Concerning the Formation and Acid-Catalyzed Aquation Reactions of Carbonato-, O-Bonded Sulfito- and Nitritopentaamminecobalt(III) Ions

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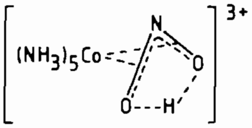
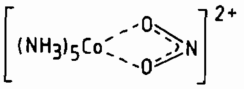
We have read with interest a recent report of a study by Sargeson and co-workers [1] which has enabled them, through use of oxygen-17 NMR, to clarify some details of their preceding findings [2] concerning intramolecular oxygen exchange during linkage isomerization and acid-catalyzed aquation reactions of nitrito-pentaamminecobalt(III). The earlier study employed oxygen-18 labelling, the analytical procedure for which prevented some of the clear-cut conclusions recently reported. It is now [1] obvious that not only does oxygen scrambling occur at a rather slow rate during isomerization (very close to that of the isomerization rate) but the very rapid scrambling previously ascribed [2] to the synthesis process can now be identified with acid-catalyzed aquation.

This latter conclusion is rather surprising, and has not been interpreted mechanistically by Sargeson *et al.* [1], though they provide a plausible interpretation of the scrambling during the spontaneous and base catalyzed isomerization reactions. Typically in molecular eliminations, as we have shown [3–7] in a number of kinetic studies of formation and acid-catalyzed aquation reactions of transition metal carbonato and O-bonded sulfito complexes, the uptake and release reactions are very rapid (stopped-flow time scale), and do not involve metal–oxygen bond cleavage of the parent aquo complex ion. Similar studies [8, 9] of the formation reaction of the $Co(NH_3)_5ONO^{2+}$ species leave some doubt as to the exact nature of the nitrosation reagent as has previously been pointed out several times [10–13]. In contrast, the formation reactions of $Co(NH_3)_5OCO_2^+$ or $Co(NH_3)_5OSO_2^+$ have clearly been shown to proceed via simple CO_2 and SO_2 addition to $Co(NH_3)_5OH^{2+}$, retaining the Co–O bond intact [3, 4, 14–16]. However, the retention of the Co–O bond in the formation of $Co(NH_3)_5ONO^{2+}$ is also further confirmed [17] by recent NMR study [1].

The acid-catalyzed aquation reaction of $Co(NH_3)_5$-ONO^{2+} is very rapid [2, 8] so no simple Co–O bond fission is to be expected [18–20]. The rapid oxygen exchange during the aquation of the nitrito species thus requires an entirely different type of mechanism from that proposed for the carbonato and O-sulfito analogues. The products of the reaction [8] are $Co(NH_3)_5OH_2^{3+}$ and an as yet unidentified acidic form of NO^+. Whatever this mechanism, it cannot involve the same π-bonded intermediate proposed by Sargeson, *et al.* [1] to account for the scrambling during isomerization, since the latter is a slow process. However, a protonated version of this such as:



might be quite unstable and could lead to the observed 50% retention of label in the aquo product. Another pseudo-chelate of the form:



could also account for the 50% label retention during aquation. Clearly, a detailed analysis of this acid-catalyzed aquation process and its reaction products is needed in order to resolve the seemingly anomalous behavior of the nitritopentaamminecobalt(III) complex.

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