



Thus, conformational preference was observed in  $\text{Ni}(\text{en})_3^{2+}$  ( $\text{en}$  = ethylenediamine)<sup>6</sup> even though there is no conformational preference in  $\text{Ni}(\text{en})_2^{2+}$ .<sup>2</sup>

A recent paper<sup>7</sup> has reported some contact shift data for the complexes  $\text{Ni}(\text{meso-bn})_3^{2+}$  and  $\text{Ni}(\text{d-bn})_3^{2+}$ . We believe the data reported in the above paper are incorrect. The purpose of this paper is to present a more detailed study of this interesting system.

### Experimental Section

The pmr spectra for all species except  $\text{Ni}(\text{meso-bn})_3^{2+}$  were obtained with a Varian HA-100 spectrometer by the method previously reported.<sup>2</sup> Pmr spectra of  $\text{Ni}(\text{meso-bn})_3^{2+}$  were obtained by modulation through the V3521A unit at 3100 Hz and operating in the usual HR mode.

Anhydrous nickel chloride (Alfa Inorganics) was used without purification. 2,3-Diaminobutane was prepared by the method of Dickey, *et al.*,<sup>8</sup> and was also obtained from Wyandotte Chemical Corp. The meso and racemic isomers were separated by a published method.<sup>8</sup> The purity of the meso and racemic isomers was checked by the method of Sudmeier and Reilley.<sup>9</sup> The center of the methyl doublet of  $\text{meso-bn} \cdot 2\text{HCl}$  is at  $-1.50$  ppm while for  $\text{rac-bn} \cdot 2\text{HCl}$  the center of the methyl doublet is at  $-1.45$  ppm. The  $\text{bn} \cdot 2\text{HCl}$  was recrystallized until only one methyl doublet was observed for the meso isomer and until a constant meso:racemic ratio was obtained for the racemic isomer. It is estimated that the meso isomer is about 99% pure and the racemic isomer about 93% pure. The *dl* racemic mixture was not resolved. All solutions were made in deuterium oxide (99.77%, Columbia Organics) and were prepared by mixing anhydrous nickel chloride with the appropriate amount of butylenediamine dihydrochloride and neutralizing with potassium deuterioxide, followed by evaporation at reduced pressure and redissolving in deuterium oxide two times to remove any residual water. TMS\* (sodium 3-(trimethylsilyl)-1-propanesulfonate) (Eastman Organics) was used as an internal reference in all solutions. All solutions were 0.5–1 M in complex except for the tris complexes. The  $\text{Ni}(\text{rac-bn})_3^{2+}$  data were obtained from a saturated solution of the chloride prepared as above. The  $\text{Ni}(\text{meso-bn})_3^{2+}$  data were obtained from a saturated solution of the sulfate prepared by removing the chloride by precipitation with silver sulfate solution.

### Results

Schematic spectra of solutions containing 1:1, 2:1, 3:1, and 4:1  $\text{bn}:\text{Ni}(\text{II})$  mole ratios are shown in Figure 1. The shifts are reported relative to the diamagnetic zinc complexes. Lines due to residual HOD and uncomplexed ligand, if present, and the reference compound are not shown.

**Spectral Assignments.**—The spectrum of the solution containing a 1:1 mole ratio of the meso isomer to nickel(II) consists of four lines. The first line at about  $-4$  ppm overlaps the residual HOD peak which is not shown. One would expect the 1:1 meso complex to have a two-line spectrum because rapid  $\delta \rightleftharpoons \lambda$  conversion between equally energetic states should average the axial and equatorial differences.<sup>2</sup> The resulting two lines would be at positions indicative of the average value for an axial and equatorial methyl and for an axial and equatorial methine. One would also expect both of these lines to obey normal Curie behavior.<sup>2</sup>

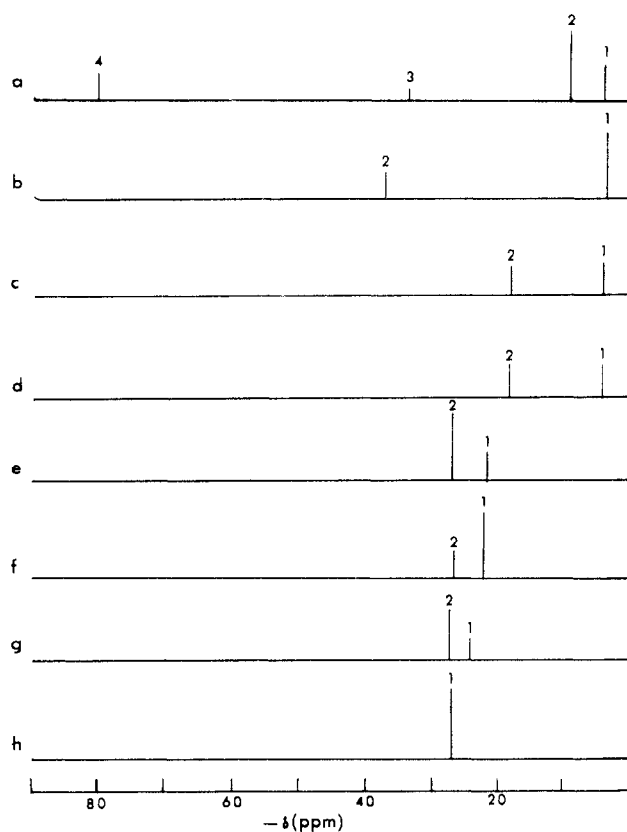


Figure 1.—Contact shift spectra of  $\text{NiCl}_2$  solutions containing various amounts of butylenediamine. The ratio of  $\text{bn}:\text{NiCl}_2$  in solution is (a) 1:1 (meso), (b) 2:1 (meso), (c) 3:1 (meso), (d) 4:1 (meso), (e) 1:1 (racemic), (f) 2:1 (racemic), (g) 3:1 (racemic), and (h) 4:1 (racemic). Chemical shifts are relative to the  $\text{Zn}(\text{bn})_2^{2+}$  complex.

Consideration of the relative formation constants for the mono, bis, and tris complexes<sup>10</sup> predicts that peaks should be observed for both mono and bis complexes in the 1:1 mole ratio spectrum. Spectra due to mono and bis complexes, for example, were observed in a study of the system  $\text{Ni}(\text{en})_x$ .<sup>6</sup> Lines 1 ( $-4$  ppm) and 3 ( $-34$  ppm) of the 1:1 mole ratio spectrum are assigned to the bis complex on the basis of peak areas and for additional reasons explained below. This interpretation is consistent with the observation of much smaller relative intensities for lines 1 and 3 in the spectrum of a 0.5:1 mole ratio solution. The spectrum of a 2:1 mole ratio solution of  $\text{meso-bn}:\text{Ni}$  consists of two peaks at approximately the same resonance positions as observed for the 2:1 isomer in the 1:1 mole ratio solution. The slight discrepancy ( $\sim 3$  ppm) between the methine resonance positions in these two solutions is due to a slight shift in the octahedral (paramagnetic)  $\rightleftharpoons$  square-planar (diamagnetic) equilibrium of the bis complex caused by a small difference in chloride ion concentration in the two solutions. That this discrepancy is not due to formation of complexes of the type  $\text{Ni}(\text{bn})_2(\text{Cl})_x(\text{H}_2\text{O})_y$  ( $x + y = 2$ ) is shown by the following experiment. Addition of a 2 molar excess of NaCl to  $\text{Ni}(\text{meso-bn})_2^{2+}$  solutions shifted the methine resonance from  $-35$  to  $-25$  ppm. If chloro complexes were

(10) F. Basolo, Y. T. Chen, and R. K. Murman, *J. Amer. Chem. Soc.*, **76**, 956 (1954).

(6) F. F.-L. Ho and C. N. Reilley, *Anal. Chem.*, **42**, 600 (1970).

(7) R. S. Fitzgerald and R. S. Drago, *Inorg. Chem.*, **8**, 2254 (1969).

(8) F. H. Dickey, W. Fickett, and S. Lucas, *J. Amer. Chem. Soc.*, **74**, 944 (1952).

(9) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1707 (1964).

formed with the octahedral form (paramagnetic), the resonance position would shift to lower fields. Because the shift is in the opposite direction, the effect of chloro complexation is small relative to the effect of chloride ion on the octahedral  $\rightleftharpoons$  square-planar equilibrium. The octahedral  $\rightleftharpoons$  square-planar equilibrium will be discussed in more detail below.

The spectrum of a solution containing 3:1 mole ratio of meso isomer to Ni(II) consists of two lines of approximately equal intensity which are assigned to methyl groups in different time-average environments (one more equatorial and the other more axial). Both of these peaks appear at field values higher than those expected for the methine protons. Because of the proximity of the residual HOD peak, accurate measurements of the area and position of line 1 in this spectrum are not possible. Furthermore both of these peaks are small because of the limited solubility of the tris complex and are quite broad. Because one would expect the methine resonances to appear much farther downfield, they would be even broader<sup>1</sup> and, in this instance, are not observed.

The spectrum of a solution containing a 1:1 mole ratio of racemic butylenediamine and Ni(II), shown in Figure 1, consists of two lines. The first line (-21.5 ppm) is assigned to both the -CH<sub>3</sub> and -CH protons on the complex Ni(*rac*-bn)<sub>2</sub><sup>2+</sup> for the same reasons used to assign the peaks due to the corresponding meso complex above. The second peak (-26.6 ppm) is assigned to all of the protons on the complex Ni(*rac*-bn)<sub>3</sub><sup>2+</sup>. The assignment of the same contact shift position to both the methine resonance and the methyl groups of the racemic compound is not unreasonable if one bears in mind that the methyl groups will be predominantly equatorial, and, hence, the methine will be predominantly axial. The methyl resonance was only 4 ppm upfield of the axial proton resonance in Ni(pn)<sub>2</sub><sup>2+</sup> (pn = propylenediamine) and the methyl and methine resonances appear at the same position in NiPDTA<sup>2-</sup> (PDTA<sup>4-</sup> = 1,2-propylenediaminetetraacetate).<sup>11</sup> The assignment of the same contact shift value to the equatorial methyl and axial methine protons in NiPDTA<sup>2-</sup> is based upon accurate integrations of the signal intensities and, hence, is not dependent upon any previous assumptions. The spectrum of a solution containing a 2:1 mole ratio of racemic bn and Ni(II) is consistent with this assignment.

The spectra of solutions containing 3:1 and 4:1 mole ratios of ligand to metal consist of a single line at the same shift position as for the 1:1 racemic complexes. These data are summarized in Table I.

The temperature dependences of the individual contact shifts of the various species are shown in Figures 2-5. The 1:1 complexes show normal Curie behavior. Both meso and racemic bis complexes show marked deviations from Curie behavior. The behavior of the spectra for the tris meso complex is analogous to that of the tris(ethylenediamine)nickel(II) complex<sup>6</sup> in that

TABLE I

SPECTRAL ASSIGNMENTS FOR THE VARIOUS SPECIES PRESENT IN SOLUTIONS OF 0.5 M NICKEL AND VARIOUS MOLE RATIOS OF BUTYLENEDIAMINE (bn)

| [bn], M                 | Line             | Contact shift, ppm | Assignment                                      |  |
|-------------------------|------------------|--------------------|---|--|
|                         |                  |                    | Species   | Protons  |
| 0.5 <sup>a</sup>        | 1                | -4                 | Ni( <i>meso</i> -bn) <sub>2</sub> <sup>2+</sup> | CH <sub>3</sub>                                |
|                         | 2                | -9.4               | Ni( <i>meso</i> -bn) <sub>2</sub> <sup>2+</sup> | CH <sub>3</sub>                                |
|                         | 3                | -34                | Ni( <i>meso</i> -bn) <sub>2</sub> <sup>2+</sup> | CH   |
| 1.0 <sup>a</sup>        | 4                | -80.5              | Ni( <i>meso</i> -bn) <sub>2</sub> <sup>2+</sup> | CH   |
|                         | 1                | -4                 | Ni( <i>meso</i> -bn) <sub>2</sub> <sup>2+</sup> | CH <sub>3</sub>                                |
| 1.5 or 2.0 <sup>a</sup> | 2                | -37                | Ni( <i>meso</i> -bn) <sub>2</sub> <sup>2+</sup> | CH   |
|                         | 1                | -5                 | Ni( <i>meso</i> -bn) <sub>3</sub> <sup>2+</sup> | CH <sub>3</sub> (ax.) <sup>c</sup>             |
|                         | 2                | -15                | Ni( <i>meso</i> -bn) <sub>3</sub> <sup>2+</sup> | CH <sub>3</sub> (eq.) <sup>c</sup>             |
|                         | 0.5 <sup>b</sup> | 1                  | -21.5   | Ni( <i>rac</i> -bn) <sub>2</sub> <sup>2+</sup> |
| 2                       |                  | -26.6              | Ni( <i>rac</i> -bn) <sub>2</sub> <sup>2+</sup>  | All  |
| 1.0 <sup>b</sup>        | 1                | -22                | Ni( <i>rac</i> -bn) <sub>2</sub> <sup>2+</sup>  | All  |
|                         | 2                | -26.5              | Ni( <i>rac</i> -bn) <sub>2</sub> <sup>2+</sup>  | All  |
| 1.5 <sup>b</sup>        | 1                | -24                | Ni( <i>rac</i> -bn) <sub>2</sub> <sup>2+</sup>  | All  |
|                         | 2                | -27                | Ni( <i>rac</i> -bn) <sub>3</sub> <sup>2+</sup>  | All  |
| 2.0 <sup>b</sup>        | 1                | -27                | Ni( <i>rac</i> -bn) <sub>3</sub> <sup>2+</sup>  | All  |

<sup>a</sup> Meso. <sup>b</sup> Racemic. <sup>c</sup> Refers to position in more abundant conformation.

the two-line spectrum collapses to a single peak at elevated temperatures.

### Discussion

**Mono Complexes.**—Previous data from these laboratories indicate that for the various substituted ethylenediamine complexes of Ni(II) the observed contact shift is roughly proportional to the formation constant of the complex.<sup>2</sup> One would not expect this relationship to be true for a wide range of ligands and metal ions. For a limited series of similar complexes, however, where the various entropy contributions to the

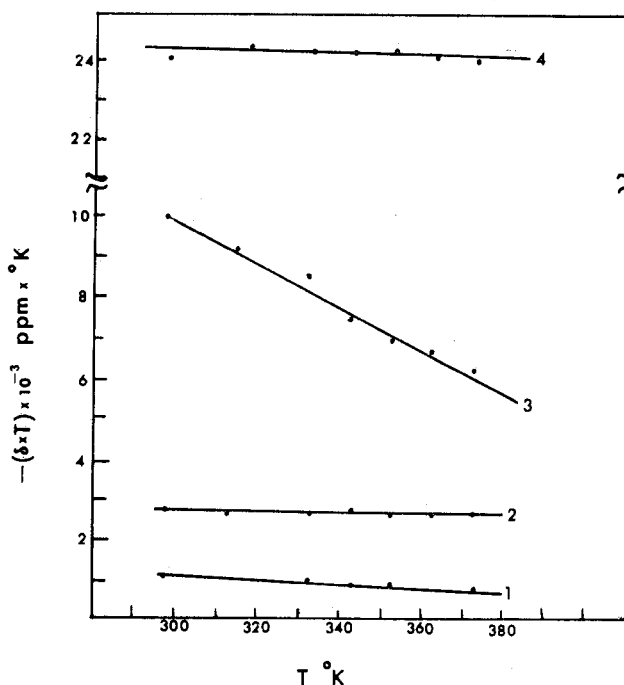


Figure 2.—Temperature dependence of the product ( $\delta T$ ) for Ni(*meso*-bn)<sub>2</sub><sup>2+</sup> and Ni(*meso*-bn)<sub>3</sub><sup>2+</sup>. Numbers refer to line number in spectrum a of Figure 1. Lines 1 and 3 are CH<sub>3</sub> and CH for Ni(*meso*-bn)<sub>2</sub><sup>2+</sup>, respectively. Lines 2 and 4 are CH<sub>3</sub> and CH for Ni(*meso*-bn)<sub>3</sub><sup>2+</sup>, respectively.

(11) L. E. Erickson, D. C. Young, F. F.-L. Ho, S. R. Watkins, J. B. Terrill, and C. N. Reilly, *Inorg. Chem.*, **10**, 441 (1971).

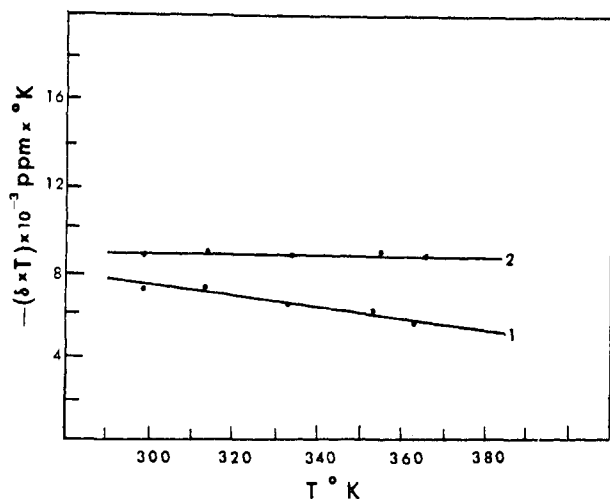


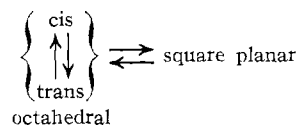
Figure 3—Temperature dependence of the product  $(\delta T)$  for  $\text{Ni}(\text{rac-bn})_2^{2+}$  and  $\text{Ni}(\text{meso-bn})_2^{2+}$ . Numbers refer to line numbers in spectrum e of Figure 1. Line 1 is for  $\text{CH}_3$  and  $\text{CH}$  of  $\text{Ni}(\text{rac-bn})_2^{2+}$ . Line 2 is for  $\text{CH}_3$  and  $\text{CH}$  of  $\text{Ni}(\text{meso-bn})_2^{2+}$ .

$\Delta G$  are approximately equal, the above relationship is not unreasonable if one also assumes that the orbitals containing the unpaired spin contribute equally to the bonding energy over the series. Within the above limitations, the observed resonance position of the methine protons of  $\text{Ni}(\text{meso-bn})_2^{2+}$  ( $-80.5$  ppm) is close to the value of  $-93.3$  ppm reported for  $\text{Ni}(\text{en})_2^{2+}$ . The appearance of only a single resonance in the  $\text{Ni}(\text{en})_2^{2+}$  spectrum was interpreted as being due to rapid  $\delta \rightleftharpoons \lambda$  conversion between configurations of equal thermodynamic stability.<sup>2</sup> The same interpretation is valid in this case and is supported by the normal Curie behavior of this species shown in Figure 2. An alternant explanation for the observation of a single methine resonance would be that the chelate ring is planar, but this alternative has been consistently disproved and is inconsistent with the racemic isomer spectrum.

The spectrum of  $\text{Ni}(\text{rac-bn})_2^{2+}$  would be expected to show deviations from Curie behavior because  $\delta \rightleftharpoons \lambda$  conversion occurs between conformational states of unequal energy, analogous to that previously observed for unsymmetrically substituted *N*-alkylethylenediamines.<sup>2</sup> The extent of the deviation is too small for detection, as is apparent from inspection of Figure 3. The explanation lies in the much greater energy required in this case, namely, to bring *two* methyl groups from equatorial to axial positions. The energy difference between  $\delta$  and  $\lambda$  forms of  $\text{Ni}(\text{pn})_2^{2+}$  was found to be about 1.2 kcal/mol.<sup>2</sup> The energy difference between  $\delta$  and  $\lambda$  forms of  $\text{Ni}(\text{rac-bn})_2^{2+}$  was approximated as  $\Delta H = 2.5$  kcal/mol and  $\Delta S = 0.5$  eu ( $\Delta G = \Delta H - T\Delta S$ ) on the basis of previous data.<sup>2</sup> From these values the deviation from normal Curie behavior was calculated to be  $\sim 0.9$  ppm at  $100^\circ$ . This deviation is within experimental error. The normal Curie behavior is, hence, consistent with previous studies.

**Bis Complexes.**—The very great difference (46.5 ppm) between the contact shift of the methine protons in  $\text{Ni}(\text{meso-bn})_2^{2+}$  and in  $\text{Ni}(\text{meso-bn})_2^{2+}$  is in sharp con-

trast to the observations made on the  $\text{Ni}(\text{en})_2$  system<sup>6</sup> where the difference between the shifts of methylene protons in  $\text{Ni}(\text{en})_2^{2+}$  and in  $\text{Ni}(\text{en})_2^{2+}$  was only 2 ppm. The large deviation from Curie behavior (line 3 of Figure 2) for  $\text{Ni}(\text{meso-bn})_2^{2+}$  is at first surprising because one would expect normal Curie behavior for meso complexes and  $\text{Ni}(\text{en})_2^{2+}$  did not exhibit any noticeable deviation. It is known, however, that the  $\text{Ni}(\text{bn})_2^{2+}$  complexes exist in two forms at room temperature: a paramagnetic octahedral form and a diamagnetic square-planar form<sup>10,12</sup>. The relative percentages of octahedral and square-planar forms of  $\text{Ni}(\text{meso-bn})_2^{2+}$  were studied by Leussing, *et al.*,<sup>12</sup> who found that between 23 and 55% of the complex is present as the square-planar form, the percentage depending strongly on the concentration and type of anions present in solution. The octahedral forms of the bis complexes can exist in both *cis* and *trans* configurations. Only a single spectrum is observed for the bis complexes, however. Thus, either the *cis* and *trans* isomers rapidly (on the nmr time scale) interconvert or no appreciable amount of *cis* isomer is formed. The octahedral  $\rightleftharpoons$  square-planar equilibrium is, therefore, represented as shown below. The present data do not allow determination of the relative amounts of *cis* and *trans* octahedral forms present. Thus, the deviations of contact shift



values from Curie behavior as well as the large difference between the contact shift of  $\text{Ni}(\text{meso-bn})_2^{2+}$  and  $\text{Ni}(\text{meso-bn})_2^{2+}$  at room temperature may be attributed to a rapid octahedral  $\rightleftharpoons$  square-planar equilibrium. Because only an averaged spectrum is observed, the interconversion must be faster than the chemical shift difference between the two forms.<sup>13</sup> An upper limit on the lifetime of either form can be calculated from the equation<sup>13</sup>

$$\tau = \frac{1}{\pi(\omega_A - \omega_B)} \quad (1)$$

The lifetime calculated for either form of the bis meso complex is  $< 4 \times 10^{-5}$  sec. Because both forms are observed independently in the optical spectra,<sup>12</sup> a lower limit of about  $10^{-15}$  sec is estimated for the lifetime of either form.

The deviation from Curie behavior can be used to calculate the energy difference between square-planar and octahedral forms as a function of temperature in the following manner. Let  $K$  be the product of the contact shift of methine protons and temperature expected for normal Curie behavior. The observed contact shift-temperature product will be the weighted average of the shift experienced at each environment ( $K = 0$  for the

(12) D. L. Leussing, J. Harris, and P. Wood, *J. Phys. Chem.*, **66**, 1544 (1962).

(13) A. Carrington and A. D. McLachlan in "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 207.

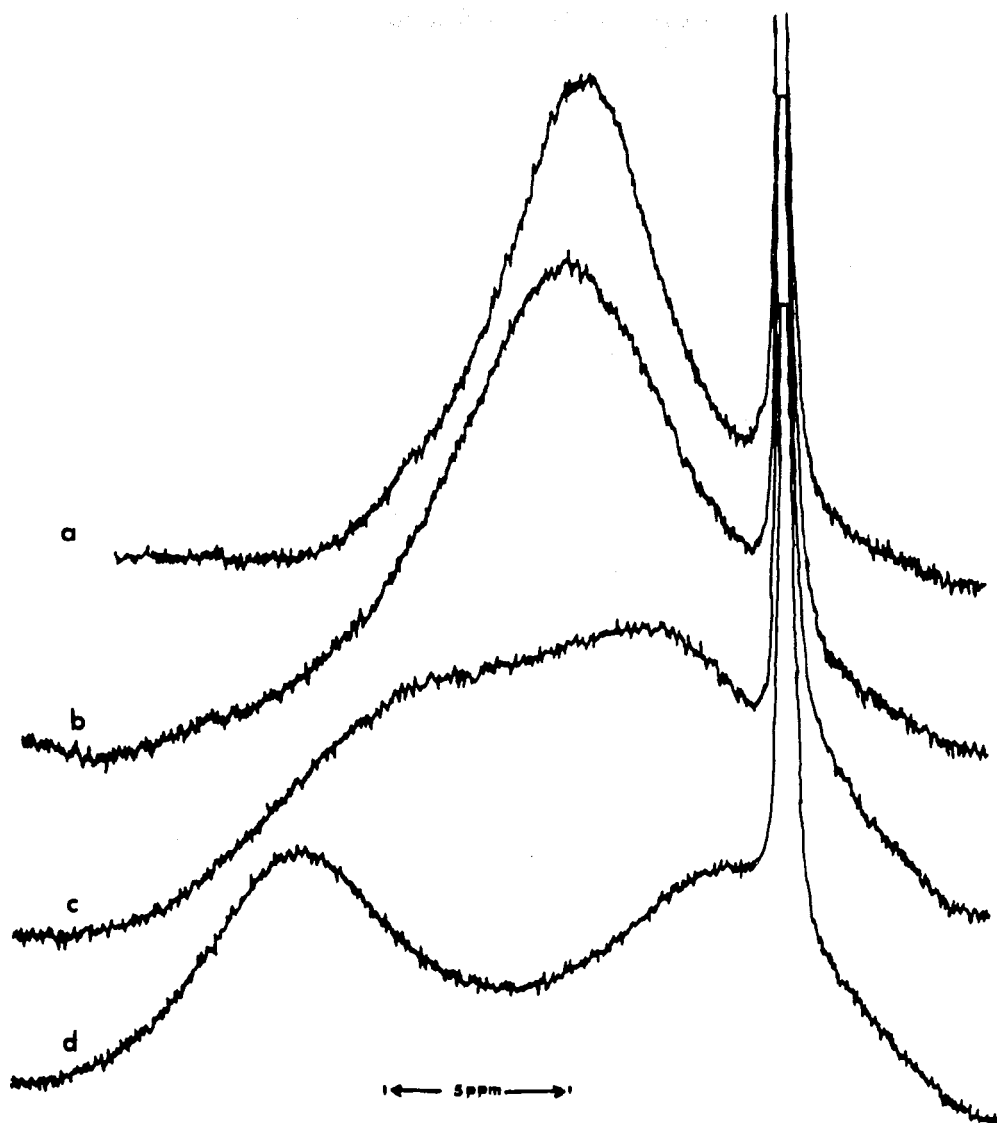


Figure 4.—Spectra of saturated Ni(*meso*-bn)<sub>3</sub>SO<sub>4</sub> solution in deuterium oxide at various temperatures: (a) 60°, (b) 50°, (c) 40°, (d) 27°.

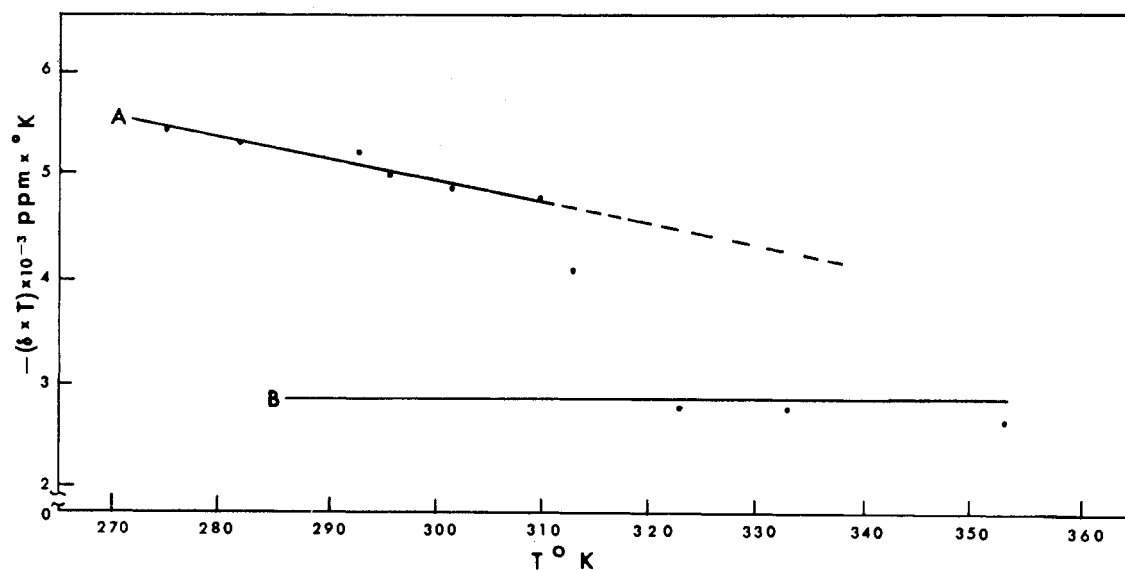


Figure 5.—Temperature dependence of the product  $(\delta T)$  for Ni(*meso*-bn)<sub>3</sub><sup>2+</sup>. The points are data points from the downfield (−15 ppm) resonance. Line A is drawn using eq 20 and values of +7.4 ppm for  $\delta_a$  and −26.6 ppm for  $\delta_b$  and expression 21 for  $\Delta G$ . Line B is the average (coalesced) position predicted from the methyl resonance position of Ni(*meso*-bn)<sup>2+</sup>.

diamagnetic species). This is stated mathematically in the equation

$$(\delta T) = \frac{1}{1 + e^{-\Delta G/RT}K} \quad (2)$$

$\Delta G$  will be a function of temperature because of the finite entropy contribution

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

In order to use eq 2, a value of  $K$  for the pure paramagnetic form must be obtained. This value was approximated as  $-23,244 \text{ ppm } ^\circ\text{K}$  ( $-78 \text{ ppm} \times 298^\circ\text{K}$ ). This value was determined by assuming that the methine shift of the octahedral bis complex would be about 2 ppm less than the shift of mono complex ( $-78$  instead of  $-80 \text{ ppm}$ ) as observed in the  $\text{Ni}(\text{en})_2^{2+}$  system.<sup>6</sup> This value of  $K$  was tested by fitting the data to the assumed value of  $K$  through a least-squares procedure; a value of  $K$  equal to  $-23,244$  was found to give the smallest standard deviation in the calculated values of  $\Delta G$ .

Using eq 2, the value of  $K$  above, and the data shown in Figure 2,  $\Delta G$  as a function of temperature is obtained.  $\Delta G$  obeys the equation

$$\Delta G = 2150 \pm 70 - (7.7 \pm 0.2)T \quad (4)$$

The analysis of the data for  $\text{Ni}(\text{rac-bn})_2^{2+}$  follows an analogous scheme except that a value of  $-8046 \text{ ppm } ^\circ\text{K}$  ( $-27 \text{ ppm} \times 298^\circ\text{K}$ ) was used for  $K$ .  $\Delta G$  obeys the equation

$$\Delta G = 3700 \pm 500 - (9.0 \pm 1.5)T \quad (5)$$

The greater experimental error in the racemic case is due to the very small amount of square-planar form present; this leads to smaller shift differences and, hence, larger relative errors. The lifetime of the bis racemic complex in either the octahedral or square-planar form is estimated from eq 1 to be less than  $10^{-4} \text{ sec}$ .

The above free energy expressions show that the octahedral square-planar interchange is a large endothermic enthalpy change, but, because of the large entropy contribution, the free energy change is negative for the meso isomer and only slightly positive for the racemic isomer. We believe that this entropy term arises from the coordinated axial water molecules being "pushed" out of the coordination sphere by the methyl groups of the ligand. Obviously, the axial methyl group of the meso isomer will be more effective in this respect than the equatorial methyl groups of the racemic isomer. This analysis is consistent with previous observations that increasing methyl substitution on the ethylenediamine backbone increases the stability of the square-planar form.<sup>10</sup>

**Tris Complexes.**—Earlier, Fitzgerald and Drago reported contact shift data which they claimed to be for the complexes  $\text{Ni}(\text{meso-bn})_3^{2+}$  and  $\text{Ni}(\text{d-bn})_3^{2+}$ .<sup>7</sup> They observed essentially identical pmr and optical spectra for both complexes and were unable to account for the difference in formation constants for  $\text{Ni}(\text{meso-bn})_3^{2+}$  and  $\text{Ni}(\text{rac-bn})_3^{2+}$  on the basis of their spectra.

One possible reason why essentially identical spectra were observed by these workers is that their mixture of meso and racemic butylenediamine was not completely separated and the data reported were obtained, in fact, from the racemic form. This explanation is consistent with their observation of only a single resonance line at the same field position for both  $\text{Ni}(\text{meso-bn})_3^{2+}$  and  $\text{Ni}(\text{d-bn})_3^{2+}$ . The present data for  $\text{Ni}(\text{rac-bn})_3^{2+}$  agree with the previous data for  $\text{Ni}(\text{d-bn})_3^{2+}$  but disagree with their data for  $\text{Ni}(\text{meso-bn})_3^{2+}$ . Table II

TABLE II  
COMPARISON OF THE OPTICAL SPECTRA OF  
 $\text{Ni}(\text{meso-bn})_3^{2+}$  AND  $\text{Ni}(\text{rac-bn})_3^{2+}$

| Compd                              | $10^{-2}\nu_{\text{max}}, \text{cm}^{-1}$ |                     |                    |
|------------------------------------|---|---------------------|--------------------|
|                                    | This work <sup>a</sup>                    | Ref 12 <sup>b</sup> | Ref 7 <sup>a</sup> |
| $\text{Ni}(\text{meso-bn})_3^{2+}$ | 11.0                                      | 10.9                | 11.268             |
|                                    | 18.0                                      | 18.0                | 18.484             |
|                                    | 28.7                                      | 28.3                | 29.240             |
| $\text{Ni}(\text{rac-bn})_3^{2+}$  | 11.6                                      |                     |                    |
|                                    | 18.7                                      |                     |                    |
|                                    | 29.5                                      |                     |                    |
| $\text{Ni}(\text{d-bn})_3^{2+}$    |   |                     | 11.416             |
|                                    |   |                     | 18.553             |
|                                    |   |                     | 29.586             |

<sup>a</sup> Excess ligand was present in these solutions. <sup>b</sup>  $\bar{n}$  (average number of bond ligands) = 3.05.

compares the optical spectra reported previously<sup>7,12</sup> and the spectra obtained in this work. The optical spectra are consistent with the above analysis. If the previous workers had obtained their pmr spectra from aqueous solutions, rather than deuterium oxide solutions, as their Experimental Section suggests, the large water absorption would have made observation of the small meso isomer peaks reported here impossible.

The previous workers compared the difference in  $Dq$  between  $\text{Ni}(\text{meso-bn})_3^{2+}$  and  $\text{Ni}(\text{d-bn})_3^{2+}$  with the difference in  $Dq$  between  $\text{Ni}(\text{NH}_3)_6^{2+}$  and  $\text{Ni}(\text{CH}_3\text{-NH}_2)_6^{2+}$ . They argued that, because the  $\Delta Dq$  was much less for bn than for  $\text{NH}_3$  and because the contact shifts were essentially identical, the difference in total stability constants between the tris complexes was not due to an "... intrinsic difference in metal-ligand bond strengths." The present data, however, argue against this analysis. The present and previous data are compared in Table III. Clearly, the present data are con-

TABLE III  
COMPARISON OF SPECTRAL DATA FOR  $\text{Ni}(\text{meso-bn})_3^{2+}$  AND  
 $\text{Ni}(\text{rac-bn})_3^{2+}$  WITH SPECTRAL DATA FOR  $\text{Ni}(\text{CH}_3\text{NH}_2)_6^{2+}$

| Compd   | $Dq, \text{cm}^{-1}$ | $\Delta Dq, \text{cm}^{-1}$ | $\Delta\nu, \text{Hz}$ | $\Delta\Delta\nu, \text{Hz}$ |
|---|----------------------|-----------------------------|------------------------|------------------------------|
| $\text{Ni}(\text{NH}_3)_6^{2+}$ <sup>a</sup>    | 1053                 |                             |                        |                              |
|   |                      | 60                          |                        |                              |
| $\text{Ni}(\text{CH}_3\text{NH}_2)_6^{2+}$      | 993                  |                             |                        |                              |
| $\text{Ni}(\text{meso-bn})_3^{2+}$ <sup>b</sup> | 1127                 |                             | -2422                  |                              |
|   |                      | 15                          |                        | -29                          |
| $\text{Ni}(\text{d-bn})_3^{2+}$ <sup>b</sup>    | 1142                 |                             | -2451                  |                              |
| $\text{Ni}(\text{meso-bn})_3^{2+}$ <sup>c</sup> | 1100                 |                             | $\sim -900$ (av)       |                              |
|   |                      | 60                          |                        | -1760                        |
| $\text{Ni}(\text{rac-bn})_3^{2+}$ <sup>c</sup>  | 1160                 |                             | -2660                  |                              |

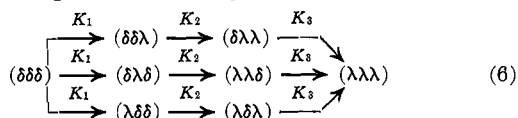
<sup>a</sup> R. S. Drago, D. W. Meek, R. Longhi, and M. D. Soeston, *Inorg. Chem.*, **2**, 1056 (1963). <sup>b</sup> From ref 7. <sup>c</sup> Present data.

sistent with the lower formation constant of the meso complex.

The pmr data reported here are entirely consistent with a similar study of  $\text{Ni}(\text{en})_3^{2+}$ . Figure 4 shows the effect of temperature upon the spectrum of  $\text{Ni}(\text{meso-bn})_3^{2+}$ . Figure 5 summarizes the spectra as a Curie-law plot as reported in previous studies.<sup>2,6</sup> The variation of peak 1 ( $-4$  ppm at room temperature) is not shown because its overlap with the residual HOD peak (as well as TMS\* and uncomplexed ligand peaks when present) made accurate observation of its position impossible. Despite the relatively greater solubility of the sulfate salt, it was not possible to identify the methine resonance positions.

The temperature dependence of the spectrum of  $\text{Ni}(\text{en})_3^{2+}$  was analogous to that reported in Figures 4 and 5 except that the two peaks did not coalesce until  $101^\circ$  while the peaks of  $\text{Ni}(\text{meso-bn})_3^{2+}$  coalesce at  $50^\circ$ . The  $\text{Ni}(\text{en})_3^{2+}$  data were explained on the basis of non-bonded atom interactions giving rise to an energy difference between the conformations  $\Delta(\delta\delta\delta)$  and  $\Delta(\lambda\lambda\lambda)$ . The difference in contact shift between the two observed lines was related to the energy differences between the two conformations.<sup>6</sup>

The present data were analyzed in the following manner. The process of conformational interchange is shown as (for a particular configuration)



$$K_1 = \frac{(\delta\delta\lambda)}{(\delta\delta\delta)} = \frac{(\delta\lambda\delta)}{(\delta\delta\delta)} = \frac{(\lambda\delta\delta)}{(\delta\delta\delta)} \quad (7)$$

$$K_2 = \frac{(\delta\lambda\lambda)}{(\delta\delta\lambda)} = \frac{(\lambda\lambda\delta)}{(\delta\lambda\delta)} = \frac{(\lambda\delta\lambda)}{(\lambda\delta\delta)} \quad (8)$$

$$K_3 = \frac{(\lambda\lambda\lambda)}{(\delta\lambda\lambda)} \quad (9)$$

Clearly,  $(\delta\delta\lambda) = (\delta\lambda\delta) = (\lambda\delta\delta)$  and  $(\delta\lambda\lambda) = (\lambda\lambda\delta) = (\lambda\delta\lambda)$ . Let  $f_1$  = mole fraction of  $(\delta\delta\delta)$  form,  $f_2$  = mole fraction of  $(\delta\delta\lambda)$  or  $(\delta\lambda\delta)$  or  $(\lambda\delta\delta)$  form,  $f_3$  = mole fraction of  $(\lambda\delta\lambda)$  or  $(\delta\lambda\lambda)$  or  $(\lambda\lambda\delta)$  form, and  $f_4$  = mole fraction of  $(\lambda\lambda\lambda)$  form; then

$$f_1 = \frac{(\delta\delta\delta)}{(\delta\delta\delta) + 3(\delta\delta\lambda) + 3(\delta\lambda\lambda) + (\lambda\lambda\lambda)} \quad (10)$$

Solving eq 7-9 yields

$$(\delta\delta\lambda) = (\delta\lambda\delta) = (\lambda\delta\delta) = K_1(\delta\delta\delta) \quad (11)$$

$$(\delta\lambda\lambda) = (\lambda\lambda\delta) = (\lambda\delta\lambda) = K_2K_1(\delta\delta\delta) \quad (12)$$

$$(\lambda\lambda\lambda) = K_3K_2K_1(\delta\delta\delta) \quad (13)$$

Substituting (11)-(13) into (10) yields

$$f_1 = \frac{1}{1 + 3K_1 + 3K_2K_1 + K_3K_2K_1} \quad (14)$$

$f_2, f_3,$  and  $f_4$  can be determined in a similar manner.

The observed contact shift of a predominantly equatorial proton will be the weighted average of all the conformations; thus

$$\delta_{\text{obsd}}T = \frac{(3f_1 + 2(3f_2) + 3f_3)K_e + (3f_2 + 2(3f_3) + 3f_4)K_a}{3} \quad (15)$$

$$= (f_1 + 2f_2 + f_3)K_e + (f_2 + 2f_3 + f_4)K_a \quad (16)$$

where  $K_e$  is the "frozen" equatorial contact shift temperature product and  $K_a$  is the "frozen" axial contact shift temperature product. Substituting the values of  $f_1, f_2, f_3,$  and  $f_4$  yields

$$\delta_{\text{obsd}}T = \frac{(1 + 2K_1 + K_2K_1)K_e + (K_1 + 2K_2K_1 + K_3K_2K_1)K_a}{1 + 3K_1 + 3K_2K_1 + K_3K_2K_1} \quad (17)$$

Putting eq 17 into exponential form yields

$$\begin{aligned} & \left[ 1 + 2 \exp\left(-\frac{\Delta G_1}{RT}\right) + \exp\left(-\frac{\Delta G_1 + \Delta G_2}{RT}\right) \right] K_e + \\ & \left[ \exp\left(-\frac{\Delta G_1}{RT}\right) + 2 \exp\left(-\frac{\Delta G_1 + \Delta G_2}{RT}\right) + \right. \\ & \left. \exp\left(-\frac{\Delta G_1 + \Delta G_2 + \Delta G_3}{RT}\right) \right] K_a \\ \delta_{\text{obsd}}T = & \frac{\hspace{10em}}{1 + 3 \exp\left(-\frac{\Delta G_1}{RT}\right) + 3 \exp\left(-\frac{\Delta G_1 + \Delta G_2}{RT}\right) +} \\ & \exp\left(-\frac{\Delta G_1 + \Delta G_2 + \Delta G_3}{RT}\right) \hspace{10em} \end{aligned} \quad (18)$$

If one assumes that  $\Delta G_1 = \Delta G_2 = \Delta G_3 = \Delta G$ , eq 18 can be simplified to

$$\delta_{\text{obsd}}T = \frac{K_e + \exp\left(-\frac{\Delta G}{RT}\right) K_a}{1 + \exp\left(-\frac{\Delta G}{RT}\right)} \quad (19)$$

Adding

$$\frac{K_a - K_e}{1 + \exp\left(-\frac{\Delta G}{RT}\right)}$$

to eq 19 yields

$$\delta_{\text{obsd}}T = K_a + (K_e - K_a) \left[ \frac{1}{1 + \exp\left(-\frac{\Delta G}{RT}\right)} \right] \quad (20)$$

Equation 20 was previously presented without sufficient discussion in ref 6. The "frozen" resonance positions were determined in the following manner. The resonance position of the racemic complex ( $-26.6$  ppm) was used for the "frozen" equatorial value because the temperature dependence of the shift indicates essentially no axial contribution (see above). The methyl resonance position of  $\text{Ni}(\text{meso-bn})_3^{2+}$  ( $-9.4$  ppm) was considered an average value of the "frozen" equatorial (above) and axial positions and was used to calculate the "frozen" axial resonance position ( $+7.4$  ppm). The data were analyzed using eq 20.

A least-squares procedure yielded a best fit of

$$\Delta G = 1700 \pm 90 - (3.9 + 0.3)T \quad (21)$$

This value of  $\Delta G$  and the "frozen" values above were used to generate line A of Figure 5. The energy of  $\delta \rightleftharpoons \lambda$  conversion of  $\text{Ni}(\text{meso-bn})_3^{2+}$  is thus 530 cal/mol at room temperature ( $300^\circ\text{K}$ ) compared to 300 cal/mol for  $\text{Ni}(\text{en})_3^{2+}$ .

Coalescence of the two-line spectrum occurs at elevated temperature because of rapid (relative to the chemical shift difference between the two peaks) racemization about the central metal ion. Racemization results in axial and equatorial substituents exchanging with each other.<sup>6</sup> Because the configurations  $\Delta(\delta\delta\delta)$  and  $\Delta(\lambda\lambda\lambda)$  have the same energy, fast interconversion averages the contact shift differences to a single line.

The rate of racemization can be estimated from the contact shift difference between the two peaks which would be observed if racemization did not occur (extrapolation of the theoretical  $\delta T$  curve (Figure 5, line A) to the coalescence temperature).<sup>6</sup> Equation 22 is used to calculate the rate of racemization,<sup>13</sup> where  $\Delta$  is the pre-

$$\text{rate} = \frac{1}{\tau_c} = \frac{\pi\Delta}{\sqrt{2}} \quad (22)$$

dicted contact shift difference ( $\text{sec}^{-1}$ ). The contact shift difference determined by extrapolation was estimated as  $1052 \text{ sec}^{-1}$  and the corresponding rate of racemization was  $2.3 \times 10^3 \text{ sec}^{-1}$  at  $50^\circ$ .

The free energy of activation,  $\Delta G^\ddagger$ , at the temperature of coalescence can be estimated from the rate of racemization and the temperature by use of the equation<sup>6</sup>

$$\frac{1}{\tau_c} = \frac{k}{h} T \exp(-\Delta G^\ddagger/RT) \quad (23)$$

where  $k$  is the Boltzmann constant,  $h$  is Planck's constant, and the other terms have their usual significance. A  $\Delta G^\ddagger$  of 14.0 kcal/mol was found.

The above values of the rate of racemization and activation energy of racemization are similar to the values found for  $\text{Ni}(\text{en})_3^{2+}$ ,  $5.5 \times 10^3 \text{ sec}^{-1}$  and 15.7 kcal/mol, respectively.<sup>6</sup>

The reasonable agreement between the racemization parameters of  $\text{Ni}(\text{meso-bn})_3^{2+}$  and  $\text{Ni}(\text{en})_3^{2+}$  is consistent with the trigonal-twist mechanism of racemization previously suggested.<sup>6</sup> The greater energy difference between  $\Lambda(\delta\delta\delta)$  and  $\Lambda(\lambda\lambda\lambda)$  conformations for  $\text{Ni}(\text{meso-bn})_3^{2+}$  (1.6 kcal/mol) compared to that for  $\text{Ni}(\text{en})_3^{2+}$  (0.9 kcal/mol) is consistent with the greater nonbonded atom interaction expected of the methyl groups. An energy difference of 1.7 kcal/mol was reported for the corresponding conformations in  $\text{Co}((-)\text{pn})_3^{3+}$ .<sup>14</sup> The greater energy difference noticed for  $\text{Co}((-)\text{pn})_3^{3+}$  compared to that for  $\text{Ni}(\text{meso-bn})_3^{2+}$  probably arises from the smaller size of cobalt(III) which increases steric

interactions and the preference of the methyl group for the equatorial environment.

No information on  $\delta \rightleftharpoons \lambda$  conversion of the racemic complexes is obtainable from these data because the energy difference between conformations is too great for observable amounts of the higher energy form to be present.

No peaks were observed for the tris racemic complex which could be attributed to mixed optically active forms (*i.e.*,  $\text{Ni}(d\text{-bn})_2(l\text{-bn})^{2+}$ , etc.). It is not possible to tell whether mixed isomers are not formed or whether they are formed but have the same spectrum.

It should be pointed out that the differences between the spectra of meso and racemic complexes are expected because these two ligands are different species; they are not diastereoisomers of each other as previously stated.<sup>7</sup>

**Ring Puckering.**—From the values for the "frozen" equatorial and "frozen" axial methine contact shifts, the nonplanarity of the chelate ring can be evaluated by making use of the angular dependence of the hyperfine coupling constant<sup>2,5</sup>

$$A = k_0 + k_2 \cos^2 \theta \quad k_2 \gg k_0 \quad (24)$$

The "frozen" contact shift values were evaluated as above and, solving for the negative square root, yielded a value of  $\theta = 72^\circ$ . This value is close to the value reported for  $\text{Ni}(\text{en})_3^{2+}$ ,  $76^\circ$ , and in fair agreement with the X-ray value of  $64^\circ$ <sup>15</sup> for  $\text{Ni}(\text{en})_3^{2+}$ . A  $\theta$  value of  $107^\circ$  is obtained when the positive square root is evaluated. The negative value was used because it is more reasonable and is in better agreement with the X-ray data.

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