-\overset{\vert}{\underset{\vert}{\text{C}}}\text{H}$	$-\text{CH}_3$	$-\text{CH}_3$
metn·2HCl	1.0	44.05	31.51	15.72	1.70[6.7]
fac-[Co(metn)$_3$]Cl$_3$	0.09	45.70	31.60	17.56	1.38[6.0]
		45.51			
mer-[Co(metn)$_3$]Cl$_3$	0.13	45.97	31.90	17.81	1.43
		45.73	31.78	17.65	1.41
		45.58	31.58		1.36
		45.18			1.34

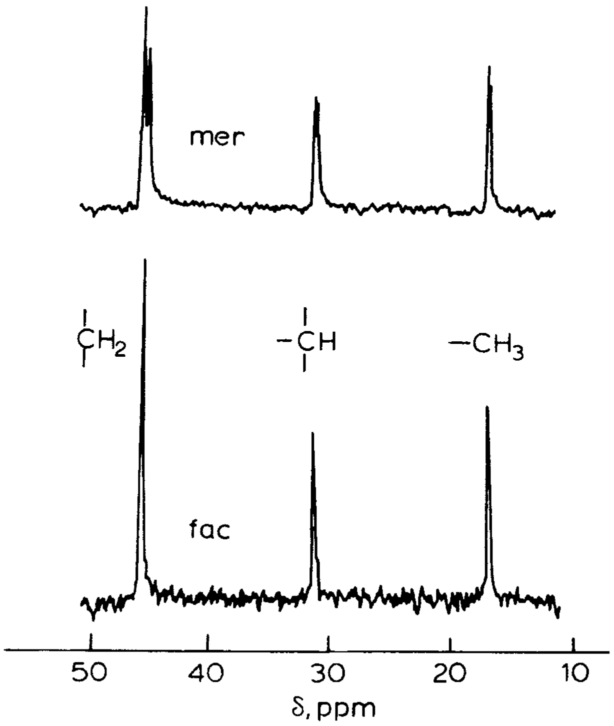


FIGURE 2 ^1H-decoupled ^{13}C NMR spectra of *fac*- and *mer*-$[Co(metn)_3]^{3+}$ in D_2O solution.

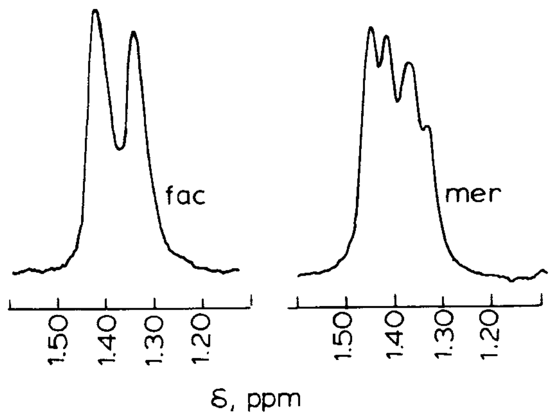


FIGURE 3 Methyl-region ^1H NMR spectra of *fac*- and *mer*-$[Co(metn)_3]^{3+}$ in D_2O solution.

methyl group) and two enantiomeric skew-boat forms (Figure 4).[14] The boat conformer is unfavorable and not expected to be a contributing form.[14] Isomer enumeration methods[15] allow us to calculate that owing to this chelate ring isomerism, either the Δ or the Λ forms of *mer*-$[Co(metn)_3]^{3+}$ and *fac*-$[Co(metn)_3]^{3+}$ can exist as 64 and 24 unique conformers, respectively. Owing to the sinambic nature of 2-methyl-1,3-propanediamine, many more conformers are possible for tris chelates of this ligand than for tris chelates of the parent ligand, 1,3-propanediamine ("tn").[14] Our NMR spectra are for the time-averaged conformers, as a result of the highly flexible nature of six-membered chelate rings. We have proposed that NMR differentiation of facial and meridional isomers owing to symmetry differences is enhanced when the chelate ring is flexible.[12] Thus, in the C_1-symmetry complex *mer*-$[Co(metn)_3]^{3+}$, where the three chelate rings are nonequivalent (as in all meridional octrahedral tris chelates), each ring is expected to exhibit a different time-averaged conformation (*i.e.*, the fraction of time spent in each conformational form will differ from ring to ring) and, therefore each ring will have different chemical shifts for its NMR-active atoms. This is the situation found for *mer*-$[Co($*ms*-bn$)_3]^{3+}$.[13] With $[Co($*cis*-cpn$)_3]^{3+}$ ("cpn" = 1,2-cyclopentanediamine),[6] where the relatively rigid cyclopentanediamine ring tends to maintain a more fixed conformation of the chelate ring, and in $[Co(pn)_3]^{3+}$ ("pn" = 1,2-diaminopropane),[16] where the chelate ring is locked into a fixed conformation by the requirement that the methyl substituent be equatorial, NMR fails to identify the facial and meridional isomers. In fact, however, we recognize that this is a somewhat overly simplified model since it is necessary that the conformational differences be reflected in NMR chemical shift differences. Work on other complexes indicates that such may be the case for ^{13}C

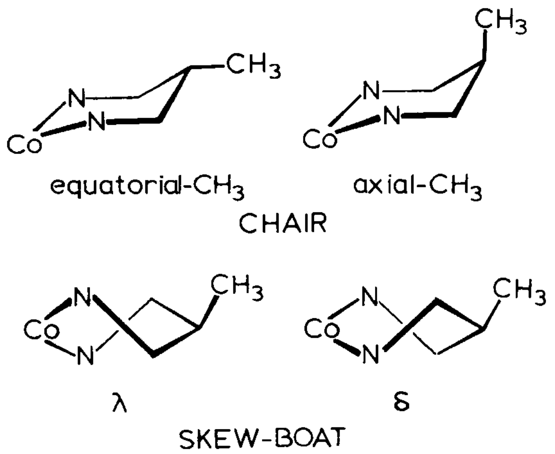


FIGURE 4 Conformations of 2-methyl-1,3-propanediamine chelate rings.

NMR if bond angles in the vicinity of the carbon of interest vary with the conformer.[17]

Force-field calculations on $\mathrm{M(tn)_3}$ complexes[18] indicate that although the all-chair form is the lowest energy conformer, other conformational forms are sufficiently close in energy that several conformations will exist in equilibrium in solution owing to entropy effects – a result which is in agreement with experimentation.[19] Unfortunately calculations are not available for 2-methyl-1,3-propanediamine complexes; however, ^{1}H NMR data for $\mathrm{Ni(ettn)^{2+}}$ ("ettn" = 2-ethyl-1,3-propanediamine) indicate that the presence of a substituent at the 2-position increases the probability of a chair conformation for the chelate ring.[20] On the other hand, the x-ray diffraction results (*vide infra*) show the presence of only skew-boat conformers in the solid state structure of $\mathrm{[Co(metn)_3]^{3+}}$. Moreover, the ^{13}C NMR and visible spectra discussed below indicate that the skew-boat conformation may be significant in our system.

Atoms which are enantiotopic in free bidentate ligands become diastereotopic in chiral complexes such as octahedral tris chelates. Of the four tris chelates containing diamine sinambic ligands with enantiotopic donor atoms (in the free ligand) whose ^{13}C NMR spectra have now been reported, two ($[\mathrm{Co}(\mathit{ms}\text{-}\mathrm{bn})_3]^{3+}$[13] and $[\mathrm{Co}(\mathit{cis}\text{-}\mathrm{chn})_3]^{3+}$[5]) contain five-membered chelate rings and two ($[\mathrm{Co}(\mathit{ms}\text{-}\mathrm{ptn})_3]^{3+}$[4] and $\mathrm{[Co(metn)_3]^{3+}}$) contain six-membered chelate rings. Spectra of the facial isomers of the first two compounds show a much greater ^{13}C chemical shift differential between diastereotopic carbon atoms ($\Delta\delta$ = 1.0 to 5.9 ppm)[5,13] than do those of the last two compounds ($\Delta\delta$ = 0.2 to 0.3 ppm).[4] This is not unexpected since in the five-membered rings, diastereotopic atoms are in conformationally dissimilar portions of the ligand. For example, in *fac*-$[\mathrm{Co}(\mathit{ms}\text{-}\mathrm{bn})_3]^{3+}$, diastereotopic methyl groups differ in axiality.[13] On the other hand, in the six-membered rings, whether chair or skew-boat, the conformational environments of diastereotopic carbon atoms are similar.

Downfield shifts of the ^{13}C NMR resonances of the methylene and methine carbon atoms of 2-methyl-1,3-propanediamine relative to the free ligand (as the dihydrochloride) occur upon coordination. This observation contrasts with the upfield shifts of central carbon atoms of 1,3-propanediamine which are observed upon coordination.[21] We have determined δ values for the central and terminal carbon atoms of 1,3-propanediamine of 36.75, 40.05 ppm for tn, 26.55, 38.62 ppm for tn·2HCl, and 25.68, 38.97 ppm for $\mathrm{[Co(tn)_3]^{3+}}$. It may be that the upfield shift of the central carbon atom ^{13}C NMR resonance in the 1,3-propanediamine system is due to a γ or gauche shift[22,23] associated with coordination of a metal ion γ to the central carbon of the six-membered chelate ring. Molecular models indicate and calculations from x-ray structure results[24] show that the M-N-C-C dihedral angle for coordinated 1,3-propanediamine decreases upon going from a skew-boat to a chair conformer. A decrease in a gauche dihedral angle is often associated with an upfield ^{13}C NMR shift.[22,23] Moreover, this change causes a decrease in the C-C-C angle of the six-membered ring.[24] There is some evidence that a decrease in a bond angle at a carbon atom as a result of structural modifications in a coordination complex is correlated with an upfield ^{13}C NMR shift for that atom.[17] It may be, therefore, that the downfield ^{13}C NMR shift of the central atom of the chelate ring which occurs with coordination of 2-methyl-1,3-propanediamine compared to the upfield shift which occurs with 1,3-propanediamine indicates a relative stabilization of the skew-boat conformer in the former system.

Visible Spectroscopy

There is little difference in the positions of the d-d bands for the facial and meridional isomers of $\mathrm{[Co(metn)_3]^{3+}}$. The bands corresponding to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions lie at 484.0 ($\epsilon = 72.7 \pm 0.7$ l mol^{-1} cm^{-1}) and 348.5 nm for the facial isomer and at 485.0 ($\epsilon = 78.3 \pm 0.8$ l mol^{-1} cm^{-1}) and 348.0 nm for the meridional. As found for $[\mathrm{Co}(\mathit{ms}\text{-}\mathrm{ptn})_3]^{3+}$[4] and $[\mathrm{Co}(\mathit{cis}\text{-}\mathrm{chn})_3]^{3+}$[5] (but not for $[\mathrm{Co}(\mathit{ms}\text{-}\mathrm{bn})_3]^{3+}$!),[3] the lower symmetry isomer exhibits a higher extinction coefficient – not an unexpected result.

Studies on several cobalt(III) complexes of 1,3-propanediamine and its derivatives indicate that the lowest energy d-d absorption band lies at lower energies for chair conformations of the chelate rings than for skew-boat conformations.[25-27] Thus, $\mathrm{[Co(tn)_3]^{3+}}$, *fac*- and *mer*-$[\mathrm{Co}(\mathit{ms}\text{-}\mathrm{ptn})_3]^{3+}$, and the four diastereomers of $[\mathrm{Co}(S\text{-}1,3\text{-}\mathrm{bn})_3]^{3+}$ ("1,3-bn" = 1,3-butanediamine), which contain chelate rings which are expected to be in primarily chair conformations, have lowest energy d-d bands which lie between 489 and 491 nm.[26-28] On the other hand, the two isomers of $[\mathrm{Co}(RR\text{-}\mathrm{ptn})_3]^{3+}$, where the ring conformations are skew-boat, have lowest energy absorption bands at 482 and 487 nm, which bracket the values found for *fac*- and *mer*-$\mathrm{[Co(metn)_3]^{3+}}$. Thus, the absorption spectra are consistent with a skew-boat conformation for the 2-methyl-1,3-propanediamine chelate rings in the tris complex.

X-ray Diffraction Results

The disorder found for *fac*-[Co(metn)$_3$]Cl$_3$ in the x-ray study was not entirely unexpected. Earlier, IR spectroscopy had shown spectra which were identical for both the facial and meridional isomers as the chloride salts. Identical spectra are likely only if the complex ions sit at sites of the same symmetry, which can happen only if there is disorder (in this case giving a pseudo D_3 symmetry to the complex ion). Despite the disorder, however, the x-ray results clearly show a skew-boat chelate ring conformation and thus provide additional evidence that this conformation may make an important contribution to the conformational geometry of [Co(metn)$_3$]$^{3+}$. We recognize, of course, that conformations in the solid state may be strongly influenced by intermolecular forces.

ACKNOWLEDGEMENTS

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