Uranium(VI) Complexes of 8-Hydroxyquinoline and Derivatives

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THE addition complexes of 8-hydroxyquinoline, $M(C_9H_6NO)_n,C_9H_6NOH$, have aroused considerable interest in regard to the nature of the forces binding the additional reagent molecule. Reports[1] suggesting that the extra molecule is an unco-ordinated crystal-lattice component conflict with those[2,3] suggesting that it is co-ordinated to the metal ion. A recent *X*-ray structure determination[4] has shown that in $UO_2(C_9H_6NO)_2,C_9H_6NOH$, the extra molecule is co-ordinated to the uranium atom but, unlike the two bidentate ligands, through the phenolate oxygen only.

We now report the location of the acidic proton in the U^{VI} complex, a series of new U^{VI} complexes of 8-hydroxyquinoline derivatives, and a method involving [^{14}C]-8-hydroxyquinoline for investigating the nature of other addition complexes.

The infrared spectrum of the 1:3 complex exhibits two bands (an unusually broad band of medium intensity centred at about 2650 cm.$^{-1}$ and a very weak one at 2050 cm.$^{-1}$, see Figure) which are not present in the sodium salt of the complex, the 1 : 2 complex $[UO_2(C_9H_6NO)_2]$ prepared thermally from the 1 : 3 compound, or in free 8-hydroxyquinoline. These bands (somewhat shifted) are present, however, in the hydrochloride salts of 8-hydroxyquinoline, its derivatives, quinoline, and pyridine. In pyridine hydrochloride, the bands (~2500, 2100 cm.$^{-1}$) are due to vibrational modes of $>NH^+$.[5,6] The broad 2500 cm.$^{-1}$ band is a composite band and its displacement from the normal $>NH^+$ stretching frequency (~3200 cm.$^{-1}$) has been attributed to strong hydrogen bonding of the type $^+N–H \cdots Cl$.[5,6] The extreme band-width is probably due to intermolecular interactions.[6] The 2100 cm.$^{-1}$ band may represent a combination band between the scissoring frequency (~1600 cm.$^{-1}$) and a low internal or lattice frequency (~400 cm.$^{-1}$).[6] The presence of the 2600 and 2050 cm.$^{-1}$ bands in the 1 : 3 compound leaves little doubt that the acidic proton is located on the ring nitrogen of the unidentate ligand and is hydrogen-bonded. Examination of Courtauld models (based on the *X*-ray structure) shows that the hydrogen bond must involve the phenolate oxygen of the neighbouring bidentate ligand, to which the proton makes a very close approach. These results confirm the speculation of Hall, Rae, and Waters.[4] Certainly, intermolecular hydrogen-bonding as suggested by Bullwinkel and Noble[2] cannot occur.

TABLE

Uranium(VI) *complexes of* 7-*substituted derivatives of* 8-*hydroxyquinoline*

Ligand	Complex[a]	Method[b]
7-Me	$UO_2(C_{10}H_8NO)_2,H_2O$	Dil. NH_3 or NaOH
	$UO_2(C_{10}H_8NO)_2,NH_3$	Urea hydrolysis
2,7-di-Me	$UO_2(C_{11}H_{10}NO)_2,H_2O$	Dil. NH_3 or NaOH
7-Bu^t	$UO_2(C_{13}H_{14}NO)_2,(H_2O\,?)$	Dil. NH_3
5,7-di-Cl	$UO_2(C_9H_4Cl_2NO)_2,Me_2CO$	Modification of procedure in ref. 1b
5,7-di-Br	$UO_2(C_9H_4Br_2NO)_2,Me_2CO$	

[a] Composition determined by elemental analysis. Presence of H_2O, NH_3, or acetone confirmed by infrared spectroscopy.

[b] In general, the complexes were prepared by the addition of a small excess of the ligand to an acid solution of uranyl nitrate, and adjustment of the final pH to 5–7 with dilute NH_3 or NaOH, or by urea hydrolysis.

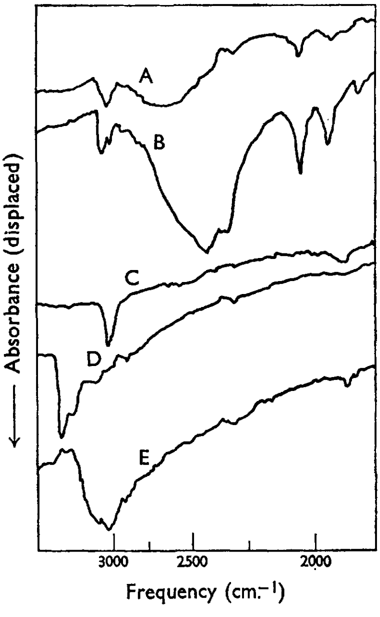

FIGURE. *Infrared spectra of* (A) $UO_2(C_9H_6NO)_2$,-C_9H_6NOH; (B) 8-*methoxyquinoline hydrochloride*; (C) $UO_2(C_9H_6NO)_2$; (D) $UO_2(C_{10}H_8NO)_2$, NH_3; (E) 8-*hydroxyquinoline. Samples were prepared as mulls in hexachlorobutadiene* (*weak absorption at* 2300 *cm.*$^{-1}$).

A survey of about 40 compounds in which $^+N–H \cdots O$ bonding occurs shows that the most probable N–O distance is 2·8—2·9 Å.[7] In the 1 : 3 compound, the N–O distance is 2·71 Å,[4] which suggests a strong hydrogen bond.

A number of 5-substituted derivatives of 8-hydroxyquinoline (Me, Ph, acetyl, Cl, NO_2) also yield 1 : 3 complexes with U^{VI}, and the absorption bands characteristic of the hydrogen-bonded $>NH^+$ are present in the infrared spectra. On the other hand, 7-substituted derivatives yield complexes in which the extra ligand is replaced by H_2O, NH_3, or acetone, depending on the conditions of preparation (Table). The diagnostic $>NH^+$ bands are absent in the spectra. The $UO_2(C_9H_4NOX_2)_2$,acetone complexes (X = Cl, Br) were prepared by slight modification of the method that Moeller and Ramaniah report[1b] as yielding 1 : 3 complexes. Their results appear to be fortuitous, arising because of the insolubility of the dihalogeno-reagents in the solvent used. Using exactly their reported procedure, we found large amounts of co-precipitated reagent in the precipitate.

As revealed by examination of models, the failure of the 7-substituted derivatives to yield 1 : 3 complexes is due to steric repulsion between, (i) the $>NH^+$ proton and the 7-substituent of the neighbouring bidenate ligand, (ii) the α-proton of the monodentate ligand and the 7-substituent of the neighbouring ligand, and (iii) the 7-substituent of the monodentate ligand and the α-proton of the neighbouring ligand. As a result of these repulsions, smaller co-ordinating species (*e.g.*, H_2O, NH_3, acetone) present in solution can successfully replace the extra reagent molecule.

On treatment of $UO_2(C_9H_6ON)_2$ with a dichloroethane solution of [^{14}C]-8-hydroxyquinoline, addition of the extra ligand occurs, the yield approaching 100% under appropriate conditions. When the product of this reaction is thermally re-converted into the 1 : 2 complex, the specific activity of the sublimed 8-hydroxyquinoline is significantly higher than that of the ligands in the residual 1 : 2 complex. This result shows that the additional reagent molecule is not equivalent to the two bidentate ligands. To determine whether the extra molecule is a unidentate ligand or a lattice component, the 1 : 3 compound was treated with a solution of [^{14}C]-8-hydroxyquinoline. After a reasonable reaction time, little activity could be detected in the isolated product. This result is contrary to that expected for a lattice-component structure and indicates that the 1 : 3 compound is a molecular entity.

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