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Stereochemical Studies on Diastereomers of Tris(2,3-butanediamine)cobalt(III)[1]

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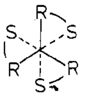
The results of ^{13}C NMR spectroscopic studies and strain energy minimization calculations on isomers of $[Co((\pm)\text{-bn})_3]^{3+}$ and $[Co(ms\text{-bn})_3]^{3+}$ (bn = 2,3-butanediamine) show the presence of highly flexible and conformationally labile complexes in the latter system, unlike the former where the species are relatively rigid. ^{13}C NMR spectroscopy easily identifies the facial and meridional isomers of the tris meso system (where the halves of the bidentate ligand are chirally distinguishable) owing to the different time-averaged conformations of the three flexible and symmetry-nonequivalent chelate rings of the meridional isomer giving rise to chemical shift variations among constitutionally similar carbon atoms. The ^{13}C NMR chemical shift variations exhibited by intermolecularly and intramolecularly diastereotopic methyl groups in the $[Co(bn)_3]^{3+}$ complexes are primarily due to axial/equatorial variations while those exhibited by diastereotopic methine carbon atoms are determined by two primary effects—the axiality of the attached methyl group and the *lel*/*ob* character of the chelate ring. The presence of tetrahedral oxyanions in solutions of the fluxional tris meso system is shown by the ^{13}C NMR studies to stabilize the *lel* chelate ring conformation, as expected.

Introduction

Meso (*R*,*S*) bidentate ligands, with donor atoms in constitutionally similar but chirally distinguishable locations, generate isomeric complexes identical in number and similar in type with those obtained with "unsymmetrical" (AB) bidentates.[2] Thus, a tris chelate containing meso bidentate ligands can exist in a facial (I) or a meridional (II) form.[3]



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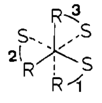

II

Among the systems for which such isomers have been reported[2] is the complex tris(*meso*-2,3-butanediamine)cobalt(III), $[Co(ms\text{-bn})_3]^{3+}$.[4] As part of a general study of conformational and steric effects in complexes with enantiotopic (before coordination) donor atoms, we have carried out ^{13}C NMR and conformational analytical studies on this system and also, for comparison, on the isomeric complexes of $[Co((\pm)\text{-bn})_3]^{3+}$. These studies not only further elucidate the conformational stereochemistry of the highly flexible *meso*-2,3-butanediamine ligand but also permit us to reach several conclusions concerning the source of ^{13}C NMR chemical shift differentiation in chelates—particularly those containing diastereotopic carbon atoms. The latter topic is of particular interest owing to the increasing application of ^{13}C NMR spectroscopy to the investigation of chelate stereochemistry and isomerism. Very limited ^{13}C NMR spectral data have been previously reported for two $[Co((\pm)\text{-bn})_3]^{3+}$ isomers.[5]

Experimental Section

Physical Measurements. Infrared spectral band positions (±3 cm^{-1}) were taken from spectra collected on a Perkin-Elmer Model 621 grating spectrophotometer using KBr pellets. Natural abundance ^{13}C NMR spectra were recorded at ca. 35 °C on a Varian XL-100/Nicolet TT-100 FT system with an observe frequency of 25.2 MHz. All ^{13}C NMR spectra were obtained by using a 2000-Hz sweep width, 2.048-s acquisition time, 50-μs pulse width (equivalent to a 90° pulse), noise modulated proton decoupling, and, unless otherwise indicated, no pulse delay. Approximately 25 000 acquisitions were taken for each spectrum.

In the preparation of the NMR samples, the chloride salts (300 mg for the tris meso complexes) were dissolved in 4 mL of D_2O and placed in a 12-mm sample tube. In some cases sodium sulfate or sodium phosphate was added. Dioxane in D_2O (ca. 5%) was employed as an external standard in a coaxial 5-mm tube. When employed as an internal standard, dioxane caused precipitation of the complexes. All chemical shifts (±0.05 ppm unless otherwise noted) have been recalculated relative to Me_4Si (dioxane solution, $\delta = 67.39$).

Preparation of the Ligands. 2,3-Butanediamine dihydrochloride was prepared by reduction of dimethylglyoxime following a reported procedure.[6] The final step of conversion to the free amine and distillation was eliminated. The meso and racemic isomers were separated by recrystallization of the dihydrochloride salt from a minimum amount of ca. 90% aqueous methanol.[6] The separation was followed by IR spectroscopy.

Since incomplete isomer separations have reportedly[7] caused errors in past work with 2,3-butanediamine ligands, the isomeric products were carefully purified and characterized. The isomeric hydrochloride salts gave satisfactory elemental analyses and their relative solubilities in methanol and their ^{1}H NMR chemical shifts agreed well with literature values and with those of authentic samples provided by Drs. C. N. Reilley and J. E. Sarneski of the University of North Carolina. Infrared and ^{13}C NMR spectroscopy, both of which proved much more sensitive than ^{1}H NMR measurements in distinguishing between the isomers and in estimating their purities, gave no indication of any racemic contaminant in the meso dihydrochloride salt (we estimate that 5% could have been easily detected) and indicated less than 5% contamination of the racemic compound by the meso. These results sharply contrast with those reported by others.[8] IR of *ms*-$C_4H_{12}N_2\cdot 2HCl$ (characteristic peaks, KBr): 1310 (w), 1198 (s) cm^{-1}. ^{13}C NMR (D_2O): δ 50.75 (s, CH), 15.75 (s, CH_3). IR of (±)-$C_4H_{12}N_2\cdot 2HCl$ (characteristic peaks, KBr): 440 (m), 1142 (s), 1005 (w) cm^{-1}. ^{13}C NMR (D_2O): δ 49.60 (s, CH), 13.49 (s, CH_3).

Preparation of the Complexes. A solution of the appropriate 2,3-butanediamine dihydrochloride salt (1.61 g, 10 mmol) in 10 mL of H_2O was added to a slurry of sodium tris(carbonato)cobaltate(III), $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (1.09 g, 3 mmol), and charcoal in 10 mL of H_2O and the mixture was stirred and heated at 60 °C for 2 h. Following the removal of the charcoal by filtration, the orange solutions were chromatographed on SP Sephadex C-25 cation-exchange resin by use of a 2.7 cm × 250 cm column for the tris meso complex and a 2.7 cm × 50 cm column for the tris racemic complex. The isomers were eluted with aqueous 0.2 M Na_2SO_4 at a flow rate of 1 mL/min. Elution curves plotted from the spectral absorbances at 470 nm were used to determine the relative isomer abundances. Extinction coefficients reported[4] for the $[Co(ms\text{-bn})_3]^{3+}$ isomers were employed in the calculations. Owing to the absence of literature values for the

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(1) Presented in part at the 173rd National Meeting of the American Chemical Society, New Orleans, LA, March 12–17, 1978.

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Table I. Thermodynamic Parameters Calculated by Strain Energy Minimization ($T = 298$ K)

complex	conformer	H,[a] kcal mol^{-1}	TS, kcal mol^{-1}	G, kcal mol^{-1}	abundance,[b] %
Δ-*fac*-[Co(*ms*-bn)$_3$]$^{3+}$	λλλ	3.12	44.70	−41.58	53
	δλλ	5.05	46.42	−41.37	37
	δδλ	6.32	46.84	−40.52	9
	δδδ	6.86	45.61	−38.75	<1
Δ-*mer*-[Co(*ms*-bn)$_3$]$^{3+}$	λλλ	4.48	46.60	−42.12	46
	λλδ	5.99	46.78	−40.79	5
	λδλ	5.29	46.62	−41.33	12
	δλλ	5.00	46.31	−41.31	12
	λδδ	6.27	46.85	−40.58	3
	δλδ	4.95	46.40	−41.45	15
	δδλ	6.36	46.70	−40.34	2
	δδδ	5.62	46.49	−40.87	6
Δ-[Co(*R,R*-bn)$_3$]$^{3+}$	λλλ	−2.95	46.62	−49.57	17
Δ-[Co(*R,R*-bn)$_2$(*S,S*-bn)]$^{3+}$	λλδ	−2.55	47.65	−50.20	49
Δ-[Co(*R,R*-bn)(*S,S*-bn)$_2$]$^{3+}$	λδδ	−2.10	47.82	−49.93	31
Δ-[Co(*S,S*-bn)$_3$]$^{3+}$	δδδ	−2.08	46.48	−48.56	3

[a] Relative to $H = 0$ for the hypothetical strucure with all bonding parameters at their equilibrium values and no nonbonded interactions. [b] Relative abundances calculated from computed free energies (G) for species within each grouping.

relative extinction coefficients of the [Co((±)-bn)$_3$]$^{3+}$ isomers, it was assumed that they were equal. Two orange bands, the first corresponding to the meridional isomer and the second to the facial,[4] were obtained upon elution of the tris meso complex. Elution of the tris racemic complex gave three well-defined bands, assigned as the *lel,lel,lel*; *lel,lel,ob*; and *lel,ob,ob* isomers[9] in the order of elution (vide infra), and a fourth, very faint band. These isomers have been previously separated.[14]

Halide salts of *fac*- and *mer*-[Co(*ms*-bn)$_3$]$^{3+}$ were prepared by addition of methanol to the concentrated chromatographic fractions to precipitate sodium sulfate followed by ion exchange with Dowex 1X-8 resin in either the chloride or the bromide form. Addition of the appropriate hydrohalic acid, removal of any precipitated sodium halides, and concentration of the solution gave the solid orange salts. Pure bromide salts were readily obtained but the chloride salts invariably contained about 20% sodium chloride. Tests for sulfate ion were negative. IR spectra of *fac*- and *mer*-[Co(*ms*-bn)$_3$]Br$_3$ and of *fac*-[Co(*ms*-bn)$_3$]Cl$_3$ were indistinguishable and differed somewhat from the IR spectrum of *mer*-[Co(*ms*-bn)$_3$]Cl$_3$. Anal. Calcd for [Co(*ms*-C$_4$H$_{12}$N$_2$)$_3$]Br$_3$: C, 25.60; H, 6.44; N, 14.92. Found (facial): C, 25.78; H, 6.49; N, 14.93. Found (meridional): C, 25.74; H, 6.12; N, 14.63.

Additions of aqueous potassium hexacyanocobaltate(III) to [Co(*ms*-bn)$_3$]$^{3+}$ solutions gave immediate precipitations of light yellow, insoluble hexacyanocobaltate(III) salts whose IR spectra allowed the facial and meridional isomers to be readily distinguished. The salt of the meridional complex exhibited an IR spectrum with three peaks in the C≡N stretching region at 2123, 2138 (sh), and 2154 cm^{-1} while the salt of the facial isomer gave an IR spectrum with only a single peak in this region at 2125 cm^{-1}. The material analyzes poorly for the anhydrous hexacyanocobaltate salt. Anal. Calcd for [Co(*ms*-C$_4$H$_{12}$N$_2$)$_3$][Co(CN)$_6$]: C, 40.15; H, 6.74; N, 31.22. Found (facial): C, 38.59; H, 6.67; N, 28.96. Found (meridional): C, 39.24; H, 6.73; N, 30.24.

Solid chloride salts free of sulfate ion were also obtained for the [Co((±)-bn)$_3$]$^{3+}$ isomers using the method described above.

For comparison of the relative abundances of the facial and meridional isomers obtained by an alternative method, [Co(*ms*-bn)$_3$]$^{3+}$ was also prepared starting with [CoBr(NH$_3$)$_5$]Br$_2$ using a reported method.[4]

Computer Calculations. Strain energy minimization calculations were carried out on the isomers and conformers of [Co(*ms*-bn)$_3$]$^{3+}$ and [Co((±)-bn)$_3$]$^{3+}$ by using a slightly modified version of the set of programs written by DeHayes[15] and employing parameters applied to other cobalt(III) diamine systems.[16] These programs permit the statistical mechanical calculation of entropy contributions once the strain energy minimized coordinates have been determined.

Results

Strain Energy Minimization Calculations. Table I gives the calculated thermodynamic parameters for all possible[17] nonenantiomeric conformers corresponding to energy minima for the two [Co(*ms*-bn)$_3$]$^{3+}$ isomers and for the lowest energy conformers only for the four [Co((±)-bn)$_3$]$^{3+}$ isomers. The calculated potential energy wells were shallow for higher energy conformers in the latter system and convergence without conversion to a lower energy conformer was achieved only with difficulty. Where convergence was achieved for a higher energy conformer in the tris racemic system, the calculated thermodynamic parameters indicated a negligible abundance (<<1%) for that conformer under equilibrium conditions ($T = 298$ K). The designations in Table I for the eight conformers of Δ-*mer*-[Co(*ms*-bn)$_3$]$^{3+}$ give the conformations of the nonequivalent chelate rings 1, 2, and 3 (II) in that order.

Carbon-13 NMR. ^{13}C NMR spectral parameters collected for the [Co(bn)$_3$]$^{3+}$ complexes are presented in Table II. The complexes [Co(*R,R*-bn)$_3$]$^{3+}$ and [Co(*S,S*-bn)$_3$]$^{3+}$ with D_3 symmetry are expected to exhibit proton-decoupled ^{13}C NMR spectra with only two resonances, corresponding to the six symmetry equivalent methyl carbon atoms and to the six symmetry equivalent methine carbon atoms. Such a spectrum is observed for the first and most intense chromatographic band eluted for [Co((±)-bn)$_3$]$^{3+}$ which we assign as that due to the *lel,lel,lel* enantiomeric pair[9] which should be present in much greater abundance than the D_3 symmetry *ob,ob,ob* pair. The latter species may constitute the very faint fourth chromatographic band observed but not characterized.

The mixed-ligand complexes [Co(*R,R*-bn)$_2$(*S,S*-bn)]$^{3+}$ and [Co(*S,S*-bn)$_2$(*R,R*-bn)]$^{3+}$ could exhibit effective symmetries as high as C_2, in which case three methyl and three methine ^{13}C NMR resonances are expected. Except for accidental overlap in the methine region, this is the spectrum observed for the third chromatographic fraction which we assign as the *lel,ob,ob* pair of isomers[9] based on the relative abundance. That this assignment is correct is indicated by the broadened methyl resonance observed in the ^{13}C NMR spectra of the remaining chromatographic fraction which must correspond to the *lel,lel,ob* pair. Such broadening, though unexplained, has been ascribed to increasing *lel* character[5] and is also observed in the spectra collected for the *lel,lel,lel* isomers.

Discussion

The thermodynamic parameters and minimized coordinates determined by strain energy minimization calculations will vary with the interaction parameter set chosen making the absolute values somewhat suspect. Nevertheless, the relative values (Table I) permit us to make some reasonable comparisons. Niketić and Rasmussen[10] have carried out strain energy

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(9) No separations of optical isomers were carried out in any of these studies. The [Co((±)-bn)$_3$]$^{3+}$ isomers can be named according to the most stable conformers.[10] Thus, employing accepted chirality and conformation labels,[11,12] we may describe the enantiomeric pair Δ(λλλ)-[Co(*R,R*-bn)$_3$]$^{3+}$, Λ(*δδδ*)-[Co(*S,S*-bn)$_3$]$^{3+}$ as the *lel,lel,lel*[13] isomers. Similarly, Δ(λλ*δ*)-[Co(*R,R*-bn)$_2$(*S,S*-bn)]$^{3+}$, Λ(*δδ*λ)-[Co(*S,S*-bn)$_2$(*R,R*-bn)]$^{3+}$ are *lel,lel,ob*; Δ(λ*δδ*)-[Co(*R,R*-bn)(*S,S*-bn)$_2$]$^{3+}$, Λ(*δ*λλ)-[Co(*S,S*-bn)(*R,R*-bn)$_2$]$^{3+}$ are *lel,ob,ob*; and Δ(*δδδ*)-[Co(*S,S*-bn)$_3$]$^{3+}$, Λ(λλλ)-[Co(*R,R*-bn)$_3$]$^{3+}$ are *ob,ob,ob*.

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Table II. ^{13}C NMR Spectral Data (δ)

complex	assignt	added anion none	 0.2 M SO_4^{2-}	 0.2 M PO_4^{3-}
fac-[Co(*ms*-bn)$_3$]Cl$_3$	CH_3	14.66 (14.59)[a] ··· (16.71)	14.58 17.01	14.55 16.74
	CH	55.25 (55.21) 57.37 (57.34)	55.16 57.38	55.12 57.18
mer-[Co(*ms*-bn)$_3$]Cl$_3$	CH_3	14.18, 14.45, 15.17 16.82, 16.91, 17.03	13.97, 14.17, 14.90 17.08, 17.25, 17.31	13.94, 14.06, 14.81 16.82, 16.89[b]
	CH	54.56, 54.66, 54.89 57.30, 57.62, 57.70	54.69, 54.93[b] 57.28, 57.79[b]	54.47, 54.74, 54.81 57.00, 57.42[b]
lel,lel,lel-[Co((±)-bn)$_3$]Cl$_3$	CH_3	18.4[c]	18.7[c]	
	CH	58.85 [58.6][d]	58.65	
lel,lel,ob-[Co((±)-bn)$_3$]Cl$_3$	CH_3	18.3[c]	18.6[c]	
	CH	57.47, 57.55 58.19, 58.28 58.59, 58.67	57.4[c] 58.13, 58.25 58.5[c]	
lel,ob,ob-[Co((±)-bn)$_3$]Cl$_3$	CH_3	18.37, 18.57, 18.67	18.35, 18.54, 18.64	
	CH	57.91,[b] 58.60	57.66,[b] 58.48	
ob,ob,ob-[Co((±)-bn)$_3$]Cl$_3$	CH	[57.4][d]		

[a] The values in parentheses were taken from a spectrum obtained with a 4-s pulse delay. [b] Area of resonance indicates the presence of two overlapping peaks. [c] Broad. [d] Values in brackets were taken from ref 5.

minimization calculations for the isomers of $[Co(bn)_3]^{3+}$ using a strikingly different parameter set; however, their computations do not include entropy calculations. Their results are very similar to ours where comparisons are possible. Calculations have also been carried out on some monokis chelates of 2,3-butanediamine.[15,16]

The strain energy minimized coordinates show trends consistent with those found in other conformational analyses on chelate systems,[10,15,16,18] and, for that reason, the detailed structural results are not reported here.[19] Angular deformations, either of the 1,3 or torsional (1,4) type, are the main source of strain relief in the tris(2,3-butanediamine) computed structures. In particular, as observed in other studies,[10,15,16] there is a flattening of the 2,3-butanediamine chelate rings (the N–C–C–N torsion angles vary from 48 to 51°) and an intraannular decrease (~4°) in the N–Co–N bond angles. Among the minor bond length deformations observed were Co–N and C–N bond length elongations.

As found by others,[10] the strain enthalpy decreases with an increased *lel* content (Table I). Although the variations within each set of structures are irregular, average values for the *lel* enthalpy stabilization per chelate ring of 1.2, 0.4, and 0.3 kcal mol^{-1} can be estimated for the facial tris meso, meridional tris meso, and tris racemic systems, respectively. These values can be compared with respective values of 0.9, 0.7, and 0.4 kcal mol^{-1} calculated by Niketič and Rasmussen.[10] Comparison of calculated enthalpies for the lowest energy conformers of the tris meso and tris racemic systems gives an estimated enthalpy decrease of 2.0 kcal mol^{-1} for conversion of an axial methyl group to an equatorial. This value compares very well with experimental[20] and calculated (by DeHayes and Busch)[16] values of 1.9 and 2.2 kcal mol^{-1}, respectively, for 2,3-butanediamine chelate rings but differs markedly from the value of 3.6 kcal mol^{-1} computed by Niketič and Rasmussen.[10]

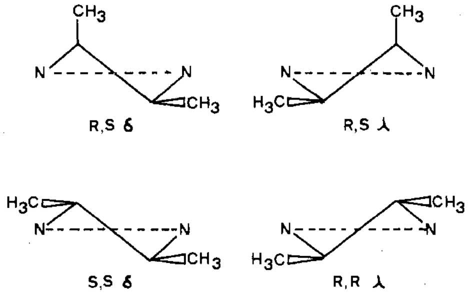

Figure 1. Conformations of 2,3-butanediamine chelate rings.

The calculated entropies are important in determining the relative free energies of the tris meso conformers. Over and above a symmetry factor contribution of $R \ln 3$ (corresponding to a free energy decrease of 0.65 kcal mol^{-1} at 298 K),[21] all of the lower symmetry C_1 conformers have calculated entropies higher than those of the two C_3 structures—facial, λλλ and facial, δδδ. This entropy increase, due primarily to vibrational contributions, indicates a more flexible structure for the lower symmetry species. On the other hand, the facial, δδδ and, even more so, the facial, λλλ conformers appear to be comparatively rigid.

Racemic 2,3-butanediamine ligands coordinated with gauche conformations must have the two methyl groups either both axial or both equatorial (Figure 1). Strain energy minimization calculations[10] indicate that a strong preference for equatorial methyl groups will essentially lock chelate rings containing the racemic ligands into a fixed conformation regardless of whether this would force the ring to be *lel* or *ob*. Thus each of the four enantiomeric pairs of isomers[9] possible for $[Co(\pm)\text{-}bn)_3]^{3+}$ are expected to exist almost entirely in a single conformational form under normal laboratory conditions. On the other hand, chelated *meso*-2,3-butanediamine ligands, whether λ or δ, must have one axial and one equatorial methyl group (Figure 1). This fact not only explains the lower stabilities observed for tris meso compared with tris racemic complexes containing symmetrically disubstituted 1,2-ethanediamine ligands[2] but also explains the results of our calculations indicating that tris meso complexes—in particular, the meridional isomer—will exist in a number of conformers under equilibrium conditions (Table I). Thus a reported[4] agreement between facial and meridional isomer abundances determined experimentally for $[Co(ms\text{-}bn)_3]^{3+}$ and those calculated based on strain energy minimization results for only the Δ(λλλ)/Λ(δδδ) enantiomeric pairs are largely fortuitous. The results of isomer abundance calculations taking into account all possible conformers and based on the thermodynamic parameters given in Table I are presented in Table III along with the results of similar calculations for the tris racemic system and experimental abundances. Though the facial and meridional relative abundances calculated agree relatively well

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Table III. Isomer Abundances

			obsd abundances, %	
complex	isomer	calcd[a] abundances, %	synthesized from $[Co(CO_3)_3]^{3-}$	synthesized from $[CoBr(NH_3)_5]^{2+}$
[Co(*ms*-bn)$_3$]$^{3+}$	facial	26	36 (±1)[b]	22 [42][c]
	meridional	74	64 (±1)[b]	78 [58][c]
[Co((±)-bn)$_3$]$^{3+}$	*lel,lel,lel*	17	60 (±1)[d]	
	lel,lel,ob	49	28 (±1)[d]	
	lel,ob,ob	31	12 (±1)[d]	
	ob,ob,ob	3	negligible	

[a] Calculated from strain energy minimization computed thermodynamic functions. [b] Average deviation for three preparations. [c] Values in brackets are taken from ref 4. [d] Average deviation for two preparations.

with those observed in some cases, the variation in the experimental results indicates either that equilibrium was not attained in all cases or that environmental effects affect the isomer distribution.[22] We hasten to point out that the application of "gas-phase" thermodynamic calculations to the interpretation of solution equilibria is suspect at best. The relative isomer abundances calculated for the tris racemic complexes do not agree well with those found experimentally (Table III).

Our ^{13}C NMR results are best interpreted by assuming a rapid $\delta \leftrightarrow \lambda$ conformation interconversion for the coordinated *meso*-2,3-butanediamine ligand. Additional resonances, owing to mixed conformer species, are not detected in our spectra. A similar conclusion has been reached from ^{1}H NMR studies on this and related systems.[4,23,24] The presence of two methyl resonances in ^{1}H NMR spectra of the tris meso complexes has been ascribed to axial and equatorial groups whose conformational interconversions are slow on the NMR time scale;[14] however, it has been pointed out that methyl groups which are enantiotopic in the free ligand become diastereotopic and intrinsically nonequivalent in the chiral tris chelates.[3] Of course, the actual magnitude of the chemical shift nonequivalence observed may be primarily due to stabilization of one chelate conformer over another by *lel* preference (vide infra).[2,4] Thus, we assign the two methine carbon resonances and, as well, the two methyl resonances in the ^{13}C NMR spectra of *fac*-[Co(*ms*-bn)$_3$]$^{3+}$ to diastereotopic groups in a conformationally fluxional molecule with an effective[2] C_3 symmetry. The additional peaks observed in spectra of the meridional isomer result from its lower symmetry, C_1.

The methyl group ^{13}C NMR resonances observed in spectra of the *meso*-2,3-butanediamine complexes are upfield from the methyl resonances in spectra of the (±)-2,3-butanediamine complexes (Table II). This can be attributed to steric compression shifts[25] associated with a greater methyl group axiality in the *meso*-2,3-butanediamine ligands. Owing to a *lel* preference for the chelate ring, one methyl group will be primarily axial and one, primarily equatorial. We assign those methyl resonances observed at ~14–15 ppm to groups which are primarily axial and those at ~16–17 ppm to those which are primarily equatorial.

If we assume that variations in the methyl group chemical shifts observed for the tris meso complexes are due only to axial/equatorial differences (an admittedly questionable assumption), we can use the observed ^{13}C NMR methyl chemical shifts of the facial isomer to predict those of the meridional. From the thermodynamic parameters of Table I, one can easily calculate that, in a time-averaged facial isomer, one set of methyl groups is predicted to be 81% axial (19% equatorial) and the other, 19% axial (81% equatorial). These values correspond to a chelate ring being 81% *lel* in this isomer. From these percentages and the chemical shifts observed for the methyl groups in the facial isomer of 16.7 and 14.6 ppm (Table II), we calculate predicted shifts of 14.0 and 17.4 ppm for methyl groups which are completely axial and completely equatorial, respectively, in a tris meso complex. The latter value might be compared with chemical shifts of 18.3 to 18.7 ppm observed for the equatorial methyl groups in the tris((±)-2,3-butanediamine)cobalt(III) complexes.

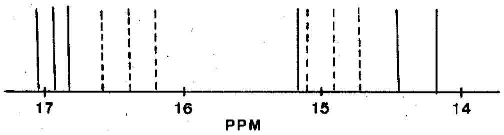

Figure 2. Calculated (---) and observed (—) methyl group ^{13}C NMR resonance positions for *mer*-[Co(*ms*-bn)$_3$]$^{3+}$.

The calculated "pure axial" and "pure equatorial" methyl carbon chemical shifts can now be used to compute the predicted methyl group resonance positions in the ^{13}C NMR spectrum of the meridional isomer. There are three nonequivalent chelate rings in this isomer. From the results of Table I, we calculate that, for a Δ absolute configuration, chelate rings 1, 2, and 3 (II) are in a λ conformation 66, 77, and 72% of the time, respectively. This means, e.g., that in chelate ring 1, one methyl group is 66% axial and the other is 66% equatorial. Using these time-average positions and the "pure axial" and "pure equatorial" resonances of 14.0 and 17.0 ppm, we calculate ^{13}C NMR resonance positions of 16.2, 16.6, and 16.4 ppm for the primarily equatorial methyl groups (those attached at the *R* absolute configuration carbon atoms in a Δ complex) in the meridional tris meso complex for chelate rings 1, 2, and 3, respectively. Similarly, resonance positions of 15.1, 14.7, and 14.9 ppm are calculated for the corresponding primarily axial methyl groups. The predicted and observed (in the absence of added oxyanions) ^{13}C NMR methyl resonances are compared graphically in Figure 2.

Despite the questionable applicability of "gas-phase" strain energy minimization calculations to solution equilibria, the magnitudes of the observed and calculated chemical shift nonequivalences (Figure 2) are sufficiently close that we may make two important points. First, the ^{13}C NMR chemical shift differences in the methyl group resonances are probably determined *primarily* by the percentages of time each group spends axial and equatorial. Second, the chemical shift differences within each "primarily axial" and "primarily equatorial" cluster of resonances in the ^{13}C NMR spectra of *mer*-[Co(*ms*-bn)$_3$]$^{3+}$ largely result from variations in time-averaged conformations of the three nonequivalent chelate rings. (A similar conclusion can be made for the methine resonances.) The second point is of particular interest since an explanation can now be advanced for the reported absence of observable chemical shift nonequivalences in the ^{13}C (and 100-MHz ^{1}H) NMR resonances corresponding to each set of constitutionally similar (but symmetry nonequivalent) carbon atoms of the C_1 symmetry complex *mer*-tris(*l*-1,2-propanediamine)cobalt(III), *mer*-[Co(*l*-pn)$_3$]$^{3+}$.[26] Here ^{13}C NMR spectra have not permitted an assignment of meridional and facial isomers. In this case, however, the presence of a single methyl group on each 1,2-propanediamine chelate ring forces a conformation where the methyl group is equatorial. Thus,

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Table IV. Time-Average Conformations of the Chelate Rings in Tris(*meso*-2,3-butanediamine)cobalt(III) Complexes

	% *lel*		
complex	no added anion	0.2 M SO_4^{2-}	0.2 M PO_4^{3-}
facial	(81)[a]	86	82
meridional[b]	92	99	93
	86	95	91
	74	82	79

[a] Calculated from strain energy minimization results. [b] Values for three nonequivalent chelate rings are given.

there will be little contribution from higher energy conformers with axial methyl groups. The three nonequivalent chelate rings of *mer*-$[Co(\textit{l}\text{-pn})_3]^{3+}$ are effectively locked into relatively fixed conformations. On the other hand, ^1H NMR spectroscopy easily shows chelate ring nonequivalence in *mer*-tris(2-methyl-1,2-propanediamine)cobalt(III), where the chelate ring must have one methyl group axial and one equatorial and will, therefore, be more flexible.[27]

Studies on methyl-substituted cyclohexanes have shown that the ^{13}C NMR resonance for a methine carbon attached to an axial methyl group is upfield from that for a methine carbon attached to an equatorial methyl.[28] Assuming that this carries over for the methine carbons of the *meso*-2,3-butanediamine chelate rings, we can assign the resonances around 55 ppm to carbons attached to axial methyl groups and those resonances around 57 ppm to carbons attached to equatorial methyl groups. The latter resonance positions observed for the tris meso complexes are similar to those observed for the methine carbon atoms of the tris racemic complexes, where the methyl groups are primarily equatorial.

There is another factor known to influence the ^{13}C NMR chemical shifts of methine carbon atoms in 2,3-butanediamine chelate rings. A study on a series of $[Co(en)_x((-)\text{-bn})_y]^{3+}$ complexes (en = 1,2-ethanediamine) has shown that the ^{13}C resonance of for a methine carbon in a *lel* (−)-2,3-butanediamine chelate ring is downfield relative to that of a methine carbon in an *ob* ring.[5] Thus, while the methine group ^{13}C chemical shift nonequivalences observed for *mer*-$[Co(\textit{ms}\text{-bn})_3]^{3+}$ are undoubtedly due in large part to inequivalent time-averaged conformations for the three chelate rings, the numerical values of the shifts are likely due to a superposition of *lel*/*ob* and axial/equatorial effects.

The methine ^{13}C resonances observed for the mixed-ligand tris racemic *lel,ob,ob*[9] enantiomeric pair (Table II) are consistent with the shifts expected for two *ob* rings and one *lel*.[5] For the *lel,lel,ob* complex the analysis is a little more obscure since the chemical shifts of resonances near 58.2 ppm, which should be due to methine carbons on *lel* rings, seem somewhat small. Moreover, this complex exhibits a small but well-defined splitting (about 0.08 ppm) of the three methine resonances expected for a C_2 complex. This splitting could be due to a symmetry lowering from strict C_2, perhaps owing to meshing of hydrogen atoms on adjacent methyl groups. The extreme broadness of the methyl resonance observed for this complex would obscure the presence of a similar splitting in the methyl region and, in fact, it could be the presence of several overlapping methyl group resonances which gives the appearance of broadening. A lowering of symmetry owing to hydrogen meshing between chelate rings has been observed in an X-ray structure determination on another system.[29] Our strain energy minimization calculations give no indication of unusually close contacts in the *lel,lel,ob* isomer compared to the other $[Co((\pm)\text{-bn})_3]^{3+}$ structures although there is a small increase in the strain energy minimized methyl carbon–methyl carbon contacts with increasing *ob* content (from 3.10 Å for the *lel,lel,lel* structure to 3.16 Å for the *ob,ob,ob*).

The value of 81% *lel* determined from the results of the strain energy minimization calculations for the time-averaged conformation of a chelate ring in the facial tris meso system at 298 K is very close to the value determined by ^1H NMR spectroscopy for the similarly flexible system $[Co(en)_3]^{3+}$ (~75% *lel* at 290 K).[30] This gives us some confidence in this value for the average conformation and, therefore, some confidence in the "pure axial" and "pure equatorial" methyl group ^{13}C NMR chemical shifts calculated earlier. There is certainly no reason to doubt that these chemical shifts are close to the correct values. From these "pure axial" and "pure equatorial" chemical shifts and the NMR data in Table II, we can calculate approximate average conformations of the three nonequivalent chelate rings of the meridional tris meso complex. The results are given in Table IV.

Additions of sulfate or phosphate anion to solutions of the tris meso complexes cause changes in the methyl group ^{13}C NMR resonances consistent with a stabilization of the *lel* conformations (Table II). The changes in the methine resonance positions are not as prominent and are not so easily interpreted, perhaps because of the superposition of the two effects discussed earlier (*lel*/*ob* and methyl group axiality). Much smaller effects are observed upon addition of sulfate ion to solutions of the more rigid tris racemic complexes. We have used the NMR results to calculate time-averaged chelate ring conformations for the tris meso complexes in the presence of the oxyanions, and these results are also given in Table IV. The results clearly indicate an increase in *lel* content similar to that found upon addition of oxyanions to $[Co(en)_3]^{3+}$.[30] The effect is greatest for the meridional complex, which appears to be less rigid than the facial isomer. Sulfate ion seems to have a greater *lel* stabilizing ability than phosphate in this system.

The ^{13}C NMR spectrum of *fac*-$[Co(\textit{ms}\text{-bn})_3]^{3+}$ in the absence of added oxyanions or a pulse delay reproducibly exhibits only three resonances (Table II). The resonance ascribable to the three equivalent, primarily equatorial methyl carbon atoms is missing. That this peak appears when there is a pulse delay indicates that the observed absence is due to saturation. The addition of sulfate or phosphate causes this peak to show up even when no pulse delay is used. A number of studies on other cobalt(III) complexes indicate that the mode of *lel* stabilization by tetrahedral oxyanions is through ion association along the threefold axis.[22,31] Molecular models indicate that the trigonal face of the facial tris meso isomer surrounded by primarily equatorial methyl groups is the least sterically congested and presumably ion association would occur preferentially at that face. Contact between equatorial methyl groups and the oxyanion could then affect the methyl group relaxation time.

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Registry No. *fac*-$[Co(ms\text{-}bn)_3]Br_3$, 71883-55-1; *mer*-$[Co(ms\text{-}bn)_3]Br_3$, 71883-56-2; *fac*-$[Co(ms\text{-}bn)_3][Co(CN)_6]$, 71884-47-4; *mer*-$[Co(ms\text{-}bn)_3][Co(CN)_6]$, 71883-58-4; *fac*-$[Co(ms\text{-}bn)_3]Cl_3$, 71883-59-5; *mer*-$[Co(ms\text{-}bn)_3]Cl_3$, 71883-608; $[Co(R,R(S,S)\text{-}bn)_3]Cl_3$, 14266-71-8; $[Co(R,R(S,S)\text{-}bn)_2(S,S(R,R)\text{-}bn)]Cl_3$, 14266-71-8; *ms*-bn·2HCl, 55536-62-4; (±)-bn·2HCl, 66427-25-6; $Na_3[Co(CO_3)_3]$, 23311-39-9.

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A Study on the Preparation and Rearrangement of the Halogenated *closo*-Carboranes $Cl_nC_2B_4H_{6-n}$ ($n = 1, 2$) and $Cl_nC_2B_5H_{7-n}$ ($n = 1, 2$)

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Dichloro as well as monochloro derivatives of 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ are prepared, and the effect of the first chlorine substituent on the position of the entering second chlorine substituent is discussed. Both mono- and dichloro derivatives of $C_2B_5H_7$ rearrange at approximately 300 °C to a mixture of isomers.

Introduction

Some monochlorinated derivatives of the small *closo*-carboranes 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$, Figure 1, have been previously prepared by reactions of the parent cage compound with molecular chlorine.[1,2] The present study was undertaken to determine the influence of the first halogen substituent on the direction of further substitution. Additionally, it was of interest to see if the product(s) from the aluminum chloride catalyzed chlorination reaction are kinetically or thermodynamically controlled. It is now known that the methylation of 2,4-$C_2B_5H_7$ using Friedel–Crafts conditions produces kinetically controlled methyl derivatives[3] which, in turn, can be thermally rearranged to more thermodynamically stable isomers.[4,5]

Experimental Section

Materials and Handling of Chemicals. Both 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ were available from R. E. Williams and J. F. Ditter, Chemical Systems, Calif. To remove a small amount (ca. 5%) of 2-CH_3-1,5-$C_2B_3H_4$ impurity from 1,6-$C_2B_4H_6$, we treated the mixture with tetramethylethylenediamine which quantitatively complexes the former but not the latter carborane over a period of several minutes at room temperature. Pure 1,6-$C_2B_4H_6$ was then obtained by passing the volatile material through a trap at −78 °C and collecting the carborane at −190 °C. Purification of Cl_2 (Matheson) was effected by fractionation through −78, −140, and −190 °C traps to remove H_2O and HCl; chlorine condensed in the −140 °C trap.

All materials were handled in conventional high-vacuum equipment or in a drybox under an atmosphere of dry nitrogen. Cold-column fractionation was carried out by using the apparatus similar to that described in the literature.[6]

Nuclear Magnetic Resonance. Proton spectra were recorded on Varian A-60 and HA-100 spectrometers. The boron-11 spectra were obtained at 32.1 MHz with the Varian HA-100 instrument. Boron-11 decoupled proton spectra at 100 MHz were observed while irradiation was done at 32.1 MHz with a General Radio Model 1061 frequency synthesizer with a power booster provided by an Electronic Navigation Industries Model 320L RD power amplifier. Proton-decoupled ^{11}B spectra at 32.1 MHz were observed while irradiation was done at 100 MHz with the above-mentioned system. Boron-11 decoupled ^1H NMR were also obtained by using a FT-Bruker WP-60 instrument equipped with a Fluke 6160 frequency synthesizer and the ENI-320L amplifier.

The boron-11 chemical shift data (Table I) are reported relative to boron trifluoride–ethyl etherate and were obtained by using boron trichloride, δ −46.8, downfield from $(C_2H_5)_2O\cdot BF_3$, as a secondary external standard. The proton chemical shifts are reported relative to internal tetramethylsilane, $\tau = 10.00$.

Mass Spectra. Mass spectra were recorded on a Varian CH-5 high-resolution mass spectrometer and GLC–MS data were gathered by using a Varian Mat 111 equipped with 10% Kel-F grease on a 60/80 mesh Chrom W 20 ft × $^1/_8$ in. column.

Synthesis of 5-Cl-2,4-$C_2B_5H_6$ and 5,6-Cl_2-2,4-$C_2B_5H_5$. After a catalytic amount of $AlCl_3$ was sublimed into a 25-mL glass flask, $C_2B_5H_7$ (3.5 mmol) was added, followed by the same quantity of Cl_2. The flask was sealed and the reaction mixture warmed from −190 °C to room temperature. The color of Cl_2 disappeared within 30 min. The product mixture was fractionated through −140 and −190 °C traps, and a small amount of noncondensable gas was observed. The material in the −140 °C trap was further purified by cold-column[6] fractionation, whereby 5-Cl-$C_2B_5H_6$ (2.2 mmol, 77% yield based upon 2.85 mmol of $C_2B_5H_7$ consumed) distilled between −73 and −47 °C. The remaining volatile material, removed from the column while warming to room temperature, was 5,6-Cl_2-$C_2B_5H_5$ (0.15 mmol, 5% yield).

Into the same 25 mL flask with the $AlCl_3$ catalyst were added 5-Cl-$C_2B_5H_6$ (1.5 mmol) and Cl_2 (1.5 mmol). The flask was sealed and warmed to room temperature. By monitoring the ^{11}B NMR of the mixture, we noted that approximately 50% of the $ClC_2B_5H_6$ had reacted in 0.5 h at room temperature and the reaction was nearly complete in a 2-h period. The product mixture was fractionated through −140 and −190 °C traps to remove HCl. The material in the −140 °C trap was further fractionated by cold-column distillation with the removal of 5,6-Cl_2-$C_2B_5H_5$ (1.08 mmol, 72% yield based on starting 5-Cl-$C_2B_5H_6$) between −17.5 and 0 °C (5,6-Cl_2-$C_2B_5H_5$ is a liquid at room temperature). There was no $Cl_3C_2B_5H_4$ observed, but an isomeric dichloro derivative, 1,5-Cl_2-2,4-$C_2B_5H_5$, having a ^{11}B NMR singlet at δ ca. +14.5 and a 1:1 doublet at +31.8, $J(BH) = 192.6$ Hz, mixed with unreacted 5-Cl-$C_2B_5H_6$, was formed in less than 5% yield.

Synthesis of 2-Cl-1,6-$C_2B_4H_5$ and 2,4-Cl_2-1,6-$C_2B_4H_4$. Friedel–Crafts Route. In a typical reaction, measured amounts of 1,6-$C_2B_4H_6$ and Cl_2 were condensed into a glass reactor with a small quantity

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