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Coordination Catalysis: The Metal Ion Induced Activation of Methylene Groups in Ethylenediaminetetracetic Acid

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The activation of the normally inert methylene group of glycine, caused by coordination of this amino acid to a transition metal, was first reported by Akabori,[1] who used Cu^{2+} ion to promote the base-catalysed condensation between acetaldehyde and glycine to give threonine. This substantial increase in the lability of the methylene group hydrogens was later directly confirmed by deuterium labelling experiments[2] and has also been shown to occur in other α-aminocarboxylate complexes of Co^{3+} [2-7] and Pt^{2+}.[8] However, there seems to have been no systematic investigation of which other metals might produce a similar effect. Therefore, we wish to make a preliminary report of a study aimed at resolving this question.

In this work EDTA was used as the ligand, in preference to glycine, since the stability constants of the metal–EDTA complexes are considerably greater than those of the most similar glycinate compounds,[9] thus allowing a wider range of complexes to be examined, without the complications associated with their decomposition in the alkaline media used.

Activation was conveniently detected by following the replacement of hydrogen by deuterium at ligand methylene groups using alkaline D_2O solutions of the metal–EDTA complexes, with exchange measured either jointly by p.m.r. and I.R. spectroscopy for diamagnetic complexes, or by I.R. alone for paramagnetic ones. Where exchange did occur it was readily observed either by disappearance of specific methylene group signals in the p.m.r. spectrum, or by characteristic shifts in the I.R. (the reduction in the C–H stretching frequency from 3100–2900 cm^{-1} to 2150–2050 cm^{-1} which follows deuteration[10] was considered to be diagnostic here, though other changes were also observed).

In every case where exchange was believed to have occurred, the observation was confirmed by carrying out the reverse reaction using alkaline H_2O solution, thereby producing complexes indistinguishable from the starting materials.

TABLE I. The Activation of EDTA by Metal Ions.[a]

Metal ions producing activation	Metal ions not producing activation (A), or having unstable EDTA complexes in alkaline solution (B)
VO^{2+}, Cr^{3+}, Fe^{2+},[b,c] Co^{2+},[c] Co^{3+}, Rh^{3+}, Ni^{2+},[c] Cu^{2+} [c]	A. Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Ti^+, Zn^{2+}, Cd^{2+}, Hg^{2+} B. Be^{2+}, Sn^{2+}, Pb^{2+}, Sb^{3+}, Hg_2^{2+}, Hg^{2+}, Mn^{2+}, Fe^{2+}, Ag^+ Pd^{2+}, Pt^{2+}

[a] Solutions approximately 10^{-1} mol dm^{-3} in both metal and EDTA were kept at pD ≃9 for two weeks at 40 °C.
[b] In order to prevent precipitation 10:1 EDTA:Fe^{2+} was used.
[c] These ions exhibit true catalytic activity in that they were able to induce complete exchange even with a large (10:1) excess of ligand.

From 30 metals tested only 7, all *d*-block transition elements, were found to produce any measurable activation (Table I). No evidence was obtained for activation by any *s* or *p* group metals. In each case, as far as could be determined, the activation was specific, being restricted to those methylene groups adjacent to a carboxylate function. In no case was activation of the methylene groups within the ethylenediamine backbone observed. Indeed, specifically deuterated EDTA, $(HOOCCD_2)_2NCH_2CH_2N(CD_2COOH)_2$ was isolated from several complexes and the pattern of labelling confirmed by separate p.m.r., I.R. and mass spectra. Similar specificity in the pattern of exchange has been noted for polyaminocarboxylate complexes of Co^{3+} examined previously.[3,5]

The origin of this activation may reasonably be ascribed to the electron withdrawing effect of the positively charged metal ion, which, transmitted across the ligand, results in a weakening of the C–H bond. The ability of the metal ion to produce this effect may be tentatively correlated with the degree of covalency in the metal–ligand bond, since those metals which were found to induce activation are just those which have significant covalent component to the metal–ligand bonds, as judged by the I.R. spectra of the complexes.[11]

Clearly, this effect is considerably more general than was hitherto considered to be the case and may be restricted only by the necessity for the complex to be stable in alkaline solution. Such changes in reactivity, in addition to having considerably potential for syntheses, reflect a gap in our knowledge of coordination compounds and further work is now in progress to ascertain what features of the ligand contribute to such effects.

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