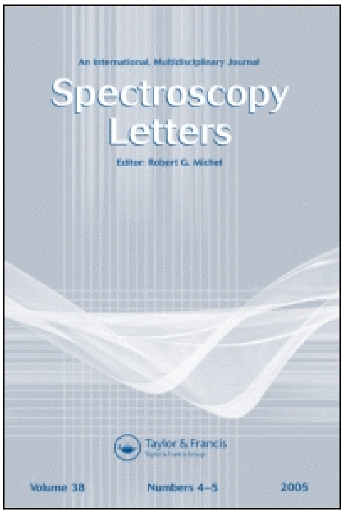

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The Infrared and ^{1}H-NMR Spectra of 8-Hydroxyquinoline Adducts of 8-Hydroxyquinoline Complexes of Dioxouranium(VI), Thorium(IV) and Scandium(III)

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THE INFRARED AND ^{1}H-NMR SPECTRA OF 8-HYDROXYQUINOLINE ADDUCTS OF 8-HYDROXYQUINOLINE COMPLEXES OF DIOXOURANIUM(VI), THORIUM(IV) AND SCANDIUM(III)

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ABSTRACT

The ^{1}H-nmr and infrared spectra of the complexes $[M(ox)_n(Hox)]$ where M = UO_2 (n = 2), Th (n = 4) or Sc (n = 3) and Hox = 8-hydroxyquinoline are discussed. The nmr spectra of the adducts are uninformative with respect to the bonding and structure of these molecules since they dissociate in solution. The solid state ir spectra show that the adducted molecule of 8-hydroxyquinoline is bound to the metal through the phenolic oxygen, the proton forming an intramolecular hydrogen bond between the nitrogen atom of the adducted molecule and the oxygen atom of a neighbouring chelate ring. The mid- and far-ir spectra are reported for the first time and assignments for the δN-H, νM-O and νM-N modes have been made.

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INTRODUCTION

The capacity which certain metal complexes have for adducting an additional molecule of ligand in the protonated form to yield complexes of formula $[ML_n(HL)]$, has elicited much interest. In 1970, one of the present authors drew attention to the fact that the compound once formulated as $H[UO_2(acac)_3]$[1] is correctly formulated $[UO_2(acac)_2(Hacac)]$.[2] 8-Hydroxyquinoline (oxine or Hox) also forms complexes of type $[M(ox)_n(Hox)]$ where M is Sc, Th, Pu or UO_2. The structural and bonding aspects of these complexes have been widely studied[3-15] by uv, ir and nmr spectroscopy and the crystal structure of $[UO_2(ox)_2(Hox)]$ has been determined.[10] The present communication reports on our study of the ^1H-nmr and ir spectra of the complexes $[UO_2(ox)_2(Hox)]$, $[Sc(ox)_3(Hox)]$ and $[Th(ox)_4(Hox)].2H_2O$. The far-ir spectra are reported for the first time.

EXPERIMENTAL

The complexes were prepared by the methods reported in the literature[3-15] Composition and purity were established by microanalysis (C,H,N). The complex $[Sc(ox)_3].H_2O$ (not previously reported) was prepared by the addition of oxine (0.135 g, 0.93 mMol) in 2-propanol (3 ml) to sodium acetate trihydrate (0.127 g, 0.93 mMol) in water (7 ml). Further 2-propanol (2 ml) was added to dissolve the precipitated sodium oxinate and the solution was added to $[Sc(acac)_3]$ (0.105 g, 0.31 mMol) in 2-propanol (7 ml). The solution was gently heated (2 hr) and cooled. The yellow precipitate of $[Sc(ox)_3].H_2O$ was collected by filtration, washed with ether and dried under reduced pressure over silica gel (Found: 65.40% C, 4.10% H, 8.45% N. Calcd. for $[Sc(ox)_3].H_2O$: 65.46% C, 4.07% H, 8.48% N). Nmr spectra were determined on dmso solutions with TMS as reference on a Bruker WH-90 90 Mhz spectrometer. Ir spectra were determined on a Perkin-Elmer 983 spectrophotometer and a Digilab FTS-16B/D interferometer. Samples were in the form of nujol mulls between CsI plates (4000 - 200 cm^{-1}) or polyethylene plates (500 - 50 cm^{-1}). Spectra in the region of nujol absorption were also determined on hexachlorobutadiene mulls and the overlap region (500 - 200 cm^{-1}) was determined on both instruments.

RESULTS AND DISCUSSION

The ir and nmr spectra were compared with those of the 'parent' molecules, $[UO_2(ox)_2]$, $K[UO_2(ox)_3]$, $[Th(ox)_4]$ and $[Sc(ox)_3].H_2O$.

^{1}H-NMR SPECTRA

The nmr spectra of the thorium and uranyl complexes have been discussed by Baker and Sawyer[14] but the spectrum of $[Sc(ox)_3(Hox)]$ has not previously been reported.

Three alternative opinions have existed on the structure of the uranyl complex. Moeller and Ramaniah[6] concluded that the additional ligand is held only by weak lattice forces in the solid state and that it is completely dissociated from $[UO_2(ox)_2]$ in solution while others[8] suggest that the three ligands are equivalently bound to yield the complex $H[UO_2(ox)_3]$. A third opinion is that the third ligand molecule coordinates differently from the other two through the phenolic oxygen,[16] the latter hypothesis being ultimately proven by the structural

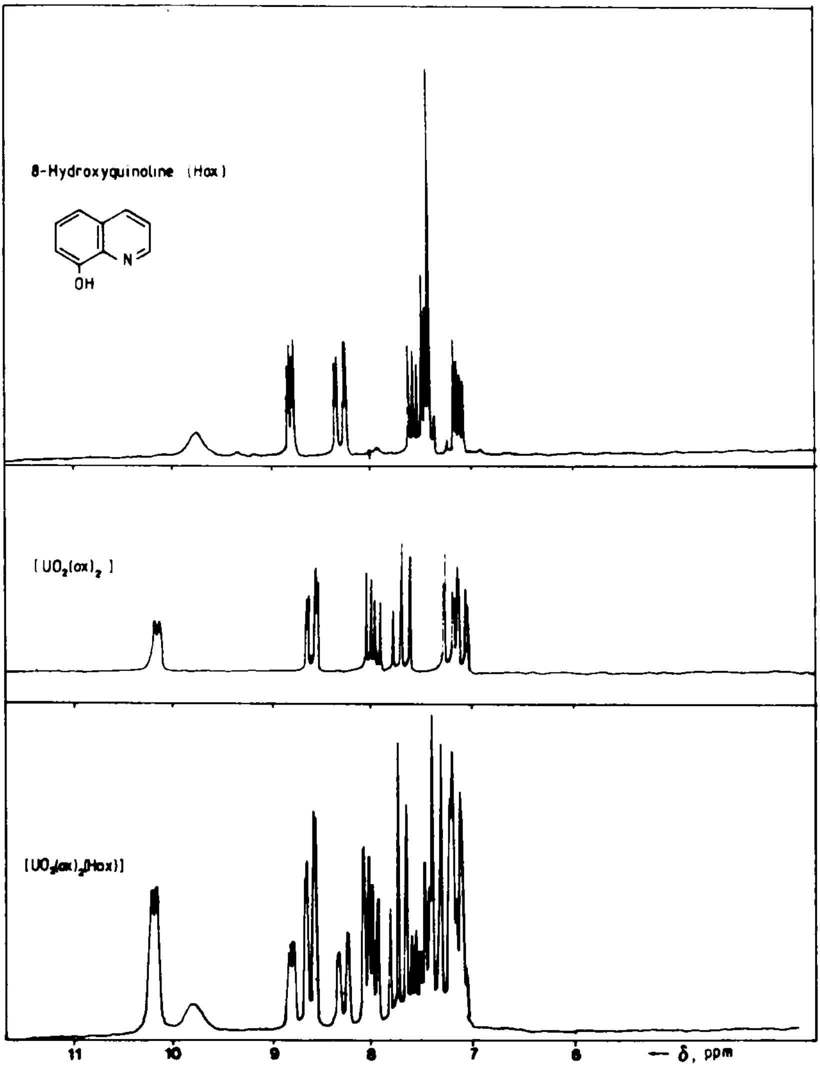

Fig. 1. ^{1}H-nmr spectra of Hox, [UO$_2$(ox)$_2$] and [UO$_2$(ox)$_2$(Hox)].

determination of Hall, Rae and Waters[10] who also established that the proton participated in hydrogen bonding between the uncoordinated nitrogen atom of the third ligand and the oxygen atom of one of the neighbouring ligands.

We find that the ^{1}H-nmr spectra of the complex $[UO_2(ox)_2(Hox)]$ is a precise superimposition of the spectra of $[UO_2(ox)_2]$ and free 8-hydroxyquinoline (Fig. 1). Likewise, the spectrum of $[Th(ox)_4(Hox)]$ amounts to that of Hox superimposed on $[Th(ox)_4]$ and the spectrum of $[Sc(ox)_3(Hox)]$ is the sum of the spectra of $[Sc(ox)_3]$ and Hox. Although it is possible that if the adducts maintained their identity in dmso solution, they could coincidentally give rise to spectra which are identical to the superimposed spectra of the unsolvated complex and free Hox, it is unlikely that this would occur in all three cases examined. We conclude therefore that dissociation is complete in dmso solution.

It is of interest to note that Baker and Sawyer did not extend their spectra to include the OH proton signal. This occurs at 9.8 ppm downfield of TMS in the free ligand and in solutions of the complexes where it is considerably broadened by hydrogen bonding and disappears on addition of D_2O. The spectrum of $[UO_2(ox)_2(Hox)]$ (Fig. 1) is typical of all three adducts.

INFRARED SPECTRA

The Uranyl Complexes

By contrast with the uninformative nature of the ^{1}H-nmr spectra, the infrared spectra provide firm evidence of a uniquely-bound ligand molecule in the uranyl complex $[UO_2(ox)_2(Hox)]$. The 4000 - 2000 cm^{-1} region of this complex

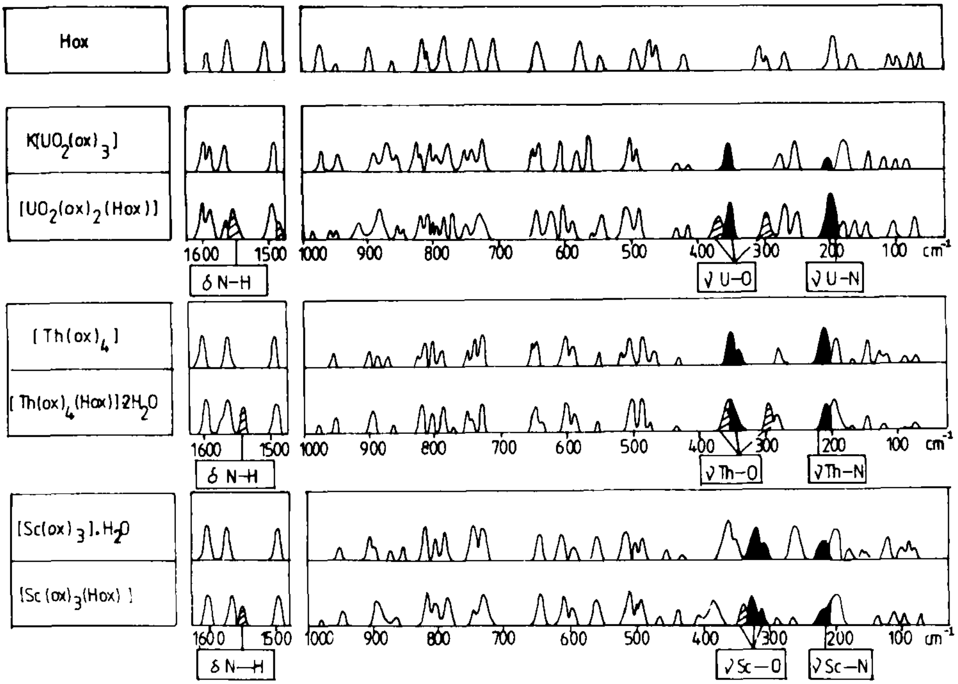

Fig. 2. Infrared spectra (1600 - 1500 and 1000 - 50 cm^{-1}) of the 'normal' and adducted molecules of 8-hydroxyquinoline. Solid bands : νM-N and normal νM-O. Shaded bands : νM-O of adducted Hox and δN-H

has been reported previously,[11] also that of the thorium complex $[Th(ox)_4(Hox)].2H_2O$.[12] In both cases, a broad band near 2650 cm^{-1} and a sharper band near 2050 cm^{-1} occur in the spectra of the oxine adducts, but are absent from the normal molecules $[UO_2(ox)_2]$ and $[Th(ox)_4]$. These bands are attributed to the N - H --- O hydrogen bonds in the adducted molecule. Our present work supports these conclusions with respect to the 4000 - 2000 cm^{-1} regions. However, we find that the spectra below 2000 cm^{-1}, which are reported here for the first time, are more informative with respect to differences between the molecules $[UO_2(ox)_2]$ and $[UO_2(ox)_2(Hox)]$. Even more appropriate is a comparison between the spectra of $K[UO_2(ox)_3]$

and $[UO_2(ox)_2(Hox)]$. Figure 2 depicts these spectra together with that of 8-hydroxyquinoline (Hox) itself. Figure 3 shows tracings of the spectra of $K[UO_2(ox)_3]$ and $[UO_2(ox)_2(Hox)]$.

The most significant differences between the mid- and far-ir spectra of $K[UO_2(ox)_3]$ and $[UO_2(ox)_2(Hox)]$ are as follows:

a) The adduct has strong additional bands at 622, 546, 363 and 296 cm^{-1}. The bands at 622 and 546 cm^{-1} are probably associated with the γ-ring bands of free Hox which occur at 636 and 545 cm^{-1}.

b) The band at 363 cm^{-1} in the spectrum of the adduct occurs in a region which is completely free from any absorptions in the spectrum of Hox. This band is absent from the spectrum of $K[UO_2(ox)_3]$ so it is assigned to the νU-O mode involving the phenolic oxygen of the adducted Hox molecule. The band at 352 cm^{-1} which is present in the spectra of both $K[UO_2(ox)_3]$ and $[UO_2(ox)_2(Hox)]$, is therefore firmly assigned to the νU-O of the 'normal' chelate rings.

c) The band at 296 cm^{-1} is also assigned to νU-O of the adducted molecule being unique to the spectrum of the adduct, although in this case, there is a ligand band near 300 cm^{-1} in the spectrum of free Hox. However this ligand band is found to recur in the spectra of both the normal and adducted molecule near 270 cm^{-1}. Similarly, the ligand band at 265 cm^{-1} in the spectrum of free Hox, recurs in the spectra of the normal and adducted molecules near 250 cm^{-1}.

d) Each of the spectra exhibits a band pair near 200 cm^{-1}. The component of higher frequency is assigned to νU-N while the component of lower frequency is probably associated with the strong ligand absorption at 194 cm^{-1}

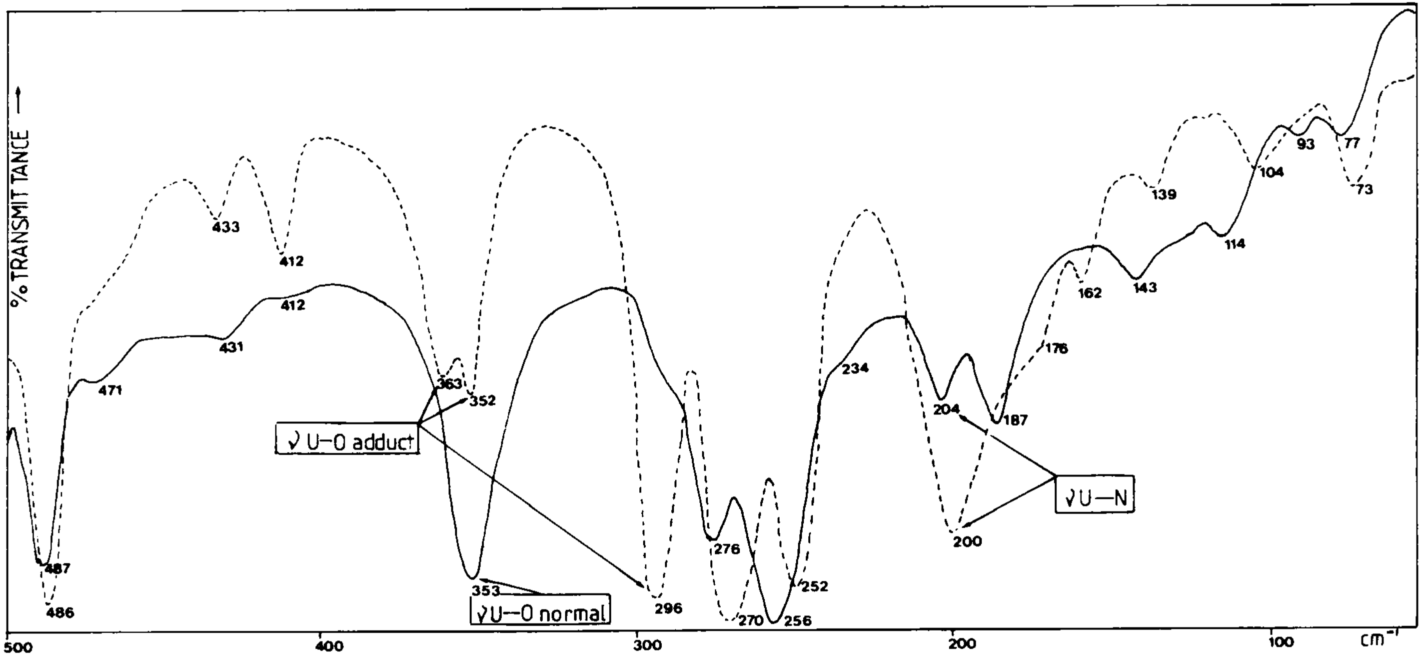

Fig. 3. Far-ir spectra of K[UO$_2$(ox)$_3$] (——) and [UO$_2$(ox)$_2$(Hox)} (- - - - - -).

in the spectrum of free Hox. The νU-N bands have frequencies which are normal for νM-N bands in the metal complexes of heterocyclic nitrogenous bases.[17]

e) In the 1600 - 1500 cm^{-1} region the spectrum of the adducted molecule exhibits an extra strong band at 1560 cm^{-1}. This band is assigned to the N-H bending mode since it is absent from the spectrum of the normal molecule. The δN-H band is also clearly observed in the adducted thorium and scandium complexes.

The Thorium Complexes

The oxine adduct of $[Th(ox)_4]$ occurs as a dihydrate and is therefore correctly formulated $[Th(ox)_4(Hox)].2H_2O$. The most distinctive differences between the spectra of the eight- and nine-coordinate thorium complexes (Fig. 2) occur in the δN-H region where the adducted molecule exhibits a strong additional band at 1545 cm^{-1}, presumably the δN-H mode of the adducted Hox molecule. The other major difference is the additional band at 296 cm^{-1} in the adducted complex which is assigned to νTh-O. There are no obvious differences between the spectra of the normal and adducted complexes in the 350 cm^{-1} region. In this respect, the thorium complexes differ from those of the uranyl ion.

The Scandium Complexes

Scandium(III) has long been known[5] to form the complex $[Sc(ox)_3(Hox)]$ with 8-hydroxyquinoline while the simple complex $[Sc(ox)_3]$ could not be synthesized. We have prepared the latter complex as a monohydrate by ligand exchange between

TABLE 1. Frequency (cm^{-1}) and assignment data for normal and adducted 8-hydroxyquinoline complexes

Complex	δN-H	$\nu M\text{-}O_{normal}$	$\nu M\text{-}O_{adduct}$	νM-N
$[UO_2(ox)_2]$[a]	-	352	-	190
$K[UO_2(ox)_3]$[b]	-	353	-	204
$[UO_2(ox)_2(Hox)]$[c]	1560	352	363,296	200
$[Th(ox)_4$	-	351	-	219
$[Th(ox)_4(Hox)].2H_2O$	1545	355	(355),296	206sh
$[Sc(ox)_3].H_2O$	-	322,310	-	223sh
$[Sc(ox)_3(Hox)]$	1550	327,309	337sh	220sh

[a] νU=O at 916 cm^{-1},
[b] νU=O at 896 cm^{-1},
[c] νU=O at 919 cm^{-1}

oxine and [Sc(acac)$_3$] in 2-propanol and assignments have been made on the basis of deuteration of the ligand and the effects of metal ion substitution.[18] On this basis νSc-O was assigned to the bands at 322 and 310 cm^{-1}, while νSc-N was found at 223 cm^{-1}. The adducted molecule exhibits an additional shoulder at 337 cm^{-1} which is undoubtedly the νSc-O band originating in the bonding of the scandium(III) ion to the phenolic oxygen of the adducted Hox molecule. There is also an additional band at 1550 cm^{-1} which is attributed to the δN-H mode of the adducted Hox. The νSc-N band occurs, as in the spectrum of the normal molecule as a shoulder at 220 cm^{-1} (Fig. 2).

The combined ir results, showing all of the important assignments are assembled in Table 1.

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