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Proton Magnetic Resonance Spectra of Metal Ammine Complexes. IX. Stereoelectronic Effect in the Activation of α-Hydrogen Atoms of Coordinated Amino Acids

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The activation of glycine methylene hydrogens caused by coordination to cobalt(III) ion has been studied by several workers [1]. In a series of investigations, Norman and Phipps [2] referred recently to different hydrogen–deuterium exchange rates exhibited by three stereochemically different glycinato ligands of *mer*-$[Co(gly)_3]$, where gly = $H_2NCH_2CO_2^-$. Their results are essentially in agreement with our previous studies [3], though we could offer no explanation for it at that time. Subsequent studies on cobalt(III) ammine compounds prompted us to propose an interpretation, which we would like to communicate here.

Our recent works [4] indicated that the chemical shift of α-hydrogen(s) of α-amino acids or α-aminocarboxylates coordinated to cobalt(III) ion can be explained, in the absence of valence angle distortion, by the effect of the magnetic anisotropy of the central metal ion. The effect on proton chemical shifts could be quantified by use of ^{59}Co chemical shift data for the compound in question or for those compounds which have similar ligators. The theory of chemical shift based on this effect has been applied to some cobalt(III) complexes [4–6]. Application of the theory to the meridional $[Co(gly)_3]$ complex reveals that the hydrogens denoted as h in the Figure suffer an upfield shift, while the l hydrogens suffer a low-field shift. Quantitative evaluation of their shifts caused by the magnetic anisotropy effect was thwarted by the absence of ^{59}Co chemical shift data for glycine-containing cobalt(III) compounds. A rough estimation can, however, be made by (i) replacing the contributions to ^{59}Co shifts from the glycine oxygen and nitrogen by those from the oxalate oxygen and ammine nitrogen, respectively, and (ii) using the crystallographically determined geometry of glycine residues [7]. The relevant data are given in ref. [4]. The calculation gave rise to about 0.4 ppm as their chemical shift difference, with h hydrogens at higher magnetic field, and the shift difference between the two l groups is much smaller than this value. The observed shift difference, 0.26 ppm, is a bit smaller but it clearly demonstrates that the high-field peak corresponds to two h protons and the low-field one to four l protons. Experimentally this is what is observed. The observed spectrum consisted of two peaks at δ 3.68 and 3.42 with an intensity ratio of 2:1. Thus, the h hydrogens rather than l are most probably the unique methylene. Coupled with the observation that the high-field peak diminishes in intensity more rapidly in alkaline D_2O than the low-field one, the above assignment establishes that it is the h hydrogen that exchanges faster with deuterium.

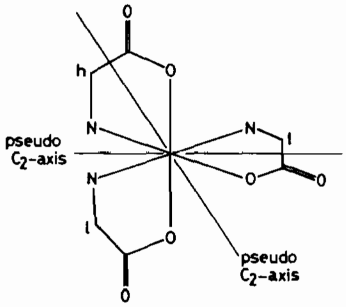

Figure. Schematic presentation of the *mer*-$[Co(gly)_3]$ complex. The structure is drawn for the Λ configuration.

Before discussing factors which may lead to different degrees of activation of h and l methylenes, we recall the following observation [5, 8]. In monosubstituted cobalt(III) pentaammine ion $[Co(NH_3)_5X]^{n+}$, the ammine hydrogens *trans* to X were activated to a different degree according to X. The strong-field ligands, *e.g.*, CN^- and NO_2^-, deactivated the *trans* ammine protons and accordingly these hydrogens exchanged with deuterium more slowly than the *cis* protons. The weak-field ligands, oxygen or halogen, worked oppositely. One may rationalize this phenomenon in terms of the *trans*-bond strengthening or weakening effect of a ligand [9]. This line of reasoning leads us to note that for the h glycinato ion the ligating atom *trans* to its carboxyl group is oxygen and that *trans* to the amino group is also oxygen. Thus, the difference among the three glycinato ligands is that the h glycinate has two oxygens as the ligating atoms *trans* to itself, whereas the two l glycinates have either two nitrogens or one nitrogen and one oxygen at their *trans* positions. From this stereochemical feature, coupled with the above observation, it is expected that the bond

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between cobalt(III) and the h glycinate is stronger than either of the two l glycinate-to-cobalt bonds. This would result in the least electron densities on the methylene carbon of the h glycinate, because the electron-withdrawing effect exerted by the positively charged cobalt ion is transferred more effectively to this carbon than to the other, and hence a high degree of activation of the h hydrogens. Of the two l methylenes, the one which has both oxygen and nitrogen at its *trans* position will be more activated. The effect proposed here explains the three different HD-exchange rates exhibited by three stereochemically different glycinate ligands in *mer*-$[Co(gly)_3]$. We conclude, therefore, that the relative efficiencies in activating the *trans* α-hydrogens of α-aminocarboxylato ligands is greater for oxygen than for nitrogen. This may add to the factors which affect the rate of HD-exchange of α-hydrogens of α-aminocarboxylato ligands. These include solution pH [1b], temperature [1b], overall charge on the complex [1d], valence angle distortion [1a], and the relative efficiencies in stabilizing the carbanion intermediate [1d].

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