ABSTRACT

The synthesis and characterization of several Binuclear complexes of cobalt(III) containing the carbonate ligand both in the terminal and in the bridge position are reported.

The possibility of μ-carbonato complex formation by the direct uptake of CO_2 by the OH groups of μ-hydroxo-dicobalt(III) complexes has been investigated thoroughly. In weakly basic solutions of carbonate the dimeric complex, Di-μ-hydroxo tetrakis (ethylenediamine) dicobalt(III), undergoes complete bridge cleavage giving two moles of the monomer, carbonato bis-ethylene diamine cobalt (III). Detailed kinetic studies reveal that the bridge cleavage proceedes via the D' mechanism.

A single hydroxo bridged intermediate is proposed in which the presence of a HCO_3^- group is found to have a profound labilising effect on the remaining OH bond cleavage. A consecutive reaction treatment was used to resolve the k_{obsd} (which is influenced neither by pH nor by $[CO_3]_T$) into its components k_1 and k_2. At 25°C, I = 0.5M ($LiClO_4$), k_1 = (0.46 ± 0.05) x 10^{-3} sec^{-1} and k_2 = (0.17 ± 0.03) x 10^{-3} sec^{-1}, and its temperature parameters are $\Delta H_1^{\ddagger}$ = 24.1 ± 2.1 kcal mol^{-1}, $\Delta H_2^{\ddagger}$ = 21.7 ± 1.3 kcal mol^{-1} $\Delta S_1^{\ddagger}$ = 6.8 ± 6.7 cal deg^{-1} mol^{-1} and $\Delta S_2^{\ddagger}$ = −3.1 ± 4.4 cal deg^{-1} mol^{-1} over the range 35–45°C.

An extension of this work to other similar complexes like, Di-μ-hydroxo bis-[tetraamminecobalt(III)] and Tris[di-μ-hydroxo tetraamminecobalt(III)] cobalt(III). confirms the conclusion that Binuclear complexes with only two bridging OH groups will undergo complete bridge cleavage in aqueous carbonate.

The reaction of a solution of the μ-amido-μ-hydroxo bis-[tetra amminecobalt(III)] chloride and sodium bicarbonate at 40°C resulted in the isolation of black needle like crystals of μ-amido

μ-hydroxo tetraammine bis(carbonato) dicobalt (III) pentahydrate. This complex has been characterized unambiguously by means of a three-dimensional X-ray diffraction study. The coordinating ligands form nearly regular octahedra about the cobalt atoms with Co(1)–N and Co(1)–O distances of about 1.92 and 1.93Å. A mechanism for the formation of μ-amido-μ-hydroxo tetraammine bis (carbonato) dicobalt(III) has been proposed, on the basis of the collective evidence from kinetics and chemical reactions, in which formation of three different ion pairs, X.OH, $X.CO_3$ and $X.HCO_3$ [X =$(NH_3)_4$ Co μ-$(NH_2,OH)Co(NH_3)_4^{4+}$] plays an important role.

Rate constants k_1 and k_2 for the consecutive reaction leading to the formation of the bis carbonato complex together with its activation parameters are as follows:
At 25°C, pH = 9.03, I = 0.5M ($LiClO_4$), k_1= (0.63 ± 0.10) x 10^{-3} sec^{-1} and k_2 = (0.21 ± 0.07) x 10^{-3} sec^{-1} and its activation parameters are $\Delta H_1^{\ddagger}$ = 26.1 ± 3.5 kcal mol^{-1}, $\Delta H_2^{\ddagger}$ = 23.9 ± 2.0 kcal mol^{-1}, $\Delta S_1^{\ddagger}$ = 14.4 ± 11.8 cal deg^{-1} mol^{-1} and $\Delta S_2^{\ddagger}$ = 5.0 ± 6.7 cal deg^{-1} mol^{-1} over the range 30 – 45°.

The synthesis and kinetics of the acid catalysed decarboxylation of μ-carbonato bis (pentaamminecobalt(III)] ion are reported. In acidic solution the dimer is found to dissociate into $(NH_3)_5CoCO_3H^{2+}$ and $(NH_3)_5CoOH_2^{3+}$. Kinetic studies indicate that the rate determining step involves the decarboxylation of mononuclear bicarbonato complex,

$$(NH_3)_5\ Co\ CO_3\ H^{2+} \longrightarrow (NH_3)_5\ Co\ OH^{2+} + CO_2 .$$

The rate of this reaction was followed by a stopped flow technique over the range $1 < pH < 8$ at 25°, I = 0.5M (phosphate/citrate). The data are satisfactorily explained by a mechanism similar to the acid-catalysed aquation of carbonatopentaammine cobalt (III)

ion, such that

$$k_{obsd} = k_1 (H^+) / [(H^+) + K_1]$$

where k_1 is the rate constant for the reaction given above and K_1 is the acid dissociation constant of $Co(NH_3)_5CO_3H^{2+}$. $k_1 = 1.09\ sec^{-1}$ at 25^o and $K_1 = 4.4 \times 10^{-7}$ M.

An interesting μ-carbonato complex, $[(NH_3)_3Co\mu(OH)_2\mu CO_3Co(NH_3)_3]SO_4 . 5H_2O$, has been prepared and its structure was determined by a three-dimensional X-ray diffraction study. This is the first well charcterised μ-carbonato complex of cobalt (III).

Several other novel μ-carbonato complexes like, μ hydroxo diμ-carbonato bis [triamminecobalt(III)]perchlorate.dihydrate; μ-amidoμ-carbonato bis [tetraamminecobalt(III)]carbonate.nitrate.hexahydrate; μ-amidoμ-carbonato tetrakis [ethylenediamine - cobalt(III)]chloride.tetrahydrate; and μ-amido,μ-carbonatoμ-hydroxo bis [triamminecobalt(III)] iodide have been prepared and characterized by convensional methods. The rather unusual infrared spectrum of all these μ-carbonato complexes have been successfully interpreted.

Finally an electrochemical investigation into the redox properties of a series of Binuclear complexes of cobalt(III) have been carried out. Cyclic voltammetry has been used to demonstrate that these redox couples are quasi-reversible to irreversible. The effect of changing the ligands on the peak potential (E_p) has been examined and a correlation has been obtained between the redox potential and the spectrochemical properties of these complexes.