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Proton Magnetic Resonance of Metal Ammine Complexes. IV. Paramagnetic Anisotropy of Cobalt(III) Ions as Exemplified in Proton Chemical Shifts

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A theory is presented which couples the proton chemical shift induced by the paramagnetic anisotropy with the chemical shift of the central cobalt-59 nucleus. The theory has been successfully applied to twenty cobalt(III) α-aminocarboxylate complexes. It is shown that it can be used not only to assign proton NMR signals but also to determine the structure of the complex and, in certain cases, the conformation of ligand molecules.

Recently, Watabe *et al.*1) have given a method for assigning proton magnetic resonance spectra of diamagnetic cobalt compounds. They have noted a general trend, with a few exceptions, for the chemical shift of a proton in a H–C–N–Co(III)–X fragment where X is a nitrogen or oxygen atom and occupies the *trans* (to N) position. The proton resonates at higher or lower field according to whether X is oxygen or nitrogen. This "through-cobalt" effect has been attributed tentatively to the polarizing power of the X atom.

During the course of an investigation on the proton chemical shifts in cobalt(III) ammine complexes, we found2) that the shifts are primarily determined by the anisotropy in the second order paramagnetism of the central cobalt ion. A theoretical relation between the proton and the cobalt-59 shielding constants was derived and used successfully to reproduce the observed ammine proton chemical shifts. In connection with this work, a recent report given by Yajima *et al.*3) gave us an impetus to study theoretically the cobalt-59 chemical shifts. We have shown that the additivity in cobalt-59 chemical shifts observed in solution3) originates from the additivity in each (xx, yy, and zz) component of the shielding tensor.4) The result, coupled with the relation between ^{1}H and ^{59}Co chemical shifts, enables us to predict the shift of protons under the influence of the paramagnetic anisotropy of the central cobalt(III) ion. Thus, the anisotropy in the second order paramagnetism of diamagnetic cobalt ions will be shown to manifest itself in proton chemical shift variations. Several cobalt(III) complexes exemplifying this situation are treated in this paper. The purpose of the present study is to substantiate the empirical rule of Watabe *et al.* in the light of magnetic anisotropies. The study has been limited to cobalt(III) α-aminocarboxylate complexes. The theoretical results derived here can be utilized not only for the assignment of proton NMR signals but also, in certain cases, for the determination of the geometrical structure of complexes.

Theory

Details of the theory were given in previous papers.2,4) It is well established that proton chemical shielding under the influence of the anisotropic magnetic susceptibility is given by5)

$$\sigma_{xx}(^1\mathrm{H}) = (1-3\sin^2\theta\cos^2\phi)\chi^{p}_{xx}/R^3 \tag{1}$$

$$\sigma_{yy}(^1\mathrm{H}) = (1-3\sin^2\theta\sin^2\phi)\chi^{p}_{yy}/R^3 \tag{2}$$

$$\sigma_{zz}(^1\mathrm{H}) = (1-3\cos^2\theta)\chi^{p}_{zz}/R^3 \tag{3}$$

where χ^{p}_{ii} (i=x, y, z) is the principal value of the magnetic susceptibility tensor of cobalt(III) ion, the superscript p refers to the paramagnetic part (*vide infra*), R is the distance between the metal ion and the proton in question, and θ and ϕ are the polar coordinates of the proton in a frame of reference which diagonalizes the susceptibility tensor. In general, magnetic susceptibility and shielding tensors are given, respectively, by

$$\begin{aligned}\chi = &-(1/2)(e^2/2mc^2)\langle 0|\sum_{\mathrm{i}}\{\boldsymbol{l}(r_{\mathrm{i}}{}^2)-\boldsymbol{r}_{\mathrm{i}}\boldsymbol{r}_{\mathrm{i}}\}|0\rangle \\ &+\sum_{n}\Delta E_n{}^{-1}\{\langle 0|\sum_{\mathrm{i}}\boldsymbol{m}_{\mathrm{i}}|n\rangle\langle n|\sum_{\mathrm{i}}\boldsymbol{m}_{\mathrm{i}}|0\rangle+\mathrm{c.c.}\}\end{aligned} \tag{4}$$

and

$$\begin{aligned}\sigma = &(e^2/2mc^2)\langle 0|\sum_{\mathrm{i}}\{\boldsymbol{l}(r_{\mathrm{i}}{}^2)-\boldsymbol{r}_{\mathrm{i}}\boldsymbol{r}_{\mathrm{i}}\}/r_{\mathrm{i}}{}^3|0\rangle \\ &-2\sum_{n}\Delta E_n{}^{-1}\{\langle 0|\sum_{\mathrm{i}}\boldsymbol{m}_{\mathrm{i}}/r_{\mathrm{i}}{}^3|n\rangle\langle n|\sum_{\mathrm{i}}\boldsymbol{m}_{\mathrm{i}}|0\rangle+\mathrm{c.c.}\}\end{aligned} \tag{5}$$

The latter is based on Ramsey's formulation.6) All the notations have their usual meaning2,4) and c.c. is to take the complex conjugate. From Eqs. (4) and (5), it has been shown,2) after some mathematical manipulation, that the following relation holds for a cobalt(III) ion.

$$\chi^{p}_{ii} = -\sigma^{p}_{ii}/2\langle r^{-3}\rangle \quad (\mathrm{i=x,\ y,\ z}) \tag{6}$$

Substitution of Eq. (6) into Eqs. (1)—(3) gives

$$\sigma_{xx}(^1\mathrm{H}) = -(1-3\sin^2\theta\cos^2\phi)\sigma^{p}_{xx}(^{59}\mathrm{Co})/2R^3\langle r^{-3}\rangle \tag{7}$$

$$\sigma_{yy}(^1\mathrm{H}) = -(1-3\sin^2\theta\sin^2\phi)\sigma^{p}_{yy}(^{59}\mathrm{Co})/2R^3\langle r^{-3}\rangle \tag{8}$$

$$\sigma_{zz}(^1\mathrm{H}) = -(1-3\cos^2\theta)\sigma^{p}_{zz}(^{59}\mathrm{Co})/2R^3\langle r^{-3}\rangle \tag{9}$$

Covalency effects have been taken into account through Eq. (6). Thus, proton chemical shifts are directly related to cobalt-59 chemical shifts. The additivity in cobalt-59 chemical shifts gives the relations

$$\sigma^{p}_{xx}(^{59}\mathrm{Co}) = \sigma^{p}(\mathrm{C}) + \sigma^{p}(\mathrm{D}) + \sigma^{p}(\mathrm{E}) + \sigma^{p}(\mathrm{F}) \tag{10}$$

$$\sigma^{p}_{yy}(^{59}\mathrm{Co}) = \sigma^{p}(\mathrm{A}) + \sigma^{p}(\mathrm{B}) + \sigma^{p}(\mathrm{E}) + \sigma^{p}(\mathrm{F}) \tag{11}$$

$$\sigma^{p}_{zz}(^{59}\mathrm{Co}) = \sigma^{p}(\mathrm{A}) + \sigma^{p}(\mathrm{B}) + \sigma^{p}(\mathrm{C}) + \sigma^{p}(\mathrm{D}) \tag{12}$$

These relations have been derived in the $\mathrm{O_h}$-approximation for a complex (Fig. 1). Thus, we obtain the following results for the chemical shift of a proton in a ligand coordinated to cobalt(III) ion.

$$\begin{aligned}\sigma_{xx}(^1\mathrm{H}) = &-(1-3\sin^2\theta\cos^2\phi) \\ &\times(\sigma^{p}(\mathrm{C})+\sigma^{p}(\mathrm{D})+\sigma^{p}(\mathrm{E})+\sigma^{p}(\mathrm{F}))/2R^3\langle r^{-3}\rangle\end{aligned} \tag{13}$$

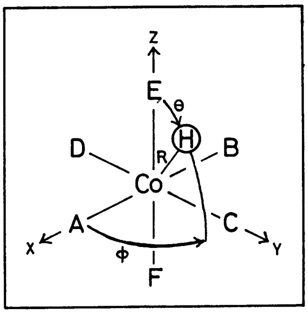


Fig. 1. The coordinate system for a complex [Co(AB-CDEF)]. A, B, ……, F stand for ligand molecules or ions.

$$\sigma_{yy}(^1\mathrm{H}) = -(1-3\sin^2\theta\sin^2\phi) \times (\sigma^p(\mathrm{A})+\sigma^p(\mathrm{B})+\sigma^p(\mathrm{E})+\sigma^p(\mathrm{F}))/2R^3\langle r^{-3}\rangle \quad (14)$$

$$\sigma_{zz}(^1\mathrm{H}) = -(1-3\cos^2\theta) \times (\sigma^p(\mathrm{A})+\sigma^p(\mathrm{B})+\sigma^p(\mathrm{C})+\sigma^p(\mathrm{D}))/2R^3\langle r^{-3}\rangle \quad (15)$$

Analysis of cobalt-59 chemical shift data indicates that the magnitude of $\sigma^p(\mathrm{X})$ for various ligands is in the order

$$\sigma^p(\mathrm{N}) > \sigma^p(\mathrm{O}) > \sigma^p(\mathrm{Cl}) \simeq \sigma^p(\mathrm{Br})$$

Typical values of $\sigma^p(\mathrm{X})$ for several ligands are given in Table 1.[4] The proton chemical shift to be observed in solution is given by

$$\sigma_{iso}(^1\mathrm{H}) = (\sigma_{xx}(^1\mathrm{H})+\sigma_{yy}(^1\mathrm{H})+\sigma_{zz}(^1\mathrm{H}))/3 \quad (16)$$

TABLE 1. σ^p (X) VALUES FOR SEVERAL LIGANDS[4]

X	σ^p (X) ppm	X	σ^p (X) ppm
NH_3	−4860	N_3^-	−5655
en	−9205	OH^-	−6345
Cl^-	−5910	H_2O	−6255
Br^-	−5865	CO_3^{2-}	−12090
NO_2^-	−4073	ox^{2-}	−11440
CN^-	−2760	Phen	−9135

Application to Cobalt(III) α-Aminocarboxylates Geometry. Quantities necessary for the calculation of Eqs. (13)—(15) can be estimated in the following way. An average of r^{-3} over a metal 3d orbital is transferred from that of $[Co(NH_3)_6]^{3+}$; $\langle r^{-3}\rangle=5.77$ a.u.[2] Chemical shift values of cobalt-59 nuclei do not seem to have been reported for aminoacidato complexes. The best values might be the data for simple cobalt compounds for which shift data are available. Setting $\sigma^p(\mathrm{O})$ and $\sigma^p(\mathrm{N})$ at around −6000 and −4600 ppm, respectively, we obtain the result $\sigma^p(\mathrm{N})-\sigma^p(\mathrm{O})\simeq 1400$ ppm. This value was used for all the complexes we examined. Although this is a drastic approximation, the final results were not seriously affected (*vide infra*).

Geometrical factors R, θ, and ϕ were taken from data on α-aminocarboxylate backbones of NH_4[Co-(EDTA)]·$2H_2O$[7] and $(+)_{495}$-[Co(L-glu)(en)$_2$]ClO_4.[8] In the former complex, two structurally different glycine residues are present, the in-plane and out-of-plane groups. It has been reported that the out-of-plane ring is almost flat. The five-membered chelate ring in the latter complex formed by cobalt ion and L-glutamate ion is also nearly flat. This is in line with the observation that chelated α-aminoacidato rings are planar.[9–11] Thus, we assume the planar conformation for α-aminocarboxylate residues in the following. The cobalt-proton distance, R, is calculated for these complexes at about 3.47 A (6.56 a.u.). The relevant quantities are illustrated in Fig. 2. Under these conditions, we obtain

$$(\sigma^p(\mathrm{N})-\sigma^p(\mathrm{O}))/R^3\langle r^{-3}\rangle \simeq 0.859\ \mathrm{ppm} \quad (17)$$

Unless otherwise stated, this value will be used for all complexes.

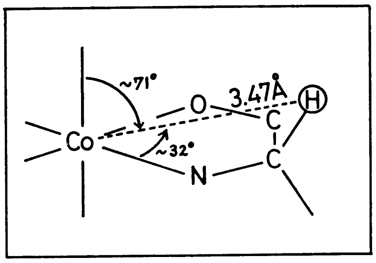


Fig. 2. The geometry of the α-aminocarboxylate residue.

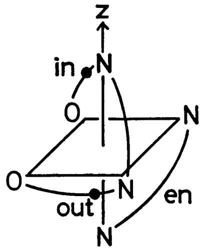


Fig. 3. Schematic presentation of *β-cis*-[Co(EDDA)(en)]$^+$ molecule. Closed circles refer to glycine methylene protons in question.

Illustrative Examples. [*Case I*] cis-O_2N_4 *Type*; *β*-cis-[*Co(EDDA)(en)*]$^+$: This complex contains two equivalent glycine methylene groups, in-plane and out-of-plane methylenes, designated as in-CH_2 and out-CH_2, respectively (Fig. 3). The ligand EDDA conformation in this inert chelate was reported to be fixed.[12] From Eqs. (13)—(16), the chemical shift of the methylene protons is given by

$$\sigma_{iso}(^1\mathrm{H}) = (1-3\cos^2\theta)(\sigma^p(\mathrm{N})-\sigma^p(\mathrm{O}))/6R^3\langle r^{-3}\rangle \quad (18)$$

The geometrical factors, coupled with Eq. (17), give

$$\sigma_{iso}(\text{in-CH}_2) \simeq -0.168\ \mathrm{ppm} \quad (19)$$

$$\sigma_{iso}(\text{out-CH}_2) \simeq +0.099\ \mathrm{ppm} \quad (20)$$

Thus, our estimation indicates that the out-CH_2 resonates at higher field and the in-CH_2 at lower field, the separation being about 0.26 ppm. Not much significance can be attached to this figure. Coleman *et al.*[13] observed a singlet at 3.71 ppm (from NaTMS) and an AB quartet at 3.59 ppm. Assignment was made based on a comparison with the spectra of *β-cis*-[Co(EDDA)(ox)]$^-$ and *β-cis*-[Co(EDDA)(mal)]$^-$, on the signal intensities, and the well established fact that, in coordinated EDDA, in- and out-CH_2 appear as a singlet and an AB quartet, respectively.[14,15] The assignment was further substantiated by the isotopic deuterium exchange experiment. It was thus concluded that the singlet at higher field is the in-CH_2, which is in line with our prediction. The observed chemical shift difference between the in- and out-CH_2 is about 0.14 ppm smaller than that expected from the theory. This seems to be due to the valence angle distortion.

β-cis-[Co(EDDA)$(NH_3)_2$]$^+$ can be treated similarly. It suffices to say that the theory leads to a correct assignment.[16)]

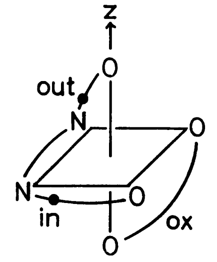


Fig. 4. *β-cis*-[Co(EDDA) (ox)]$^-$ molecule. Closed circles stand for the in- and out-methylenes.

[*Case II*] cis-N_2O_4 *Type*; *β*-cis-[*Co(EDDA)(ox)*]$^-$: The coordinate system is shown in Fig. 4. The two glycine methylene protons, in- and out-CH_2, can be treated in a similar manner to that for Case I if we replace (σ^p(N)$-\sigma^p$(O)) in Eq. (18) by (σ^p(O)$-\sigma^p$(N)). This leads to the conclusion that the out-CH_2 should appear at a higher field, which is also in line with the observation by Coleman *et al.*[13)]

[*Case III*] mer-N_3O_3 *Type*; [*Co(ED3A)(NO*$_2$*)*]$^-$: It can easily be shown that the proton chemical shift is given by

$$\sigma_{\rm iso}(^1{\rm H}) = \sin^2\theta\cos 2\phi(\sigma^p({\rm N})-\sigma^p({\rm O}))/2R^3\langle r^{-3}\rangle \quad (21)$$

Note that we have placed three oxygen atoms in the xz plane. We see at once that the resonance field of B methylene protons is higher than that of groups A and C (Fig. 5). A subtlety is involved in positioning A and C methylenes. There is clearly a minor difference in the chemical shift of these protons. All these predictions have been confirmed by observation.[13)]

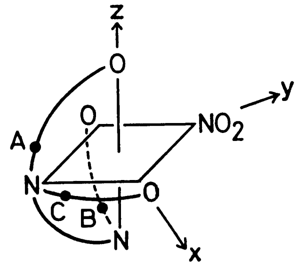


Fig. 5. [Co(ED3A)(NO_2)] ion. A, B, and C differentiate three methylene groups.

Assignments. c_1-cis-[*Co(gly)*$_2$*(en)*]$^+$: This molecule is of the *cis*-O_2N_4 type and can be treated as in Case I. The two acetate methylene groups are designated as A and B (Fig. 6). It is predicted by theory that group A should resonate at a higher field than B by about 0.2 ppm. Matsuoka *et al.*[17)] observed two singlets at 3.60 and 3.44 ppm corresponding to two acetate methylenes. In this case, the valence angle distortion is irrelevant and we may safely assign the former singlet to the B protons.

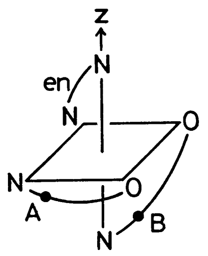


Fig. 6. c_1-*cis*-[Co(gly)$_2$(en)]$^+$ ion. A and B are the methylenes under consideration.

c_1-cis-[*Co(gly)*$_2$*(ox)*]$^-$: The difference between the two glycine methylene groups is shown in Fig. 7. According to our prediction B is situated in a higher field than A. It was reported[17)] that two singlets at 3.58 and 3.43 ppm can be assigned to two glycine methylenes. Although the predicted separation around 0.05 ppm is rather small as compared with the observed value (0.15 ppm), it is highly probable that group B resonates at a higher field.

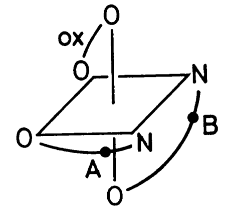
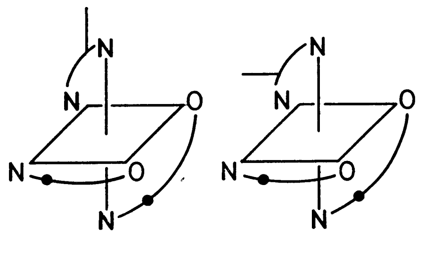


Fig. 7. c_1-*cis*-[Co(gly)$_2$(ox)]$^-$ ion. A and B stand for the two acetate groups in question.

cis(*O*),cis(*N*)-[*Co(gly)*$_2$*(l-pn)*]$^+$: Two geometrical isomers exist in this *cis*-O_2N_4 type compound (Fig. 8). The complexes were obtained by the reaction of *trans*-[$CoCl_2$(l-pn)$_2$]$^+$ with glycine in an alkaline medium. Kojima and Shibata[18)] obtained complexes 8a and 8b as more soluble and less soluble isomers, respectively. The glycine methylene chemical shifts are reported at 3.62 and 3.46 ppm for 8a and 3.59 and 3.46 ppm for 8b. The proton chemical shifts in these complexes can be treated in the same way as for c_1-*cis*-[Co(gly)$_2$(en)]$^+$. Thus, protons resonating at a higher field can be assigned to methylene group *trans* to the oxygen atom in both isomers.

cis-[*Co(IDA)*$_2$]$^-$: Cooke[19)] measured the proton NMR spectrum and observed two signals at 3.75 and 3.635 ppm corresponding to two methylene groups.



(8a) (8b)

Fig. 8. Two possible isomers of *cis*(*O*), *cis*(*N*)-[Co(gly)$_2$-(l-pn)]$^+$ molecule. Closed circles refer to protons in question.

This complex is of the *cis*-N_2O_4 type and can be treated as in Case II. We assign the high field signal to the out-of-plane methylenes.

mer-[*Co(gly)*$_2$*(*L*-glu)*]: Kawasaki and Shibata[20] prepared this complex by the reaction of $[Co(gly)_2(CO_3)]^-$ with glutamate ion in the presence of activated charcoal. They did not succeed in determining the structure. There are two possibilities; *cis(O),trans(N)*- and *cis(N), trans(O)*-isomers. The chemical shift values have not been given but can be estimated from the spectrum. Two singlets at about 3.4 and 3.65 ppm can be observed. Thus, the shift difference is close to that found between groups B and C in $[Co(ED3A)(NO_2)]^-$. For the *cis(O),trans(N)*-structure, the shift difference should be much smaller, which follows from the analogy of the difference between groups A and C in $[Co(ED3A)(NO_2)]^-$. We are thus inclined to presume that the complex assumes the *cis(N),trans(O)*-structure (see Fig. 9). If this is the case, the glycine protons designated as B should appear at a higher field.

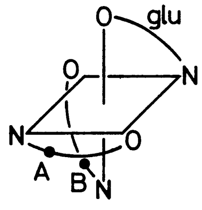


Fig. 9. *mer*-[Co(gly)$_2$(L-glu)] molecule. A and B are methylene groups.

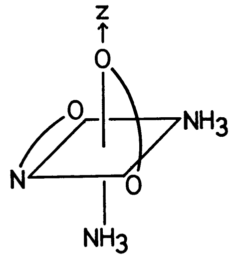


Fig. 10. *mer(cis)*-$[Co(CO_3)(gly)(NH_3)_2]$ ion.

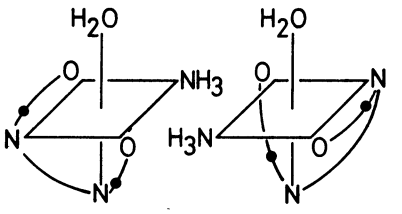
mer*(*cis*)*-[*Co(CO*$_3$*)(gly)(NH*$_3$*)*$_2$]: Let us examine the chemical shift of ammine protons of coordinated ammonia molecules (see Fig. 10). Kanazawa and Shibata[21] measured the NMR spectrum in trifluoroacetic acid. They observed the chemical shifts of ammonia protons at 5.1 and 5.8 ppm. The separation is larger as compared with separations found for glycine methylene protons discussed above. This is caused by the decrease in Co–H distance *R*. For the ammonia protons situated on the z-axis, the NH_3-rotation about its C_3-axis renders the factors $(1-3\sin^2\theta\cos^2\phi)$ and $(1-3\sin^2\theta\sin^2\phi)$ both averaged to $(2-3\sin^2\theta)/2$. It follows that protons of this ammonia molecule do not experience the magnetic anisotropy of the cobalt(III) ion. For the other ammonia protons, the following relation can be derived by taking the NH_3-rotation into account.

$$\sigma_{\mathrm{iso}}(^1\mathrm{H}) = -(3\cos^2\theta'-1)(\sigma^{\mathrm{p}}(\mathrm{N})-\sigma^{\mathrm{p}}(\mathrm{O}))/4R^3\langle r^{-3}\rangle \quad (22)$$

Note here that θ' represents the angle between the Co–H vector and the x-axis. The geometrical factors are R=2.52 A (4.77 a.u.) and θ'=22.0.[2] These values, coupled with $(\sigma^{\mathrm{p}}(\mathrm{N})-\sigma^{\mathrm{p}}(\mathrm{O}))\simeq 1400$ ppm, give $\sigma_{\mathrm{iso}}(^1\mathrm{H})$ value of about −0.883 ppm. Thus, it can be concluded that this ammonia is shifted to low field.

mer*(*cis*)*-[*Co(CO*$_3$*)(β-ala)(NH*$_3$*)*$_2$], mer*(*cis*)*-[*Co(ox)(gly)(NH*$_3$*)*$_2$], mer*(*cis*)*-[*Co(ox)(β-ala)(NH*$_3$*)*$_2$]: These three complexes can be treated in the same way as above. The protons of the ammonia molecule *trans* to the nitrogen should appear at a lower field and those *trans* to the oxygen at a higher field.

α-cis-[*Co(EDDA)(NH*$_3$*)H*$_2$*O*]$^+$: As expected, the glycine methylene protons exhibit two AB quartets. From a comparison of the spectrum with that of *β-cis*-$[Co(EDDA)(NH_3)_2]^+$ and *β-cis*-$[Co(EDDA)(H_2O)]^+$, the quartet at a lower field has been assigned[23] to glycine protons near the coordinated ammonia molecule. However, this assignment seems to be open to question. There are two possible ways of coordination for ammonia molecule, 11a and 11b. In either case, the theory based on the magnetic anisotropy of cobalt ion leads to an assignment just the opposite; the high field quartet should be due to the methylene near the coordinated ammonia.



(11a) (11b)

Fig. 11. Two possible ways of coordination of ammonia molecule in *α-cis*-$[Co(EDDA)(NH_3)H_2O]^+$. Closed circles stand for two glycine methylene groups.

Discussion

Several criteria have been proposed for the assignment of proton NMR spectra. They include valence angle distortions (and the consequential elongation of Co–O bonds),[25] bond anisotropies,[13–15,19] steric compressions,[24] selective labilization of α-hydrogen atoms,[26] and the paramagnetic anisotropy in the central metal ion.[1,2,4,27] The first effect, which is the most relevant to our problem, tends to vitiate a prediction based only on the paramagnetic anisotropy of metal ions. $[Co(EDTA)]^-$ and its derivatives offer such examples.

The molecular structure of $[Co(EDTA)]^-$ was determined by Weakliem and Hoard.[7] Their X-ray analysis revealed that while the out-of-plane rings are nearly flat, the in-plane rings suffer severe valence angle distortions, leading to a substantial elongation of the Co–O bonds. In accordance with this fact, the in-plane protons have been shown[14,25,28] to be more shielded than the out-of-plane ones. Similar situations have been noted for $[Co(PDTA)]^-$ and $[Co(CyDTA)]^-$.[26] These molecules belong to *cis*-N_2O_4 symmetry. From the result on *cis*-$[Co(IDA)_2]^-$, it is readily seen that the prediction based only on the paramagnetic anisotropy of the cobalt ion is contrary to observation. Thus, the valence angle distortion acts in these cases to offset paramagnetic anisotropy.

Another example of similar situation is provided by β-*cis*-[Co(EDDA)(mal)]$^-$. Coleman *et al.*[13] measured a spectrum consisting of a singlet and an AB quartet for glycine methylenes. The former resonates at a higher field, the separation being *ca.* 0.06 ppm. The assignment was based on the argument for β-*cis*-[Co(EDDA)(ox)]$^-$. The selective HD exchange experiment provided further support to this assignment. The out-of-plane methylene was shown to be more labilized and amenable to the isotopic exchange reaction. Thus, their assignment can be considered to be sound. Consideration of only the paramagnetic anisotropy leads to an erroneous conclusion, though the predicted separation between the in- and out-of-plane protons is rather small (0.05 ppm). All these examples indicate that we should be careful in applying the theory to ligands with valence angle distortions.

Watabe *et al.*[1] observed that in a number of cobalt(III) α-aminocarboxylate complexes, α protons adjacent to the amino group which is *trans* to N atom are shifted to low field and those *trans* to O atom to high field. This seems to be an over simplification. As Eqs. (13)—(15) indicate, the proton chemical shift is dependent on all the six coordinating atoms and on the position of the proton in question.

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Appendix. Abbreviations

EDTA =ethylenediaminetetraacetato ion.
glu =glutamato ion.
en =ethylenediamine.
EDDA =ethylenediaminediacetato ion.
ox =oxalato ion.
mal =malonato ion.
ED3A =ethylenediaminetriacetato ion.
gly =glycinato ion.
pn =propylenediamine.
IDA =iminodiacetato ion.
ala =alaninato ion.
PDTA =propylenediaminetetraacetato ion.
CyDTA =cyclohexanediaminetetraacetato ion.
phen =phenanthroline.

References

1) M. Watabe, K. Onuki, and S. Yoshikawa, to be published.

2) (a) H. Yoneda and Y. Nakashima, This Bulletin, **47**, 669 (1974). (b) Y. Nakashima, U. Sakaguchi, and H. Yoneda, *Chem. Lett.*, **1974**, 503.

3) F. Yajima, Y. Koike, A. Yamasaki, and S. Fujiwara, This Bulletin, **47**, 1442 (1974).

4) Y. Nakashima, U. Sakaguchi, and H. Yoneda, to be published.

5) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

6) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

7) H. A. Weakliem and J.L. Hoard, *J. Amer. Chem. Soc.*, **81**, 549 (1959).

8) R. D. Gillard, N. C. Payne, and G. B. Robertson, *J. Chem. Soc.*, *A*, **1970**, 2579.

9) H.C. Freeman, M.R. Snow, I. Nitta, and K. Tomita, *Acta Crystallogr.*, **21**, 1463 (1964).

10) G. M. Gramaccioli, *ibid.*, **21**, 600 (1966).

11) G. M. Gramaccioli and R. E. March, *ibid.*, **21**, 594 (1966).

12) G. L. Blackmer, R. E. Hamm, and J. I. Legg, *J. Amer. Chem. Soc.*, **91**, 6632 (1969).

13) P. F. Coleman, J. I. Legg, and J. Steele, *Inorg. Chem.*, **9**, 937 (1970).

14) J.I. Legg and D.W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

15) J.I. Legg and D.W. Cooke, *ibid.*, **5**, 594 (1966).

16) K. Kuroda, *Chem. Lett.*, **1972**, 197.

17) N. Matsuoka, J. Hidaka, and Y. Shimura, This Bulletin, **40**, 1868 (1967).

18) Y. Kojima and M. Shibata, *Inorg. Chem.*, **9**, 238 (1970).

19) D. W. Cooke, *ibid.*, **5**, 1141 (1966).

20) K. Kawasaki and M. Shibata, This Bulletin, **45**, 3100 (1972).

21) S. Kanazawa and M. Shibata, *ibid.*, **44**, 2424 (1971).

22) K. Nakai, S. Kanazawa, and M. Shibata, *ibid.*, **45**, 3544 (1972).

23) K. Kuroda, *ibid.*, **45**, 2176 (1972).

24) J. C. Dabrowiak and D. W. Cooke, *J. Amer. Chem. Soc.*, **92**, 1097 (1970).

25) D. H. Williams and D. H. Busch, *ibid.*, **87**, 4644 (1965).

26) J. B. Terrill and C. N. Reilly, *Inorg. Chem.*, **5**, 1988 (1966).

27) (a) R. V. Emanuel and E. W. Randall, *J. Chem. Soc.*, *A*, **1969**, 3002. (b) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960). (c) A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, **1964**, 2747.

28) R. J. Day and C. N. Reilly, *Anal. Chem.*, **36**, 1073 (1964).