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Coordination Catalysis: Inter and Intra-ligand Selectivity in the Activation of Glycine and Ethylenediaminetetracetic Acid Complexes of Cobalt(III)

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The activation of the normally inert methylene group of glycine, caused by the coordination of this aminoacid to cobalt(III), has been reported by several workers [1]. Williams and Busch [2] have demonstrated the increased reactivity of the glycine directly, using p.m.r. spectroscopy to monitor the ^1H–^2H exchange in alkaline deuterium oxide, and in certain cases [3–5] it has been shown that the pro-chiral methylene hydrogens may be distinguished and thus a degree of stereoselectivity introduced into the reaction. Nevertheless, it has been shown that when optically active aminoacids were used as ligands in place of glycine, the rate of ligand racemisation (mutarotation) and exchange at the methine hydrogen are comparable, thus suggesting a carbanion intermediate [6].

In contrast, an entirely different type of stereoselectivity has been reported in the activation of polyaminocarboxylate complexes. Here, Williams and Busch [2] noted that for $[Co^{III}EDTA]^-$, which has two stereochemically distinct pairs of glycinate-like rings [7], Figure 1, the methylene group hydrogens in the out-of-plane rings underwent ^1H–^2H exchange at a much greater rate than did those in the pair of in-plane rings. Interestingly, similar selectivity has also been reported in the acid-catalysed ^1H–^2H exchange [8] where it was suggested that exchange of hydrogens at the in-plane methylene groups was indirect, and occurred only via the scrambling of in-plane and out-of-plane rings. Therefore, we have re-examined the base-catalysed exchange in $[Co^{III}(EDTA)]^-$ and have extended our observations to the activation of glycine in *trans*-trisglycinatocobalt(III), which also has two stereochemically distinct types of ligand ring.

When $[Co^{III}(EDTA)]^-$ was dissolved in ^2H_2O and the solution made alkaline (pD = 8.6), the p.m.r. spectrum, which initially consisted of the two AB patterns of the distinct in-plane and out-of-plane glycinate-type rings overlapping the A_2B_2 pattern of the ethylenediamine back-bone, slowly changed. The downfield AB pattern which has been assigned to the out-of-plane methylenes [2, 8] gradually diminished (the half-life for this reaction at pD 8.6 and 37 °C ≃ 2.5 hr) but the high field AB pattern of the in-plane methylene showed no significant decrease with respect to the ethylenediamine methylene peaks which provide an internal standard.

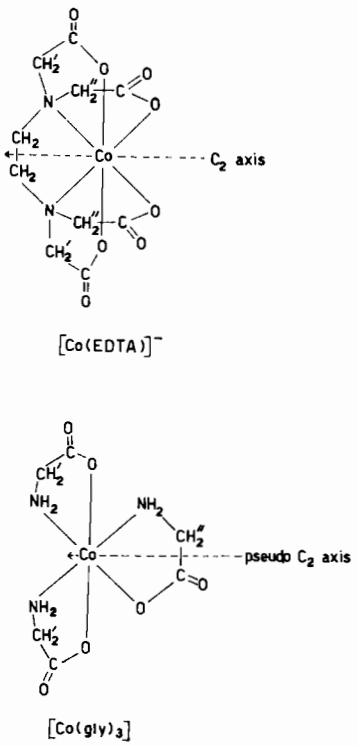

Figure. The structures of $[Co(EDTA)]^-$ and *trans*-$[Co(gly)_3]$ showing the in-plane (H″) and out-of-plane (H′) hydrogen in EDTA and the related (H′) and unique (H″) glycinate hydrogens.

However, in agreement with Williams and Busch [3], it was found that if the sample was heated, or if the concentration of alkali was increased, then the intensity of the signals attributed to the in-plane groups did decrease, though part of the effect could be attributed to decomposition of the complex since the A_2B_2 pattern was also affected. Because of this the collection of accurate kinetic data was not possible, though reasonable estimates of the half-life could be obtained. Thus $t_{1/2}$ for the apparent ^1H–^2H exchange at the in-plane methylenes (pD = 12.5 and 80 °C) was found to be comparable with the half-life for the overall racemisation of the complex *i.e.* in-plane to out-of-plane scrambling, when determined under the same conditions [9].

Therefore, it appears likely that the incorporation of deuterium into the in-plane methylene groups occurs largely by interchange of in-plane and out-of-plane ligand rings, as was found to be the case in the acid-catalysed reaction, and that direct exchange at the in-plane methylenes is insignificant.

In the case of *trans*-$[Co^{III}(gly)_3]$ two types of glycinate rings also occur. Two of the ligands are related by the pseudo two-fold and three-fold axes derived from the D_3 symmetry of the parent tris-bidentate chelate *i.e.* $[Co^{III}(en)_3]^{3+}$, with the third ligand having no such simple relationship to the preceeding pair, Figure 1. This stereochemical relationship is confirmed by the p.m.r. spectrum of the complex. In neutral or acid ^2H_2O the spectrum consists of two broad peaks (whose exact shift was pD dependent) and partially obscured by the $^1HO^2H$ resonance, together with two triplets, J = 8 Hz, relative intensity 2:1 at 3.68 ± 0.02 p.p.m. and 3.42 ± 0.02 p.p.m. downfield from DSS (3-(trimethylsilyl)-1-propanesulphonate). These may be assigned to the NH_2 protons, the pair of similar methylene groups and the unique glycine methylene respectively.

On the addition of base, the broad NH_2 signals disappeared immediately, and the triplets collapsed to two singlets, relative intensity 2:1 at 3.73 ± 0.02 p.p.m. and 3.47 ± 0.02 p.p.m. downfield of DSS. The slight shift may be ascribed to change in solvation and hydrogen bonding of the ligands [10].

The intensity of the two methylene group signals then underwent a further slow decrease which could be reversed by using ^1H_2O as solvent, and was therefore ascribed to ^1H–^2H exchange. Interestingly though, the rates of exchange at the two types of methylene groups were not equivalent. The smaller of the two signals, that at higher field, representing the unique methylene groups disappeared quite rapidly (at pD = 10.7 and 37 °C, $t_{1/2}$ = 60 hr), whilst the larger lower field signal of the two pseudo-equivalent methylenes remained unaffected under these conditions. However, on heating the sample, or raising the pD the larger signal slowly disappeared, but only at a rate which was comparable to the decomposition of the complex and therefore it seems likely that for this pair of methylenes ^1H–^2H exchange occurs only after ligand scrambling.

At first sight this selectivity appears surprising, since with $[Co^{III}(EDTA)]^-$ the selectivity may be ascribed to the different conformations necessarily adopted by the in-plane and out-of-plane rings [2, 8]. Thus, the out-of-plane rings, which are relatively strain free, react directly since they are able to accommodate the negative charge caused by loss of the α-hydrogen, whereas the highly-strained in-plane rings are unable to undergo ^1H–^2H exchange in this fashion since they are unable to adopt a suitable conformation. However, in the case of the trisglycinatocobalt(III) complex it is not obvious how or why such differences in ligand conformation might arise. Nevertheless, the relatively large difference in the chemical shifts between the methylene groups does lead to the conclusion that there are two distinct environments for the glycinate rings. However, since in this case it is the methylene group giving rise to the upfield signal which is the more reactive (unlike the $[Co^{III}(EDTA)]^-$), it is uncertain whether the shift differences arise soley from conformational preferences or from a combination of solvation and hydrogen-bonding effects. Nevertheless, it is significant that the two types of ring have such profoundly different reactivities and these observations reinforce the need for further precise structural data in this area.

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