

**(Carbonato)bis(diamine)cobalt(III) Complexes of the Sinambic Ligands
meso-2,3-Butanediamine and 2-Methyl-1,3-propanediamine**MARÍA FE GARGALLO,¹ J. DOUGLAS MATHER, EILEEN N. DUESLER, and ROBERT E. TAPSCOTT*

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Owing to rotational nonequivalence of donor atoms in the meso ligand *meso*-2,3-butanediamine (*ms-bn*) and in the prochiral ligand 2-methyl-1,3-propanediamine (*metn*), these ligands, when complexed, generate isomers equal in number to those obtained with unsymmetrical ("AB") bidentates. All possible diastereomers of the complexes $[\text{Co}(\text{ms-bn})_2\text{CO}_3]^+$ and $[\text{Co}(\text{metn})_2\text{CO}_3]^+$ have been prepared and their ¹³C NMR spectra determined. The surprising results that ¹³C NMR spectra of the C₂(*syn*) and C₂(*anti*) isomers in either system are virtually identical and differ strikingly from spectra of the C₁ isomers indicate that conformations of corresponding ligands in the C₂ isomers are similar and differ significantly from those of ligands in the C₁ isomers. A structure determination on crystals of the least soluble fraction of $[\text{Co}(\text{ms-bn})_2\text{CO}_3]\cdot\text{H}_2\text{O}$ (*P*₂, *Z*₁, *Z* = 4, *a* = 7.877 (4) Å, *b* = 11.889 (5) Å, *c* = 17.107 (7) Å) shows a monohydrate containing a single enantiomer (refined as Δ(λλ)) of the C₂(*anti*) diastereomer.

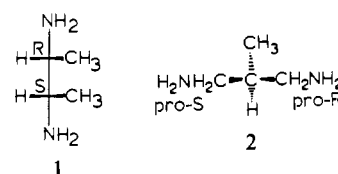
Introduction

Sinambic (from L. sine + ambitus: "without rotation") ligands are bidentates having rotationally nonequivalent donor atoms ("ligators").² If the heterotopic³ ligators are diastereotopic or constitutionally heterotopic, the ligands are the well-known unsymmetrical ("AB") bidentates. If the ligators are enantiotopic, the free ligand can possess nontrivial symmetry (depending on the conformation). Enantiotopic ligators may be found in meso ligands in oppositely chiral portions of the molecule (where the chiralities can usually be designated as "*R*" and "*S*"⁴), or they may be found in prochiral ligands in oppositely prochiral portions of the molecule (designated "*pro-R*" and "*pro-S*"⁵ or, in this paper, "*pR*" and "*pS*"). Just as unsymmetrical sinambic ligands are termed "AB" bidentates to denote that the ligators are chemically unique, sinambic ligands with enantiotopic donor atoms can be termed "*RS*" or "*pR-pS*".²

When coordinated, meso and prochiral sinambic ligands give rise to isomers equal in number (but not always in symmetry) to those obtained with AB bidentates, though the former isomers have not been so widely studied.² Thus, for example, octahedral tris meso and tris prochiral chelates exist in both facial and meridional forms as do tris AB complexes.⁶ Similarly, and of greater interest here, tris chelates containing two meso or prochiral ligands and a third symmetrical ("AA") bidentate can exhibit three diastereomeric forms—two having C₂ symmetry and one having C₁ symmetry (ignoring the presence of Δ,Λ optical isomerism). Separation of such diastereomers has been reported previously for a complex containing a meso sinambic ligand (*meso*-2,4-pentanediamine)⁷ but not for a complex containing prochiral ligands.

In a continuation of our studies on the differentiation of diastereotopic carbon atoms by ¹³C NMR spectroscopy and on diastereoisomerism in complexes of meso and prochiral sinambic ligands,⁸⁻¹¹ we report here studies on complexes containing two meso or two prochiral ligands and a third symmetrical bidentate ligand—the complexes $[\text{Co}(\text{ms-}$

bn)₂CO₃]⁺ ("*bn*" = 2,3-butanediamine (1)) and $[\text{Co-}$



(*metn*)₂CO₃]⁺ ("*metn*" = 2-methyl-1,3-propanediamine (2)), whose diastereomers are pictured in Figures 1 and 2. In these figures and in subsequent discussion, the terms "*anti*" and "*syn*" distinguish the two C₂ isomers according to whether methyl groups on planar rings would point away from or toward each other. It happens that these designations also indicate whether the 6-membered chelate rings of $[\text{Co}(\text{metn})_2\text{CO}_3]^+$ would fold away from or toward each other if the rings have a chair conformation with the methyl group equatorial (as found for $[\text{Co}(\text{metn})_2\text{Cl}_2]^+$ complexes¹¹).⁷ Tris complexes of *metn*⁹ and *ms-bn*^{8,12} with Co(III) have been reported as have the syntheses and structures of *cis*- and *trans*- $[\text{Co}(\text{metn})_2\text{Cl}_2]^+$.¹¹

Experimental Section

Ligands. 2,3-Butanediamine was obtained commercially and the meso isomer was separated from the racemic as described elsewhere.⁸ 2-Methyl-1,3-propanediamine was prepared by a previously described method.⁹

$[\text{Co}(\text{ms-bn})_2\text{CO}_3]^+$. The dihydrochloride salt of *ms*-2,3-butanediamine (25.8 g, 0.16 mol) in a minimum of water was treated with NaOH (12.8 g, 0.32 mol) to give the free diamine. Methanol was added to precipitate NaCl, which was filtered off, and the resulting solution was added to 200 mL of a methanolic solution of CoCl₂·6H₂O (19 g, 0.080 mol) containing 1 mL of glacial acetic acid. The mixture was aerated to oxidize the Co(II) to Co(III), and 25 mL of 12 M HCl was added to give a clear green solution, which was reduced to dryness under vacuum. The residue was allowed to react for 30 min with a 20% excess of Li₂CO₃ dissolved in 450 mL of hot water, and insoluble solids were removed by filtration. The volume of the filtrate was reduced to ca. 150 mL, an excess of potassium iodide was added, and the solution was allowed to evaporate to give red crystals.

Fractional recrystallization gave two solids. The less soluble fraction (A) consisted of a mixture of large thick rectangular plates, elongated rectangular plates with slightly concave sides ("bowties"), and hexagonal plates. Crystal structures and ¹³C NMR spectra (vide infra) showed that these forms were isostructural and that fraction A contained only the C₂(*anti*) isomer. IR (KBr, peaks characteristic of fraction): 3640 (s), 1027 (s), 810 (w) cm⁻¹. Anal. Calcd for $[\text{Co}(\text{C}_4\text{H}_{12}\text{N}_2)_2\text{CO}_3]\cdot\text{H}_2\text{O}$: C, 24.55; H, 5.91; N, 12.73. Found: C, 24.58; H, 5.99; N, 12.42.

The more soluble fraction, B, consisting of clusters of exceedingly thin plates, was shown by subsequent studies to contain a mixture

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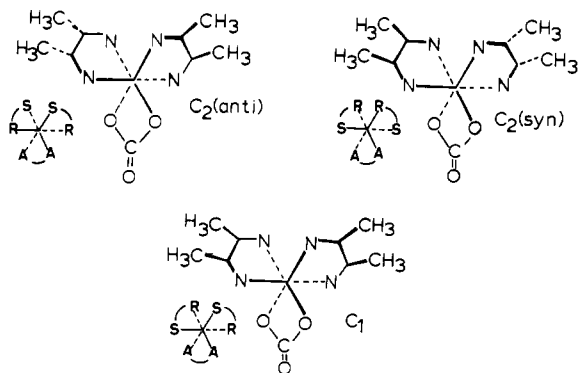


Figure 1. Diastereomers (shown as Δ enantiomers) of $[\text{Co}(\text{ms-bn})_2\text{CO}_3]^+$.

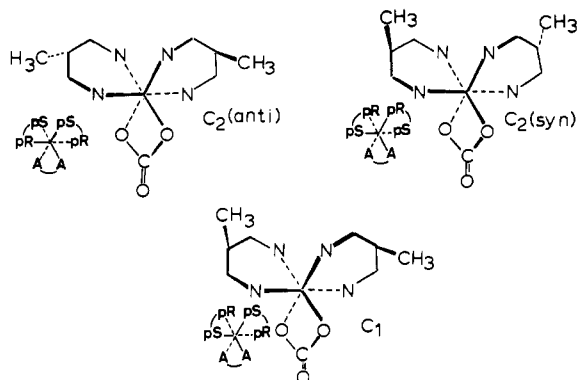


Figure 2. Diastereomers (shown as Δ enantiomers) of $[\text{Co}(\text{metn})_2\text{CO}_3]^+$.

of the C_1 and $C_2(\text{syn})$ isomers. Repeated crystallizations failed to separate these two diastereomers. Despite the uniform appearance of the crystals, both the IR spectrum, which differed significantly from that of fraction A, and the analysis, which most often showed the presence of three water molecules of crystallization, were somewhat variable. This may be due to a varying ratio of two diastereomeric salts. IR (KBr, approximate positions of peaks characteristic of fraction B): 1215, 1015, 830 (m), 822 (m) cm^{-1} . Anal. Calcd for $[\text{Co}(\text{C}_4\text{H}_{12}\text{N}_2)_2\text{CO}_3]\cdot 3\text{H}_2\text{O}$: C, 22.69; H, 6.30; N, 11.79. Found (average): C, 22.91; H, 6.34; N, 11.75.

An initial reaction mixture containing all isomers was chromatographed on SP Sephadex C-25 cation-exchange resin in a 2.7 cm \times 250 cm column using 0.15 M Na_2SO_4 eluent at a flow rate of 1 mL min^{-1} . Two well-defined red bands were obtained along with a third extremely broad band engulfing the two sharper bands. Addition of some fraction A to a mixture before chromatographing increased the intensity of the first well-defined band to be eluted. Chromatography of fraction B by itself gave one well-defined band preceded by and overlapped with a broad diffuse band.

$[\text{Co}(\text{metn})_2\text{CO}_3]^+$. To a solution of *trans*- $[\text{Co}(\text{metn})_2\text{Cl}_2]\text{Cl}^{11}$ (1.0 g, 3.0 mmol) in a minimum of water was added solid Na_2CO_3 (0.33 g, 3.0 mmol). The mixture was stirred to effect dissolution, and the solution was then heated on a steam bath for 10 min. Evaporation at room temperature gave a red solid, which was filtered off. Anal. Calcd for $[\text{Co}(\text{C}_4\text{H}_{12}\text{N}_2)_2\text{CO}_3]\text{Cl}\cdot 2\text{H}_2\text{O}$: C, 29.47; H, 7.62; N, 15.28. Found: C, 29.47; H, 7.97; N, 14.79.

Chromatography on a 2.5 cm \times 200 cm column packed with SP Sephadex C-25 cation-exchange resin using 0.15 M aqueous Na_2SO_4 eluent gave a clean separation of the carbonate complex into three bands that eluted with a retention time of 25 h. The relative abundances were determined from the relative spectral absorbances at 515 nm with extinction coefficients assumed to be equal. In order of elution, the abundances of the three fractions were 0.60:1.0:0.40. From the ^{13}C NMR spectra and steric considerations (vide infra), these respective fractions are assigned as the $C_2(\text{anti})$, C_1 , and $C_2(\text{syn})$ isomers.

Sodium sulfate was removed by a series of methanol additions and evaporations and was filtered off as it appeared. The solutions were finally allowed to evaporate to dryness, and the complex salts were extracted with methanol, in which the salts are partially soluble.

Table I. Summary of Crystal and Data Collection Parameters for $[\text{Co}(\text{ms-C}_4\text{H}_{12}\text{N}_2)_2\text{CO}_3]\cdot\text{H}_2\text{O}$

fw	440
F_{000}	880
a , Å	7.877 (4)
b , Å	11.889 (5)
c , Å	17.107 (7)
V , Å ³	1603 (1)
Z	4
ρ (calcd), g cm^{-3}	1.82
space group	$P2_12_12_1$
cryst shape	hexagonal plate
cryst dimens, mm	$0.5 \times 0.5 \times 0.2$
radiation	Mo $K\alpha$ ($\lambda = 0.71069$ Å)
monochromator	graphite
abs coeff, $\mu(\text{Mo } K\alpha)$ cm^{-1}	29.9
est min and max transmission	0.363 and 0.856
coeff	
scan speed, deg min^{-1}	variable, 5.0–29.3
scan range	1.25° below $2\theta(K\alpha_1)$ to 1.3° above $2\theta(K\alpha_2)$
2θ limits, deg	1.0–60.0
bkgd counting time	0.5 (scan time)
stds monitored	3 every 94 reflns
reflncs collected	5175
unique reflncs	4702
m , no. of unique data used	3930 with $ F > 5\sigma(F)$
n , no. of variables refined	172
erf =	1.11
w^{-1}	$[\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$
$R(F)$	$\sigma^2(F_o) + (gF_o)^2$, $g = 0.032$
$R_w(F)$	0.041
	$[\sum w(F_o - F_c)^2 / w F_o ^2]^{1/2}$
	0.043

Evaporation of the methanol extracts gave pink-red solids.

Spectroscopy. Natural-abundance, proton-decoupled ^{13}C NMR spectra were collected on a Varian FT-80 NMR spectrometer at 20.0 MHz using D_2O solvent and an external Me_4Si reference. ^{13}C NMR spectra of $[\text{Co}(\text{ms-bn})_2\text{CO}_3]\text{I}$ solutions were obtained by using a 0.5-s acquisition time, a 10- μs pulse width (equivalent to a 50° pulse), and no pulse delay. Concentration studies showed no observable concentration dependence of the ^{13}C chemical shifts. Spectra of ca. 0.15 M solutions of $[\text{Co}(\text{metn})_2\text{CO}_3]^+$ diastereomers as the sulfate salts were collected by using a 0.4-s acquisition time, a 4- μs pulse width (equivalent to a 40° pulse), and a 0.1-s pulse delay.

Visible spectra of $[\text{Co}(\text{metn})_2\text{CO}_3]^+$ diastereomers in aqueous solution with sulfate counterions were recorded on a Cary Model 219 spectrophotometer.

Crystal Structure Determination on $[\text{Co}(\text{ms-bn})_2\text{CO}_3]\cdot\text{H}_2\text{O}$ (Fraction A). All diffraction data were collected on a Nicolet P3/F diffractometer system at ambient temperature ($\sim 27^\circ\text{C}$). The SHELXTL series of programs¹³ was used for the structure solution, refinement, and plotting.

Crystal data and data collection parameters for a hexagonal plate grown by evaporation of an aqueous solution and mounted in a glass capillary are summarized in Table I. The systematic absences of $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$) were consistent with the space group $P2_12_12_1$. Moreover, the E statistics obtained from data reduction strongly indicated a noncentric space group. The data were corrected for Lorentz and polarization factors and for absorption by using an empirical correction based on ψ scans and by assuming a thin plate with the prominent face indexed as 010. The agreement factors for the ψ -scan reflections before and after the absorption correction were 0.129 and 0.027.

The structure was solved by direct methods, from which starting positions for cobalt and iodine were obtained. The agreement factor for isotropic refinement of all non-hydrogen atoms (with no hydrogen atoms located) was $R = 0.097$. This fell to $R = 0.047$ when the

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Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters with Their Estimated Standard Deviations for $[\text{Co}(ms\text{-}bn)_2\text{CO}_3]\cdot\text{H}_2\text{O}$

atom	x	y	z	$U_{\text{equiv}}, \text{\AA}^2$
I	-0.09927 (5)	-0.24061 (3)	0.67023 (2)	0.0408 (1)
Co	0.46777 (8)	-0.05711 (5)	0.78523 (3)	0.0210 (2)
N(1)	0.6810 (5)	-0.1054 (3)	0.8310 (2)	0.025 (1)
C(2)	0.7886 (6)	-0.0059 (4)	0.8493 (3)	0.020 (1)
C(3)	0.6714 (7)	0.0853 (4)	0.8822 (3)	0.030 (1)
N(4)	0.5237 (5)	0.0915 (3)	0.8289 (2)	0.027 (1)
C(5)	0.9373 (7)	-0.0395 (5)	0.9017 (4)	0.042 (2)
C(6)	0.6095 (9)	0.0623 (5)	0.9654 (3)	0.046 (2)
N(7)	0.5706 (5)	-0.0221 (3)	0.6829 (2)	0.028 (1)
C(8)	0.4346 (6)	-0.0026 (4)	0.6237 (3)	0.029 (1)
C(9)	0.2924 (6)	0.0593 (4)	0.6644 (3)	0.030 (1)
N(10)	0.2564 (6)	-0.0056 (4)	0.7382 (2)	0.027 (1)
C(11)	0.3867 (10)	-0.1170 (5)	0.5866 (3)	0.046 (2)
C(12)	0.1336 (8)	0.0772 (6)	0.6173 (4)	0.049 (2)
C(13)	0.3382 (6)	-0.2161 (4)	0.8388 (3)	0.029 (1)
O(1)	0.4079 (5)	-0.2118 (3)	0.7679 (2)	0.029 (1)
O(2)	0.3493 (5)	-0.1182 (3)	0.8729 (2)	0.028 (1)
O(3)	0.2773 (5)	-0.3022 (3)	0.8674 (2)	0.040 (1)
O(4)	0.6214 (6)	-0.2341 (4)	0.9829 (2)	0.053 (2)

^a $U_{\text{equiv}} = 1/3(U_{11} + U_{22} + U_{33})$ with the U_{ii} 's in an orthonormal coordinate system. The anisotropic thermal parameters used were of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. See: Willis, B. T. M.; Pryor, A. W. "Thermal Vibrations in Crystallography"; Cambridge University Press: Cambridge, 1975; pp 101-102.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[\text{Co}(ms\text{-}bn)_2\text{CO}_3]\cdot\text{H}_2\text{O}$

Distances			
Co-N(1)	1.940 (4)	Co-N(10)	1.948 (4)
Co-N(4)	1.968 (4)	Co-O(1)	1.922 (3)
Co-N(7)	1.973 (4)	Co-O(2)	1.910 (3)
Angles			
N(1)-Co-N(4)	85.3 (2)	Co-N(7)-C(8)	109.9 (3)
N(7)-Co-N(10)	85.3 (2)	Co-N(10)-C(9)	110.2 (3)
O(1)-Co-O(2)	68.8 (1)	Co-O(1)-C(13)	89.8 (3)
Co-N(1)-C(2)	110.1 (3)	Co-O(2)-C(13)	91.2 (3)
Co-N(4)-C(3)	111.4 (3)		

structure was refined anisotropically. The hydrogen atoms of the chelate rings were then fixed at calculated positions, and those of the water molecule were fixed at the positions found in a difference map. Isotropic temperature factors of all hydrogen atoms were fixed at 1.3 times the values of U_{equiv} of the atoms to which they were attached. The final difference map showed the four highest peaks, with intensities of $1.08\text{--}1.32 \text{ e \AA}^{-3}$, to be near the iodine atom. Final agreement factors are tabulated in Table I, and the final fractional coordinates and equivalent isotropic thermal parameters are listed in Table II. Tables of anisotropic thermal parameters, hydrogen atom positions and thermal parameters, observed and calculated structure factors, interatomic distances and angles, and torsion angles are available as supplementary material.

Structure determinations on fraction A crystals having both "bowtie" and rectangular plate habits showed these to be isostructural with the hexagonal plates.

Results and Discussion

Structure of $[\text{Co}(ms\text{-}bn)_2\text{CO}_3]\cdot\text{H}_2\text{O}$ (Fraction A). The crystal contains a single enantiomer—either $\Delta(\lambda\lambda)$ or $\Lambda(\delta\delta)$, where the δ and λ labels denote the conformations of the nonplanar 2,3-butanediamine chelate rings. The refinement was carried out on the $\Delta(\lambda\lambda)$ form, which gave a slightly better final agreement factor than that obtained with $\Lambda(\delta\delta)$ ($R = 0.041$ vs. $R = 0.044$). The conformers, with one methyl group axial and one equatorial in each ring, are *lel,lel*, as expected.⁸ The cationic complex, pictured in Figure 3 (supplementary material) as the $\Delta(\lambda\lambda)$ enantiomer, has the $C_2(\text{anti})$ structure though there is no crystallographic symmetry. Some selected interatomic distances and angles are given in Table III, and atom designations are presented in Figure 4. The unit cell

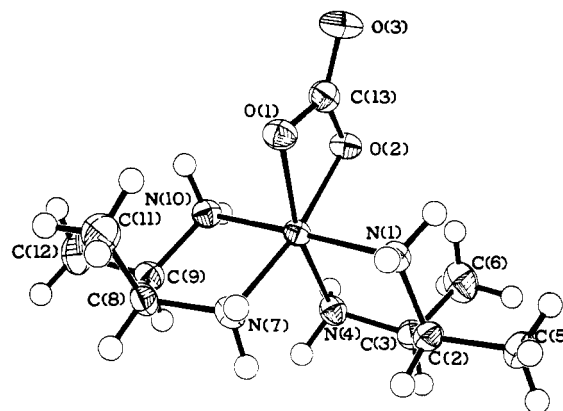


Figure 4. Atom designations for the complex $[\text{Co}(ms\text{-}bn)_2\text{CO}_3]^+$ found in the structure determination on $[\text{Co}(ms\text{-}bn)_2\text{CO}_3]\cdot\text{H}_2\text{O}$.

Table IV. Chelate Ring Torsion Angles (deg) for Cobalt(III) 2,3-Butanediamine Complexes^a

angle	$[\text{Co}(ms\text{-}bn)_2\text{CO}_3]^+$	<i>lel,lel,lel</i> - $[\text{Co}(\pm)\text{-}bn)_3]^{3+}$ ^b
N-C-N	-48.4 (12)	55.1
C-C-N-Co		
eq ^c	40.0 (3)	-42.8
ax	35.7 (20)	
C-N-Co-N		
eq	-16.6 (10)	25.2
ax	-11.2 (14)	

^a Average values for two crystallographically distinct angles are given for the *ms-bn* structure with average absolute deviations. Only one value is available for each angle in the $(\pm)\text{-}bn$ structure owing to its higher symmetry. The difference in sign between corresponding angles in the two structures is due only to the choice of enantiomers for the asymmetric units. ^b Reference 14. ^c The terms "eq" and "ax" distinguish between that portion of the chelate ring containing an equatorial methyl group and that containing an axial group.

contents are shown in Figure 5 (supplementary material).

Crystal structures of the racemic 2,3-butanediamine complexes *lel,lel,lel*- $[\text{Co}(\pm)\text{-}bn)_3]\text{Cl}_3$ ¹⁴ and *lel,lel,lel*- $[\text{Rh}(\pm)\text{-}bn)_3]\text{Br}_3$ ¹⁰ and of the *meso*-2,3-butanediamine complex $[\text{Pd}(ms\text{-}bn)\text{Cl}_2]$ ¹⁵ have been completed. A comparison of the *lel,lel,lel*- $[\text{Co}(\pm)\text{-}bn)_3]\text{Cl}_3$ structural data with those for $[\text{Co}(ms\text{-}bn)_2\text{CO}_3]\cdot\text{H}_2\text{O}$ shows significant chelate ring flattening in the latter structure as seen in the smaller chelate ring torsion angles (Table IV). Flattening of chelate rings containing *meso*-2,3-butanediamine ligands—apparently owing to the presence of axial methyl groups—is predicted by molecular mechanics calculations.^{8,16,17} However, the differences between corresponding torsion angles in the nonequivalent portions of the *ms-bn* chelate ring (i.e., portions differing according to whether they contain an axial or an equatorial methyl group) that we observe in $[\text{Co}(ms\text{-}bn)_2\text{CO}_3]^+$ (Table IV) are less than half of those predicted by some molecular mechanics calculations.¹⁷

¹³C NMR Spectra of $[\text{Co}(ms\text{-}bn)_2\text{CO}_3]^+$. The ¹³C NMR spectrum of a solution of fraction A, the less soluble material, exhibits precisely the number of resonances expected for a complex of C_2 symmetry—two bands in the methyl region and two bands in the methine region. Since fraction A has been shown to contain the $C_2(\text{anti})$ isomer by X-ray diffraction techniques, the observed NMR spectrum can be reliably as-

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Table V. ^{13}C NMR Chemical Shifts for Diastereomers of $[\text{Co}(\text{ms-bn})_2\text{CO}_3]^+$ and $[\text{Co}(\text{metn})_2\text{CO}_3]^+$

compd	δ		
	$-\text{CH}_3$	CH_2	$-\text{CH}$
$C_2(\text{anti})\text{-}[\text{Co}(\text{ms-bn})_2\text{CO}_3]^+$	14.60		55.95
	15.57		56.89
$C_2(\text{syn})\text{-}[\text{Co}(\text{ms-bn})_2\text{CO}_3]^+$	14.60		55.94
	15.55		56.87
$C_1\text{-}[\text{Co}(\text{ms-bn})_2\text{CO}_3]^+$	13.86		54.66
	14.72		56.19
	16.07		56.87
	16.30		57.07
$C_2(\text{anti})\text{-}[\text{Co}(\text{metn})_2\text{CO}_3]^+$	16.95	46.58	32.59
		47.06	
$C_2(\text{syn})\text{-}[\text{Co}(\text{metn})_2\text{CO}_3]^+$	16.94	46.50	32.58
		47.07	
$C_1\text{-}[\text{Co}(\text{metn})_2\text{CO}_3]^+$	17.22	46.26 ^a	32.35
	17.38	47.08	32.87
		47.50	

^a Intensity indicates two overlapping peaks.

signed to this isomer. The spiking experiment described earlier shows that fraction A is one of the constituents of the first chromatography band obtained. The ^{13}C NMR spectrum of this band contains four peaks with chemical shifts identical with those obtained for fraction A plus an additional set of eight resonances (four methyl and four methine) that can be assigned to the C_1 isomer. As expected, this latter set of eight peaks varies in intensity relative to the set of four peaks attributed to the $C_2(\text{anti})$ isomer depending on the precise portion collected during chromatography.

In solution, fraction B, the more soluble material, exhibits a ^{13}C NMR spectrum with peaks whose chemical shifts are identical with those found for peaks in the spectrum of the second well-defined chromatographic band to be eluted. Eight of the resonances are identical with those assigned (above) to the C_1 symmetry diastereomer. The remaining four resonances must be due to the $C_2(\text{syn})$ isomer. Again, the intensities of the peaks assigned to the C_2 isomer vary relative to those assigned to the C_1 isomer depending on the precise chromatographic fraction obtained.

These results and the observation that chromatography of fraction B gives one well-defined band preceded by and overlapped with a broad, diffuse band show that the first well-defined chromatographic band arises from the $C_2(\text{anti})$ isomer and the second, from the $C_2(\text{syn})$ isomer. Both of these bands are overlapped with and contaminated by a third broad, diffuse band from the C_1 isomer. This allows the assignment of the ^{13}C NMR spectra as given in Table V.

Of particular interest is the observation that, within experimental error, ^{13}C NMR spectra of the $C_2(\text{anti})$ and $C_2(\text{syn})$ isomers are identical while the spectrum of the C_1 isomer is strikingly different. There is no apparent explanation as to why intermolecularly diastereotopic carbon atoms of the two C_2 isomers have identical chemical shifts while intramolecularly diastereotopic carbon atoms of the C_1 isomer show large shift differences. Before carrying out this experiment, we had expected that the spectrum of the C_1 isomer, where methyl groups on one chelate ring point toward the carbonate ligand while those on the other ring point away, might approximate a superposition of spectra of the two C_2 isomers, where methyl groups of both rings point away from carbonate in one case and toward carbonate in the other.

^{13}C NMR of $[\text{Co}(\text{metn})_2\text{CO}_3]^+$. Owing to steric crowding, the $C_2(\text{syn})$ isomer is expected to be less stable than the C_2 -

(anti) species.^{7,18} From consideration of these relative expected stabilities and from the ^{13}C NMR spectra, the chromatographic fractions are easily assigned as $C_2(\text{anti})$, C_1 , and $C_2(\text{syn})$ in the order of elution. That the C_1 isomer is present in largest abundance is probably due to a symmetry-dependent entropy contribution of $R \ln 2$ to its stability relative to the C_2 diastereomers. The ^{13}C NMR spectral data based on these assignments are presented in Table V.

Though the ligand systems are quite different, like the $[\text{Co}(\text{ms-bn})_2\text{CO}_3]^+$ complexes, the $[\text{Co}(\text{metn})_2\text{CO}_3]^+$ system shows virtually identical ^{13}C NMR spectra for the two C_2 isomers and a strikingly different spectrum for the C_1 isomer. Again, these results are unexpected. Earlier work⁸ has indicated that ^{13}C NMR chemical shift differentiation of diastereotopic carbon atoms is often enhanced when chelating ligands are highly flexible (as they are here) and when the diastereotopic atoms are in conformationally distinct portions of the chelate ring, though there are some apparent exceptions to these conclusions.¹⁰ If these inferences are correct, it appears that the (time-averaged) conformations of the ligands in the C_2 isomers of $[\text{Co}(\text{metn})_2\text{CO}_3]^+$ and also of $[\text{Co}(\text{ms-bn})_2\text{CO}_3]^+$ are very similar to each other, while the conformations of the two chemically distinct chelate rings of each of the C_1 isomers are quite different from each other and from conformations found for the C_2 diastereomers. These conformational differences and similarities may be reflected in the electronic aqueous solution spectra of the $[\text{Co}(\text{metn})_2\text{CO}_3]^+$ diastereomers where values of 516, 517, and 509 nm are observed for the wavelengths of the lowest energy band for the $C_2(\text{anti})$, $C_2(\text{syn})$, and C_1 species, respectively. Work on tris(diamine) complexes of Co(III) with 6-membered chelate rings suggests that an increased energy for the lowest energy electronic absorption band is associated with an increased contribution from skew-boat ring conformations.⁹ If the same trend holds for carbonate bis(diamine) complexes, the spectra we observe are suggestive of an increased skew-boat character for the C_1 isomer of $[\text{Co}(\text{metn})_2\text{CO}_3]^+$. Unfortunately, we have been unable to obtain (thus far) suitable crystals of diastereomers other than $C_2(\text{anti})\text{-}[\text{Co}(\text{ms-bn})_2\text{CO}_3]\text{I}\cdot\text{H}_2\text{O}$ for X-ray structure determinations, which might shed light on these questions of conformation.

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Registry No. $C_2(\text{anti})\text{-}[\text{Co}(\text{ms-bn})_2\text{CO}_3]\text{I}\cdot\text{H}_2\text{O}$, 86852-57-5; $C_1\text{-}[\text{Co}(\text{ms-bn})_2\text{CO}_3]\text{I}$, 86852-58-6; $C_2(\text{syn})\text{-}[\text{Co}(\text{ms-bn})_2\text{CO}_3]\text{I}$, 86823-47-4; $[\text{Co}(\text{ms-bn})_2\text{CO}_3]\text{I}$, 86852-59-7; $C_2(\text{anti})\text{-}[\text{Co}(\text{metn})_2\text{CO}_3]\text{Cl}$, 86852-00-8; $C_1\text{-}[\text{Co}(\text{metn})_2\text{CO}_3]\text{Cl}$, 86852-01-9; $C_2(\text{syn})\text{-}[\text{Co}(\text{metn})_2\text{CO}_3]\text{Cl}$, 86852-02-0; $[\text{Co}(\text{metn})_2\text{CO}_2]\text{Cl}$, 86823-48-5; $\text{trans-}[\text{Co}(\text{metn})_2\text{Cl}_2]\text{Cl}$, 86823-49-6.

Supplementary Material Available: Stereoviews of the complex found in the X-ray diffraction study of $[\text{Co}(\text{ms-bn})_2\text{CO}_3]\text{I}\cdot\text{H}_2\text{O}$ (Figure 3) and of the unit cell contents (Figure 5) and tables of observed and calculated structure factors, anisotropic thermal parameters, hydrogen atom positions and thermal parameters, complete interatomic distances and angles, and torsion angles (35 pages). Ordering information is given on any current masthead page.