Thorium(IV) Complexes of 8-Hydroxyquinoline and Derivatives

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THERE has been considerable speculation concerning the nature of the forces binding the additional molecule of 8-hydroxyquinoline in the orange adduct, $Th(C_9H_6NO)_4,C_9H_6NOH$. It is thought that this molecule is either co-ordinated to the metal ion,[1] or is an unco-ordinated crystal-lattice component.[2]

We now report new evidence that the additional molecule is co-ordinated to the thorium ion, but through the phenolate oxygen only, and that the acidic proton in the complex is located on the nitrogen atom of the monodentate ligand.

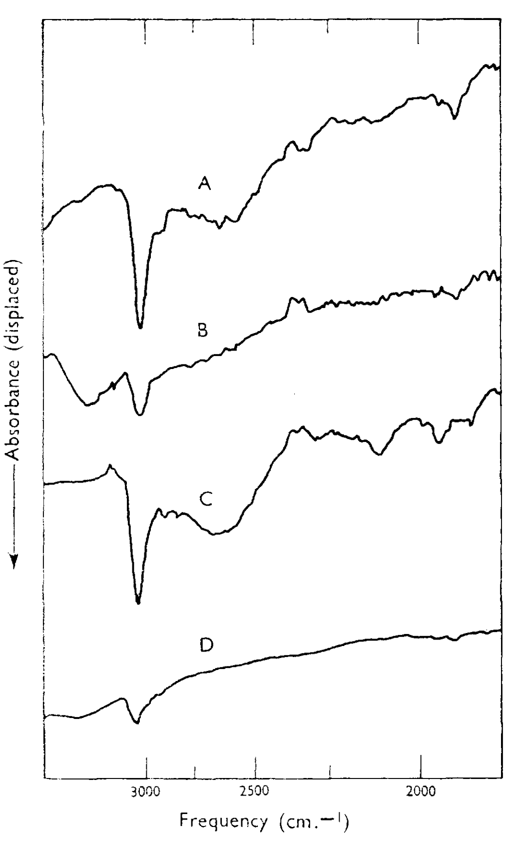

FIGURE. *I.r. spectra of* (A) *anhydrous* $Th(C_9H_6NO)_4$,-C_9H_6NOH, *dried* in vacuo *at* 50° *for* 72 *hr. and prepared for i.r. analyses in a dry-box*; (B) $Th(C_9H_6NO)_4,C_9H_6$-NOH, *dried in air at* 55° *for* 5 *hr.*; (C) *pentakis-8-hydroxy-7-phenyl-quinoline complex, dried* in vacuo *at* 130° *for* 1 *hr.*; (D) $Th(C_9H_6NO)_4$, *prepared thermally from the pentakis-compound. Samples were prepared as mulls in hexachlorobutadiene* (*weak absorption at* 2300 *cm.*$^{-1}$).

On treatment of the 8-hydroxyquinoline adduct with a dichloroethane solution containing a large excess of 8-hydroxy[^{14}C]quinoline, little activity could be detected in the compound after a reasonable reaction time. This result is contrary to that expected for a lattice compound and suggests that the adduct is a molecular entity.

The i.r. spectrum of anhydrous $Th(C_9H_6NO)_4$,-C_9H_6NOH exhibits a broad band centred at about 2625 cm.$^{-1}$ and a very weak band at about 2100 cm.$^{-1}$† (see Figure). These bands are very similar to those observed in the spectrum of $UO_2(C_9H_6NO)_2$,-C_9H_6NOH,[3] and are characteristic of hydrogen-bonded $>NH^+$.[4] They are not present in the spectrum of tetrakis-(8-hydroxyquinolinato)-thorium(IV). For the deuteriated complex, the bands are shifted to about 2050 (ν_H/ν_D = 1·29) and 1510 cm.$^{-1}$ (ν_H/ν_D = 1·37), respectively.

If the pentakis- (*i.e.*, adduct) compound is not carefully dried, a broad band due to absorption by water is observed at 3350 cm.$^{-1}$ (see Figure). This absorption could be mistakenly attributed to the presence in the compound of an 8-hydroxyquinoline molecule in the phenolic form.

The manner in which the proton is hydrogen-bonded cannot be stated, but the following possibilities exist: (i) to the oxygen of the same ligand; (ii) to the oxygen of one of the bidentate ligands bound to the same thorium ion; and (iii) to the oxygen of a ligand bound to a neighbouring thorium ion.

As suggested by the evidence, the co-ordination number of thorium in the complex is nine. Nona-co-ordination has been suggested in other Th^{IV} complexes.[5,6]

The i.r. spectra of the newly prepared pentakis-complexes formed between Th^{IV} and 5-acetyl-, 5-nitro-, 5-phenyl-, 7-methyl-, and 7-phenyl-8-hydroxyquinoline also show the bands characteristic of hydrogen bonded $>NH^+$. These compounds are likely very similar in structure to the 8-hydroxyquinoline complex.

On dissolution of the orange 8-hydroxyquinoline complex in warm dichloroethane, the yellow tetrakis-compound immediately precipitates. When a large excess of 8-hydroxyquinoline is present, however, the tetrakis-compound is not

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† The 2100 cm.$^{-1}$ band is more apparent in the anhydrous 7-phenyl-8-hydroxy-quinoline adduct.

formed and a red solution results. The solution species is probably an ion-pair between the 8-hydroxyquinolinium cation and the pentakis-(8-hydroxyquinolinato)thorium(IV) anion, in which all ligands are bidentate. Abstraction of the proton from the neutral pentakis-compound and the subsequent formation of a ten-co-ordinate species is consistent with the slow rate of ligand exchange reported above. Only a few examples of ten-co-ordinate Th^{IV} complexes have been previously reported.[5,7]

In dimethyl sulphoxide, the orange pentakis-compound yields $Th(C_9H_6NO)_4,2OSMe_2$, the $S{=}O$ stretching vibration of which is displaced to lower frequencies by about 25 cm.$^{-1}$ relative to that of free dimethyl sulphoxide. This small shift in frequency suggests that the dimethyl sulphoxide molecules are held either in the lattice,[8] or are weakly co-ordinated.

The formation of the pentakis-complex is not as sensitive to substitution in the 7-position of the quinoline ring as is the formation of the tris-U^{VI} complex.[3] The normal tetrakis-compound is obtained only on substitution of a bulky group, such as Bu^t. On the other hand, substitution in the 2-position prevents formation of the pentakis-complex. The 2-methyl derivative yields the tetrakis-compound.[9] Our attempts to prepare a complex with the 2-phenyl derivative resulted in precipitation of thorium hydroxide.

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