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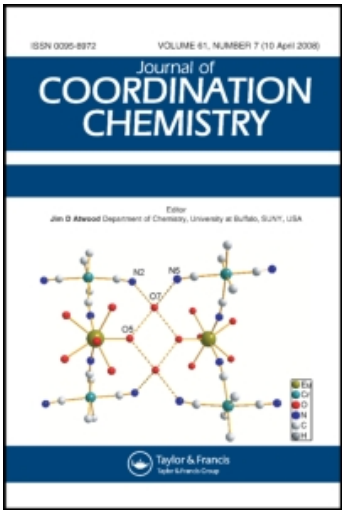

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PMR OF ISOMERS OF BIS(S-2, 3-DIAMINOPROPIONATO) COBALT(III) ION. QUANTITATIVE ANALYSIS OF EFFECT OF COBALT(III) ANISOTROPY ON PROTON CHEMICAL SHIFTS

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The proton magnetic resonance spectra of the isomers of bis(S-2,3-diaminopropionato)cobalt(III) ion, in which the tridentate ligands adopt a rigid conformation that is unchanged among the isomers, were recorded in aqueous solution and analyzed. The variation from isomer to isomer of the chemical shift of the ligand's three carbon-bound protons was found to be quantitatively attributable to cobalt(III) paramagnetic anisotropy. Estimates of some of the positional coordinates of the ligand protons were made based upon the pmr data and upon theoretical expressions for cobalt(III) paramagnetic anisotropy; they were found to be in agreement with those derived from a reported X-ray structure determination on one of the isomers.

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INTRODUCTION

The use of both coupling constant and chemical shift data from proton magnetic resonance spectrometry is well-established in the identification of geometrical isomers and in the determination of chelate ring conformations in coordination compounds. In the octahedral complexes of cobalt(III), in particular in aminocarboxylate complexes, it has been found[1–3] that geometrical isomerism can be successfully assigned using an empirical rule: the magnetic shielding of certain ligand protons – ammine protons or protons on carbons adjacent to a coordinated nitrogen atom – is increased when an acido donor is *trans* to the nitrogen donor relative to its value when another nitrogen donor occupies the same *trans* position. This "through-cobalt" effect has been ascribed to a change of polarity of the ammine in question by the *trans* acido donor.[3] However, Hendrickson and Jolly interpreted the difference between the pmr of $[Co(NH_3)_5X]^{+n}$, in which the *trans* ammine protons resonate at higher field than *cis* and $[Rh(NH_3)_5X]^{+n}$ and $[Ir(NH_3)_5X]^{+n}$ complexes, in which *trans* and *cis* ammine protons resonate at the same field, on the basis of the paramagnetic anisotropy of the cobalt(III) ion.
This paramagnetism comes from the admixture to the ground state, under the influence of the static magnetic field, of low-lying mainly metal excited states. Further development of this explanation, including quantitative expressions for $\sigma^P(H)$, has recently taken place.[5] These expressions give $\sigma^P(H)$ as a function of the location and identity of the donor atoms of the complex and the location of the proton itself. They follow from linking paramagnetic proton chemical shifts to the chemical shifts of the ^{59}Co nucleus. These ^{59}Co chemical shifts are observed in solution to be given as the sum of contributions from each donor.[6] This empirical additivity has been given a theoretical basis.[7]

The two explanations are not mutually exclusive. The usual theoretical formalism partitions the magnetic shielding exerted upon a proton into diamagnetic and paramagnetic terms.[8] The bond polarity explanation refers to the first term; the paramagnetic anisotropy refers to the second. This paper presents pmr data of isomers of a cobalt(III) complex in which a rigid conformation keeps all the factors affecting magnetic shielding – except for the "through-cobalt" effect – essentially the same from isomer to isomer.

EXPERIMENTAL SECTION

The three geometrical isomers of bis(S-2,3-diaminopropionato)cobalt(III) ion were synthesized and separated as bromide salts in the manner described previously.[9] They are represented and named in Figure 1.

The low solubilities of the bromides and other common salts of these complex ions made resort to

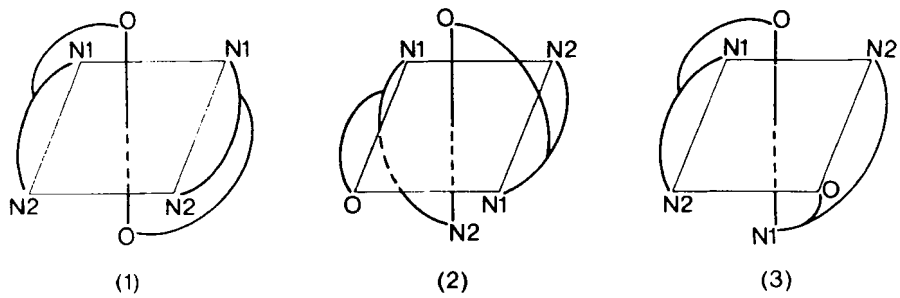

FIGURE 1 The three geometrical isomers of bis(S-2,3-diaminopropionato)cobalt(III) ion: (1) *trans,cis,cis;* (2) *cis,trans,cis;* (3) *cis,cis,trans.*

special techniques necessary to collect adequate proton magnetic resonance spectra. The spectra of the three isomers were taken on saturated solutions in D_2O of the most soluble halide salt obtainable. This was the fluoride except in the case of the *cis,cis,trans* isomer where it was the bromide. The 90 MHz high resolution proton spectra were obtained on a modified Bruker HFX-90 variable frequency spectrometer, operating in the Fourier transform mode. The magnetic field was stabilized on the deuterium resonance signal of the D_2O solvent. The method of Patt and Sykes,[10] modified by the addition of a homo-spoiling pulse, was used to minimize spectral interference from HDO. Final spectra were averages of 256 or 512 scans at temperatures of about 300 degrees K. An internal standard, tert-butanol, δ = 1.21 ppm relative to TMS, was used.

Calculations were performed on an IBM 370-158 computer.

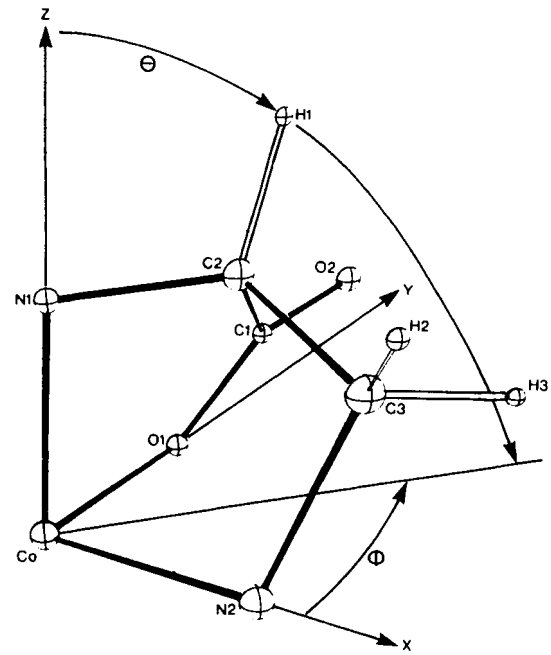

FIGURE 2 ORTEP drawing of the chelate ring system of a single S-2,3-diaminopropionate coordinated to cobalt(III). Cartesian and spherical polar coordinate systems are also indicated. Ammine hydrogens have been omitted for clarity.

RESULTS

Under the conditions of the experiment, the four nitrogen-bound protons of each ligand exchanged rapidly with the solvent deuterium. Their resonances were not observed in any of the spectra. No exchange of the 2-carbon proton was observed under the experimental conditions. The *trans,cis,cis* complex decomposed when pD was increased to favor possible 2-carbon proton exchange. Such exchange has been reported in similar cases.[11] All of the pmr spectra had eight lines. These included a low-field doublet which was in each case immediately assigned to the 2-carbon proton. This assignment was based upon the relative deshielding expected for a proton on a carbon bearing both an amine and carboxylate function (Figure 2) and also upon the observed intensity ratios. The remainders of the pmr spectra were then ascribed to the two 3-carbon protons. In all three spectra only eight of the twelve lines expected for an ABX spectrum were observed. This simplification was undoubtedly the result of degeneracy or near degeneracy in the spin energy levels.[12] Iterative analysis of the spectra, using the program LAOCOON 3[13] proceeded without difficulty. The resulting coupling constants and chemical shifts are summarized in Table I. Six parameters were determined in each case on the basis of eight independent observations, a low

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TABLE I
Results of Analysis of Pmr Spectra of the Three Isomers of Bis(S-2,3-diaminopropionato)cobalt(III) Ion

	trans,cis,cis	*cis,trans,cis*	*cis,cis,trans*
δ_1	3.861(1)[a]ppm[b]	3.840(2)ppm	3.664(1)ppm
δ_2	3.401(1)	2.957(2)	3.188(1)
δ_3	3.015(1)	2.766(2)	3.020(1)
J_{12}	3.3(3)Hz	3.0(7)Hz	3.7(4)Hz
J_{13}	0.1(3)	0.3(7)	0.5(4)
J_{23}	−13.5(3)	−12.7(6)	−13.2(3)

[a] numbers in parentheses are the estimated standard deviations, right adjusted to the last digit of the preceding number.
[b] parts per million relative to TMS.

degree of over-determination. The estimated standard deviations of the coupling constants have been adjusted upward in Table I as suggested by Ewing[14] in his discussion of the error treatment in the program LAOCOON 3. The final root-mean-square errors in the three analyses were respectively .11, .24, .13 Hz.

The sign of the geminal coupling constant, J_{23} cannot be determined from the experiment. It is cited as negative by analogy to other geminal coupling constants in saturated hydrocarbon systems.[15] The signs of the vicinal coupling constants also cannot be obtained from these experiments.

DISCUSSION

Figure 1 represents the structures of the three geometrical isomers of bis(S-2,3-diaminopropionato)-cobalt(III) ion. All of the structures are dissymmetric. They are named by giving first the spatial relationship of the two oxygen donors, then of the two α nitrogens and then of the two β nitrogens. The isomers were identified on the basis of their circular dichroism spectra, their visible-ultraviolet spectra and X-ray crystal structure determination on the *cis,trans,cis* isomer.[9,16]

In these complex ions, the coordination of each tridentate ligand leads to the formation of a chelate ring system in a rigid conformation. Each such system consists of a five-membered nitrogen-cobalt-nitrogen chelate ring locked into position by a fused five-membered α-aminocarboxylate chelate ring. The three geometrical isomers of bis(S-2,3-diamino-propionato)cobalt(III) ion can be regarded as generated at 120 degree intervals by an imaginary twist of one chelate ring system relative to the other about an axis passing through the two ligand-occupied triangular faces of the cobalt(III) coordination octahedron.

Located on each chelate ring system are the three carbon-bound protons; one on the 2-carbon and two on the 3-carbon. Since all three of the complex ion isomers have C_2 symmetry, it is necessary to consider only the individual ligand's protons when discussing proton magnetic resonance spectra.

The immediate observation about the coupling constants is their similarity from isomer to isomer. No two comparable coupling constants differ by more than 1.25 σ from isomer to isomer. This similarity, particularly among the vicinal coupling constants, argues that the same, or very nearly the same, conformation is assumed by the coordinated ligand in all three isomers. Since the vicinal coupling constants are strongly dependent upon conformation[17,18] if different conformations existed from isomer to isomer one would expect quite different vicinal coupling constants. For example, when the same ligand is coordinated as a bidentate to platinum(II) the coupling constants between protons in the same pairs are J_{12} = 4.7, J_{13} = 9.2 and J_{23} = 12.8 Hz.[19] The great difference between the observed vicinal coupling constants in that bidentate case and in these tridentate cases attests the sensitivity of the coupling constants to ligand conformation.

Fortunately the details of the tridentate conformation are known from an X-ray crystal structure determination by Liu and Ibers.[16] These results, as far the geometry of the chelate ring system is concerned, are depicted in Figure 2. Hydrogen atoms positions were not refined by Liu and Ibers but were calculated on the basis of C–H = 1.11 Å and tetrahedral angles and inserted

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in the final stages of the least-squares refinement. For this paper the positions of the three carbon-bound hydrogen atoms were recomputed[20] using Liu and Ibers' non-hydrogen positional parameters and the preferable [21]C–H distance of 0.950 Å.

From the X-ray data and the idealized H-atom positions, the dihedral angles between the planes defined by the three atoms $H_1C_2C_3$ and the planes defined by $H_2C_2C_3$ and $H_3C_2C_3$ in the complex can readily be calculated. The angles are 49(2) and 72(2) degrees. Substitution of these angles in the approximate equation derived by Karplus[22,23] for a simple dihedral angle dependence of $J_{vicinal}$ yields J = 3.4 and 0.5 Hz respectively. These value approximate those found in the three isomers. In particular the distinction in magnitude between the two vicinal coupling constants, without consideration of the other factors affecting $J_{vicinal}$ (e.g. the electronegativity of the substituents),[23] allows the assignment of the proton which is at the larger dihedral angle as H_3. This assignment is given in Figure 2.

Since the positions of all three protons are now known with reasonable accuracy and since the three protons are all now assigned in the pmr spectra of each of the isomers, we can turn to a discussion of the observed chemical shifts in terms of structure.

The isomers are all of the N_4O_2 donor type. When the theoretical expressions of Ref. (5) are specialized to this case, the following equations result for the paramagnetic chemical shifts of a protons in the three geometrical isomers:

trans,cis,cis

$$\sigma^P(H) = \frac{-2(1-3\sin^2\theta\sin^2\phi)}{6R^3\langle r^{-3}\rangle}[\sigma^P(N)-\sigma^P(0)] \quad (1)$$

cis,trans,cis

$$\sigma^P(H) = \frac{1-3\cos^2\theta}{6R^3\langle r^{-3}\rangle}[\sigma^P(N)-\sigma^P(0)] \quad (2)$$

cis,cis,trans

$$\sigma^P(H) = \frac{1-3\sin^2\theta\cos^2\phi}{6R^3\langle r^{-3}\rangle}[\sigma^P(N)-\sigma^P(0)] \quad (3)$$

where θ, ϕ and R are the spherical polar coordinates of the proton in the coordinate system of Figure 2, $\sigma^P(N)$ and $\sigma^P(O)$ are the additive contributions of the nitrogen and oxygen donors to the paramagnetic part of the ^{59}Co shielding (–4860 and –6255 ppm respectively[7]) and $\langle r^{-3}\rangle$ is the quantum mechanical average value, $\int\psi^*\frac{1}{r^3}\psi d\tau$, for a 3d cobalt orbital. Evaluation of these expressions is possible and will be presented. First however, we will test the notion that the only important source of variation in the proton magnetic shielding from isomer to isomer is the difference in cobalt(III) paramagnetic anisotropy.

In Table I, the chemical shifts of H_1 in the first two isomers, $\delta(H_1)_{trans,cis,cis}$ and $\delta(H_1)_{cis,trans,cis}$, are approximately equal. Given the above assumption this can occur only if

$$\sigma^P(H_1)_{trans,cis,cis} = \sigma^P(H_1)_{cis,trans,cis}$$

Combining Eqs. (1) and (2) it follows that $\phi(H_1)$ = 45 degrees. Furthermore, if $\phi(H_1)$ = 45 degrees, then $\sigma^P(H_1)_{cis,trans,cis}$ is of opposite sign and half the magnitude of $\sigma^P(H_1)_{trans,cis,cis}$ and $\sigma^P(H_1)_{cis,trans,cis}$. These relationships would hold regardless of the values of R, $\langle r^{-3}\rangle$ or any of the other quantities in Eqs. (1–3).

Next it is observed that:

$$\delta(H_2)_{cis,cis,trans}-\delta(H_2)_{trans,cis,cis} = \delta(H_2)_{cis,trans,cis} - \delta(H_2)_{cis,cis,trans}$$

Again, assuming that these differences are entirely from cobalt(III) paramagnetic anisotropy, combination of Eqs. (1–3) and trigonometry quickly show that $\theta(H_2)$ is 55 degrees. It follows also that:

$$\sigma^P(H_2)_{cis,trans,cis} = 0 \text{ and that}$$

$$\sigma^P(H_2)_{trans,cis,cis} = 2[\sigma^P(H_2)_{cis,cis,trans}].$$

Finally the approximate equality of $\delta(H_3)_{trans,cis,cis}$ and $\delta(H_3)_{cis,cis,trans}$ implies under the same assumption and by similar methods that $\sin\phi = \cot\theta$ for this proton and that:

$$\sigma^P(H_3)_{trans,cis,cis} = \sigma^P(H_3)_{cis,cis,trans} = -2[\sigma(H_3)_{cis,trans,cis}].$$

Thus, from the pmr data themselves we have obtained, without estimates of quantities like $\langle r^{-3}\rangle$ $\sigma^P(N)$ and $\sigma^P(O)$ or even R, knowledge of some of the coordinates of the protons in this chelate ring system. We find that for H_1 ϕ = 45 degrees – the X-ray structure-based value is 40(2) degrees. For H_2 θ = 55 degrees – X-ray structure-based value is 51(2) degrees. For H_3 $\sin\phi = \cot\theta$ – the X-ray structure-based values of 25(2) degrees and 64(2) degrees approximately fulfill this relationship.

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TABLE II
Spherical Polar Coordinates of Protons of coordinated S-2,3-diaminopropionate ligand (in coordinate system defined in Figure 2)

H_1	28(2) degrees	40(2) degrees	3.45(5)Å
H_2	51(2)	−2(2)	3.41(5)Å
H_3	64(2)	25(2)	3.53(5)Å

[a] derived from ref. 16 with modification explained in text.

None of the X-ray structure based values of proton positional coordinates differs significantly from those derived from the pmr data. This agreement is compelling especially in light of the approximations used in arriving at Eqs. (1–3), most particularly the assumption of O_h symmetry. It certainly justifies the assumption that the only important source of variation in the proton chemical shifts from isomer to isomer is cobalt(III) paramagnetic anisotropy, which, therefore, most likely is the dominant source of the empirical rule cited in the Introduction.

Values for the spherical polar coordinates of the three chelate ring proton are all given, as derived from the X-ray data, in Table II.

As a final note we can evaluate Eqs. (1–3) using these coordinates and using the $\sigma^P(N)$, $\sigma^P(O)$ and $\langle r^{-3} \rangle$ values given by Ref. 5. The equation become

trans,cis,cis

$$\sigma^P(H) = -\frac{2}{6}(1-3\sin^2\theta\sin^2\phi)F \quad (4)$$

cis,trans,cis

$$\sigma^P(H) = 1/6(1-3\cos^2\theta)F \quad (5)$$

cis,cis,trans

$$\sigma^P(H) = 1/6(1-3\sin^2\theta\cos^2\phi)F \quad (6)$$

where F = 0.78 ppm for H_1, 0.83 ppm for H_2 and 0.75 ppm for H_3.

Table III summarizes the paramagnetic chemical shifts calculated for each proton in each of the geometries.

Comparison of these calculated values within an isomer is not revealing. $\sigma^P(H_1)$ cannot be compared to $\sigma^P(H_2)$ or $\sigma^P(H_3)$ because the extra inductive effect of the two electron-with-drawing substituents on the 2-carbon is not taken into consideration; that is, the diamagnetic part of the shielding constant expression, which is sensitive to inductive effects of neighboring atoms, is not evaluated. Therefore the center from which the paramagnetic shifts are taken for the 2-carbon proton is well down-field from the comparable center for the 3-carbon protons. The same comment applies to the situation between the methylene protons, although the difference in diamagnetic shift is less.

The values given in Table III cannot be taken too seriously because they are based on *estimates* of the non-positional quantities in Eqs. (1–3). The relationships from isomer to isomer are however apparent and correspond to those discussed above.

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TABLE III
Calculated Paramagnetic Chemical Shift for Carbon-Bound Protons in Isomers of bis(S-2,3-diaminopropionato)cobalt(III) ion. Based on Coordinates in Table II[a)]

	trans,cis,cis	*cis,trans,cis*	*cis,cis,trans*
$\sigma^P(H_1)$	−0.21 ppm	−0.20 ppm	+0.09 ppm
$\sigma^P(H_2)$	−0.30	−0.03	−0.12
$\sigma^P(H_3)$	−0.16	+0.06	−0.13

[a] minus means shift down-field.

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