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Cobalt(III) Complexes of Linear Tetramines. IV. Isomers of *R*-Propylenediamine(3,7-diaza-1,9-nonanediamine)cobalt(III)

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Received August 11, 1970

Five cobalt(III) complexes having the formulation Co(2,3,2-tet)(R-pn)$^{3+}$, where 2,3,2-tet is 3,7-diaza-1,9-nonanediamine and R-pn is R-propylenediamine, have been prepared at equilibrium conditions. Circular dichroism spectra, visible absorption spectra, PMR spectra and molecular models were employed to determine the structures and absolute configurations of the isomers. All the isomers are believed to exhibit the β topology. The two most stable complexes possess the Δ(C_3) chirality and differ only in the placement of the methyl group of the R-pn. The three less stable isomers exhibit the Λ(C_3) chirality. The ratio of Δ(C_3) to Λ(C_3) isomers at equilibrium is about 10:1. The six-membered chelate ring of 2,3,2-tet is believed to exist in the skew boat conformation for one of the less stable isomers, and for another of the less stable isomers the methyl group of the R-pn is believed to occupy and axial site.

Introduction

Dwyer, MacDermott and coworkers[1-6] have extensively examined the stereochemistry of cobalt(III) complexes of propylenediamine with one of their principal objectives being the determination of relative thermodynamic stabilities of such complexes. Noteworthy is their investigation of the «tris» ethylenediamine propylenediamine cobalt(III) complexes,[3-6] $[\text{Co(en)}_n\text{–}(R\text{-pn})_{3-n}]^{3+}$, which has provided support for the now famous chelate ring conformational analysis of Corey and Bailar.[7] Relative stabilities of diastereomeric pairs of Λ(C_3)- and Δ(C_3)- $[\text{Co(en)}_n(\text{R-pn})_{3n}]^{3+}$, were expained on the basis of the expected conformational stabilities of the chelate rings.

Recently, in our laboratories and others,[8-13] there has been considerable interest in cobalt(III) complexes of the tetramine ligand 3,7-diaza-1,9-nonanediamine (2,3,2-tet) which can be thought of as two ethylenediamine moieties linked by a trimethylene bridge. Thus, the ligand is similar to triethyelenetetramine (trien) and like trien, 2,3,2-tet forms complexes analogous to those of the $(\text{en})_2$ type. Thus, complexes of the formulation Co(2,3,2-tet)(R-pn)$^{3+}$ are structurally similar to the Co$(\text{en})_2$(R-pn)$^{3+}$ complexes investigated previously. However, isomerism in the 2,3,2-tet complexes is much more complicated than that in the $(\text{en})_2$ system. For the latter complexes, isomerism is limited to the two diastereomers Δ(C_3)-R and Λ(C_3)-R neglecting chelate ring conformers. Isomerism for the 2,3,2-tet case is complicated by 3 factors: 1) α and β topologies are possible for each of the Λ and Δ chiralities; 2) the two sites of coordination of the R-pn are non-equivalent for the β topologies; and 3) the secondary nitrogen atoms of 2,3,2-tet are asymmetric. These factors lead to the possible isomers given in Figure 1.

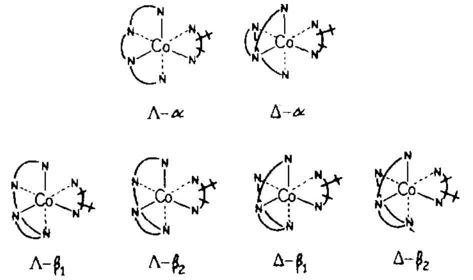

Figure 1. Isomers of Co(2,3,2-tet)(R-pn)$^{3+}$. RR,SS and RS(meso) secondary nitrogen configurations are possible for each structure.

This paper is concerned with the synthesis and characterization of isomers of Co(2,3,2-tet)(R-pn)$^{3+}$ as well as the relative stabilities of such isomers. This study together with that done previously for the Co$(\text{en})_2$(R-pn)$^{3+}$ system has proved helpful in elucidating the stereochemical behavior of 2,3,2-tet and propylenediamine with respect to complex ion formation.

Experimental Section

Ligands. R-propylenediamine (R-pn) dihydrochloride was obtained from racemic pn using the methods

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of Dwyer[1] and Bailar.[14] The method of Hamilton and Alexander[9] was employed to synthesize 2,3,2-tet.

Preparation of $[Co(2,3,2\text{-}tet)(R\text{-}pn)]^{3+}$. Two procedures were followed in preparing these complexes.

(Procedure A). To a solution of cobalt(II) chloride hexahydrate (6.0 g, 0.025 mole, in 200 ml H_2O) was added 2,3,2-tet (4.0 g, 0.025 mole), resolved *R*-propylenediamine dihydrochloride (3.67 g, 0.025 moles), diethylamine (2.6 ml, 0.025 mole) and activated charcoal (0.5 g). The resulting solution was air-oxidized for 16 hours. The charcoal was filtered and washed with water until the washings were colorless. The reaction products were absorbed on a Dowex 50W-X2, 200-400 mesh, cation exchange column ($\varnothing = 3$ cm, $h = 30$ cm). The excess cobalt(II) ($< 1\%$) was washed off the column with 0.1N HCl. A solution of 80 ml of concentrated hydrochloric acid per liter of acqueous solution was employed for eluting the column. Elution of the absorbed products indicated the presence of several cobalt(III) complexes in addition to the hexaaminecobalt(III) products which are yellow in color. The yellow band, which was eluted most slowly, was collected; the elutent was evaporated to dryness by room temperature rotatory evaporation; and the yellow solid was dried *in vacuo* at 40° overnight. The yellow solid was subjected to cellulose column chromatography.

The cellulose column ($\varnothing = 5$ cm, $h = 30$ cm) was prepared by suspending Bio-Rad Cellex-MX microcrystalline cellulose in water-saturated 1-butanol with vigorous shaking and pouring the slurry into the column with stirring. The column was impacted by allowing a constant flow of water saturated 1-butanol for 24 hours. The reaction product (0.4 g) was dissolved in a mixture of water-saturated 1-butanol (100 ml) and dry 1-butanol (35 ml) and added to the column. The layer of product absorbed at the top of the column was then eluted with a mixture of hydrochloric acid and water-saturated 1-butanol (20 ml of 12N HCl/980 ml of $BuOH{-}H_2O$). A total of six bands separated, and the elutents were collected in approximately 40 ml fractions. The absorbance of these fractions were determined at 465 mμ using a Cary 14 spectrophotometer. The complex chlorides were each extracted from the butanol solutions by shaking with water several times until no color remained in the butanol. The aqueous extracts were exaporated to dryness by room temperature rotatory evaporation. The separation was carried out several times to obtain reasonable quantities of the isomers. The two faster moving bands were identified as tris(*R*-pn)cobalt(III) chloride via visible, CD and PMR spectra. The last four bands consisted of isomers of the desired compound. Elemental analyses were not obtained because of the small amounts of the complexes. The cationic formulation was verified via PMR. These PMR data are presented in the Results section.

(Procedure B). The complex *trans-RS*-$[Co(2,3,2\text{-}tet)Cl_2]ClO_4$ (3.25 g, 0.010 mole), prepared by the standard air-oxidation technique,[8,9] was partially dissolved in methanol (125 ml). To this mixture was added *R*-propylenediamine dihydrochloride (1.6 g, 0.011 mole and diethylamine (3.3 ml, 0.032 mole). The mixture was stirred for several hours in which time a dark orange-brown color became evident. After allowing the solution to stand overnight ether was added and an orange-yellow precipitate was separated. The material was dissolved in methanol and precipitated once again using ether. The product was washed with ether after filtering and dried *in vacuo* overnight at 40°. The product was subjected to cellulose column chromatography as described in Procedure A.

Measurements. Circular dichroism spectra were recorded on a Cary 60 spectropolarimeter with a CD accessory. Proton magnetic resonance data were obtained using a Varian A60A spectrometer at ambient temperatures. The values of the chemical shifts were measured in relation to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard. All spectra were obtained using 99.77% deuterium oxide as the solvent. The deuterium oxide solutions were allowed to stand until complete amine deuteration was achieved.

Results

Isomeric mixture of $Co(2,3,2\text{-}tet)(R\text{-}pn)^{3+}$ were made by two processes: 1) the direct oxidation of a stoichiometric aqueous solution of Co(II), 2,3,2-tet and *R-pn* in the presence of activated charcoal and 2) the reaction of *R*-pn with *trans*-$Co(2,3,2\text{-}tet)Cl_2^+$ in methanol. For the mixed en *R*-pn system, reactions analogous to those above yield equilibrium mixtures of $Co(en)_x(R\text{-}pn)_{3-x}{}^{3+}$ complexes.[3,15] Thus one might predict similar behavior for the 2,3,2-tet *R*-pn system. This notion is supported experimentally since the two $Co(2,3,2\text{-}tet)(R\text{-}pn)^{3+}$ mixtures gave very similar elution profiles, exemplified in Figure 2, when subjected to a microcrystalline cellulose chromatographic column separation procedure. As can be seen from the profile four definite bands separate with the first two bands being much more intense than the last two. Also the first two bands do not separate cleanly. The relative amounts of the first two bands combined and each of the third and fourth bands are in the ratio 50:3:2, respectively. The components corresponding to fract-

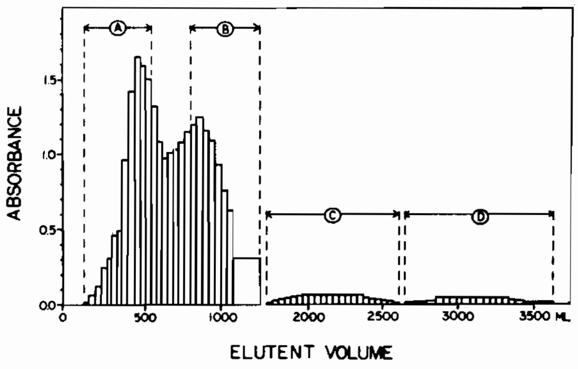

Figure 2. Elution profile fr cellulose column chromatagraphic separation of air oxidation mixture of $Co(2,3,2\text{-}tet)(R\text{-}pn)^{3+}$.

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[14] J. C. Bailar, Jr., H.B Jonassen, and A. D. Gott, *J. Am. Chem. Soc.*, *74*, 3131 (1952).

ions A, B, C, and D were characterized. Fractions A and B were taken so as to minimize mixing components of the first two bands.

Visible absorption spectra of the four components all exhibit maxima at 470±2 mμ and 340±2 mμ. The positions of these are quite similar to those in the spectrum of $Co(en)_3^{3+}$; and thus, the spectral data are consistent with a hexaamine formulation for the components.

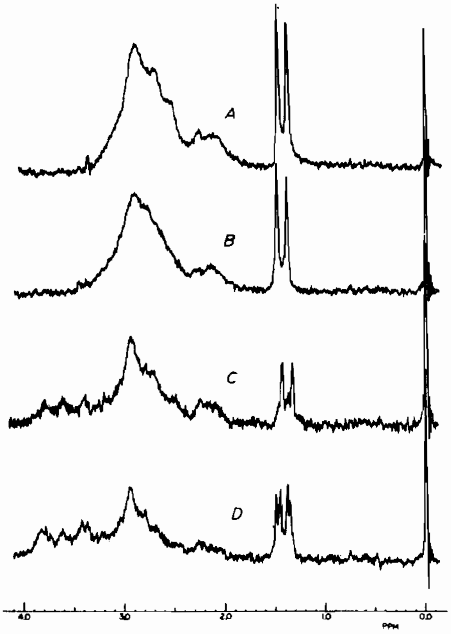

Figure 3. PMR spectra of components of Co(2,3,2-tet)(*R*-pn)$^{3+}$.

Figure 3 shows portions of the PMR spectra of the four components. The spectra of components A and B are quite similar. Each exhibits a sharp doublet (J=0.10 ppm, 6 cps) at 1.44 ppm for A and 1.46 for B downfield from DSS, which corresponds to the CH_3 group of the coordinated *R*-pn. Two broad bands are observed at 2.0-2.4 ppm and 2.4-3.3 ppm in a ratio of about 2: 15 which represent the center methylene protons of the backbone and the remaining methylene and methyne protons, respectively. The spectra of C and D are much more noisey than those of A and B because of the small amounts of these components which we obtained. Component C exhibits a doublet (J=0.10 ppm, 6 cps) at 1.39 ppm while component D shows two doublets (J=0.10 ppm, 6 cps) at 1.39 ppm and 1.49 ppm. The broad bands observed in the spectra of C and D between 3.4 and 4.0 ppm are not present in the spectra of A and B. The ratio of the intensity of the methyl signal to the intensity of all the other CH signals is nearly 3: 17 for all four components varifying the formulation of the complexes as Co-2,3,2-tet)(*R*-pn)$^{3+}$.

The CD spectra of the four components are shown in Figure 4. The spectra of A and B are quite similar and exhibit a strong negative band at 500 mμ. In the spectrum of $\Delta(C_3)$–$Co(en)_3^{3+}$ the $^1A_{1g}\rightarrow{}^1E_a$ transition results in a strong negative absorption in this region, also.[16] Since the three chelate rings of Co-(2,3,2-tet)(*R*-pn)$^{3+}$ giving rise to the overall chirality of the complex (the five-membered rings of 2,3,2-tet and the *R*-pn ring) are structurally quite similar to those of $Co(en)_3^{3+}$ and both complexes contain amine donors only, it would seem reasonable to assume that the pseudo trigonal splitting in Co(2,3,2-tet)(*R*-pn)$^{3+}$ would be similar to the splitting in $Co(en)_3^{3+}$, and that the sign of CD bands due to the $^1A_{1g}\rightarrow{}^1E_a$ transition would be the same for isomers of the two complexes with the same chirality. If one accepts this assumption, the he is forced to assign the $\Delta(C_3)$ chirality to components A and B and the $\Lambda(C_3)$ chirality to C and D. The similarity among the CD spectra of $\Delta(C_3)$–$Co(en)_2(R$–$pn)^{3+}$,[17] and components A and B; and the similarity among the CD spectra of $\Lambda(C_3)$–$Co(en)_2(R$-$pn)^{3+}$,[18] and components C and D lends support to this assumption. Furthermore, the assignment is consistent with the relative amounts of the components as will be discussed subsequently.

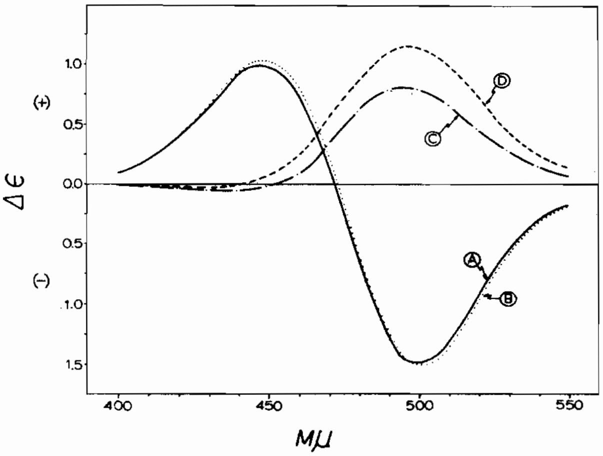

Figure 4. CD spectra of components of Co(2,3,2-tet)(*R*-pn)$^{3+}$.

Discussion

Several complexes of 2,3,2-tet exhibiting *cis* topologies have been prepared previously, among which are *cis*-$[Co(2,3,2\text{-tet})Cl_2]^+$, *cis*-$Co(2,3,2\text{-tet})CO_3^+$, $Co(2,3,2\text{-tet})C_2O_4^+$ $Co(2,3,2\text{-tet})(O_2CCH_2CO_2)^+$.[10,19-21] All of these complexes are belived to possess β-*cis* topologies with the secondary nitrogen atoms exhibiting *RR* and *SS* configurations for $\Lambda(C_3)$ and $\Delta(C_3)$ configurations, respectively.[13,19-21] These configurational assignments agree quite well with what one would predict on the basis of conformational considerations of the six-mem-

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bered chelate ring.[22-24] Examine Figure 5 for the *RR* configuration. The six-membered ring may assume the preferred chair conformation with one aminoethyl group occupying an equatorial site and the other an axial site. The equatorial aminoethyl group can readily coordinate yielding a chelate ring coplanar with the six-membered ring while the axial aminoethyl group will readily coordinate producing a ring perpendicular to the six-membered ring. This results in the absolute configuration, $\Lambda(C_3)$–β–*cis*. For the *RR* configuration to yield an α-*cis* topology the six-membered ring would need to assume the boat or skew boat conformation with both aminoethyl groups occupying axial sites. On the basis of the behavior of cyclohexane the conformations necessary for the α-*cis* topology should be much less favorable than that which yields the β-*cis* topology.

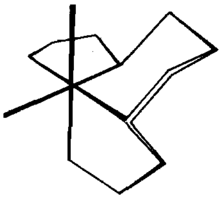

Figure 5. Backbone of 2,3,2-tet in β-*cis*-*RR* configuration. No hydrogen atoms are depected.

Similar considerations indicate that the *RS* configuration can give a β-*cis* topology only if the six-membered ring is in the boat or skew boat conformation with one aminoethyl group axial and the other equatorial. The α-*cis* topology is even more unlikely for the *RS* configurations being $\Lambda(C_3)$–$(RR)_N$ and $\Delta(C_3)$–$(SS)_N$. to form a chelate ring perpendicular to the six-membered ring from an equatorial site on a skew boat ring; for the chair conformation both aminoethyl groups occupy axial sites on the same side of the six-membered ring.

These considerations might lead one to predict that the mixtures of Co(2,3,2-tet)(*R*-pn)$^{3+}$ consist of complexes all of which possess the β-*cis* geometry with the configurations being $\Lambda(C_3)$–$(RR)_N$ and $\Delta(C_3)$–$(SS)_N$. The results concerning the separations of the components of the mixtures and characterization of the components agree with this prediction except in the case of component D for which the PMR spectrum cannot be explained solely on this basis.

For the above configurations four isomers are possible $\Lambda(C_3)$–$(RR)_N$–β_2, $\Delta(C_3)$–$(SS)_N$–β_1 and $\Delta(C_3)$-$(SS)_N$–β_2 (ref. to Figure 1). These could correspond to components A, B, C, and D from the chromatographic separation. From the work with the Co(en)$_2$(*R*-pn)$^{3+}$ system the above Δ isomers would be expected to be more stable and thus should predominate in the mixture. Therefore components A and B should be the two Δ–β isomers. The Δ chirality is consistent with the CD data. These isomers differ only in the orientation of the *R*-pn. Such isomerism has been observed in related systems namely Co(*R*-pn)$_3^{3+}$, Co(*R*-pn)$_2$(en)$^{3+}$, Co(*R*-pn)$_2$Cl$_2^+$, Co(EDDA)(*R*-pn)$^+$ and in these systems such isomers are of nearly equal stability and give nearly the same CD spectra.[4,6,25,26] This is what is observed for components A and B. Components C and D could be the corresponding Λ–β isomers. The Λ chirality is consistent with the CD spectra.

Compare the relatives stabilities of Δ and Λ isomers of Co(en)$_2$(*R*-pn)$^{2+}$ to those of the corresponding Δ and Λ isomers of Co(2,3,2-tet)(*R*-pn)$^{3+}$. For the (en)$_2$ case $K_{eq} = \Delta/\Lambda = 2$ and for 2,3,2-tet $K_{eq} = \Delta/\Lambda = 10$. Hence the stereospecificity in the 2,3,2-tet system is considerably greater than in the (en)$_2$ system. This significant result is readily explainable by using molecular models. Consider the Δ isomers (Figure 6-a,b). In these models the five-membered chelate rings of 2,3,2-tet are placed in the λ conformation. For these conformations the non-bonding interactions and strain within 2,3,2-tet appear to be at a minimum. For both of the two Δ isomers the *R*-pn chelate ring can exist in the preferred λ conformation with the methyl group at an equatorial site. There is very little interaction between the equatorial methyl group and the rest of the complex for both β_1 and β_2 isomers. In this conformation for *R*-pn one of the equatorial amine hydrogens of *R*-pn lies between two axial hydrogens of the six-membered ring minimizing interaction between these hydrogens. For these two isomers the PMR spectra should be very similar. This is consistent with the assignment of A and B being the Δ isomers. However, it is not possible to tell which of A and B is the β_1 or β_2 isomer.

For the Λ isomers the situation is quite different and it is because of this difference that the greater stereo-

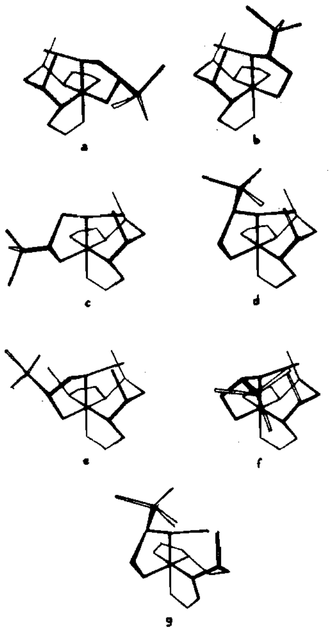

Figure 6. Structures of Co(2,3,2-tet)(*R*-pn)$^{3+}$: (a) $\Delta(C_3)$-β_1-$(SS)_N$; (b) $\Delta(C_3)$-β_2-$(SS)_N$; (c) $\Lambda(C_3)$-β_1-$(RR)_N$; (d) $\Lambda(C_3)$-β_2-$(RR)_N$; (e) $\Lambda(C_3)$-β_1-$(RR)_N$; (f) $\Lambda(C_3)$-$\beta_2(RR)_N$; (g) $\Lambda(C_3)$-$(RS)_N$. The pn rings are in the λ conformation in structures a, b, e, f, and g and in the δ conformation in structures c and d. Only pertinent hydogens are shown for all structures.

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specificity is observed in the 2,3,2-tet system. For the *R*-pn to exist in the λ conformation there is much interaction between one of the axial amine hydrogens of *R*-pn and an axial methylene hydrogen on the six-membered ring in the chair conformation (Figure 6-c,d). This interaction can be reduced to that present in the Δ isomers if the *R*-pn chelate ring is placed in the δ conformation. However, this places the methyl group in an axial position. For the β_1 isomer this would place the methyl group close to a primary amine group of 2,3,2-tet which would lead to more nonbonding interaction bteween the CH_3 group and the rest of the complex (Figure 6-e). However, models indicate that this interaction would be less than the afore-mentioned interaction between amine hydrogen of *R*-pn in the λ conformation and the 2,3,2-tet methylene. Thus we believe an axial methyl group would be preferred. For such a complex a single methyl doublet would be observed in the PMR. This is the case for the spectrum of component C and not D, and thus we assign C to be Λ–β_1 isomer. This would account for the difference in stability between the Δ–β_1 and Λ–β_1 isomers.

In the case of Λ–β_2 isomer, if the conformation of *R*-pn is changed to the δ conformation to reduce the interaction between the amine hydrogen of *R*-pn and the hydrogen of 2,3,2-tet, the methyl group will again occupy an axial site. However, this axial position is in close proximity to a methylene of the six-membered ring in 2,3,2-tet (Figure 6-f). Nonbonding interactions involving the methyl at this axial position should be greater than in the case of an axial methyl in the β_1 isomer. Another possibilty exists for the Λ–β_2 isomer. If the configuration of the secondary nitrogen bridging the coplanar six-membered ring and five-membered ring is changed to the *S* configuration the six-membered ring would likely assume the skew boat conformation which in turn would decrease the nonbonding interaction involving the hydrogen of this ring with the amine hydrogen of *R*-pn in the λ conformation (Figure 6-g). This would allow the methyl group to remain in an equatorial location. The presence of both these isomers, Δ–*RR*–β_2 and Δ–*RS*–β_2, in component D would explain the existence of two methyl doublets in the PMR spectrum of D. It would also explain the slight decrease in the stability of the Δ–β_2 isomers relative to the Δ–β_1 isomer. Furthermore, the presence of the two isomers in component D would explain the greater difference between the CD spectra of C and D relative to the difference between the spectra of A and B.

It was noted that the PMR spectra of C and D exhibited some C–H signals significantly downfield from the C–H bands present in the spectra of A and B. Downfield shifts of the magnitude observed in the present case have been observed in organic systems in which significant non-bonding interactions exist.[27,28] Such non-bonding interactions are thought to cause appreciable deshielding. This could be the explanation for the downfield bands in question.

Conclusions

There are three results of this study which are quite significant with respect to the coordination stereochemistry of propylenediamine and 2,3,2-tet. Firstly, propylenediamine is much more stereospecific in the 2,3,2-tet cobalt(III) system than in the analogous $(en)_2$ system. Secondly, evidence was obtained indicating that *R*-propylenediamine can form stable coordination complexes in which the methyl group occupies an axial site. No previous complexes in which *R*-propylenediamine shows such behavior have been reported. Finally, results were obtained suggesting that 2,3,2-tet can coordinate in the β topology with the *RS* nitrogen configurations. This behavior has not been observed previously.

Acknowledgment. We are indebted to the National Science Foundation for its support under grant GP-6813. We also wish to acknowledge the National Science Foundation and the Research Corporation for grants with which the Cary 60 Spectropolarimeter was purchased.

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