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ACETYLACETONE AND β-KETOIMINE SOLVATES OF DIOXOBIS(ACETYLACETONATO)URANIUM(VI)

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WHILE MANY solvates of uranyl acetylacetonate have been described, considerable confusion exists with respect to the composition and structures of certain of these compounds. Thus the acetylacetone adduct of uranyl acetylacetonate (1) usually formulated $UO_2(AA)_2.HAA$ (HAA = acetylacetone) has been reported by Szoke (2) to exist in an alternative form designated $H[UO_2(AA)_3]$ in which three bidentate acetylacetonate ligands are presumed to be in an equivalent environment. Furthermore, while the infrared spectrum (3) and heat of solvation (4) of an ammonia adduct formulated $UO_2(AA)_2.NH_3$ have been reported, analyses were not given and the method of synthesis employed has been shown (5) to yield a product which contains a third molecule of acetylacetone. We report here the results of the application of infrared (i.r.) and proton magnetic resonance (p.m.r.) methods in an attempt to resolve these anomalies. The acetylacetone adduct of uranyl acetylacetonate (found: C, 31.74; H, 3.85; U, 41.80%; calcd. for $C_{15}H_{22}O_8U$: C, 31.71; H, 3.90; U, 41.88%) and the product of the reaction of uranyl nitrate and acetylacetone in the presence of ammonia (found: C, 31.81; H, 3.96; N, 2.52; U, 41.70%; calcd. for $C_{15}H_{23}NO_7U$: C, 31.77; H, 4.08; N, 2.47; U, 41.95%) were prepared by the methods (1, 5) previously described.

The i.r. spectra of anhydrous $UO_2(AA)_2$ and its acetylacetone adduct (Fig. 1a,b) show that the C-O and C-C stretching frequencies of the former (in the range 1500-1620 cm^{-1}) are doubled in the spectrum of the adduct

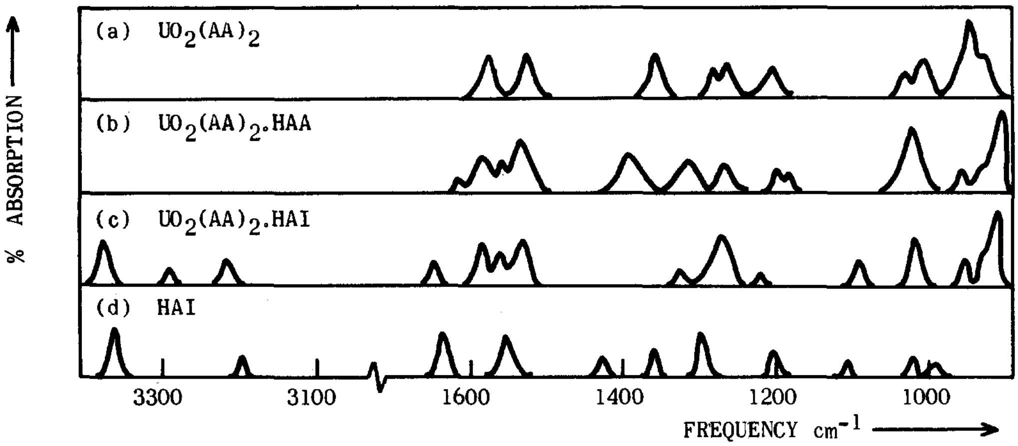


FIGURE 1. I.r. spectra of uranyl complexes (a - c in nujol; d as liquid film).

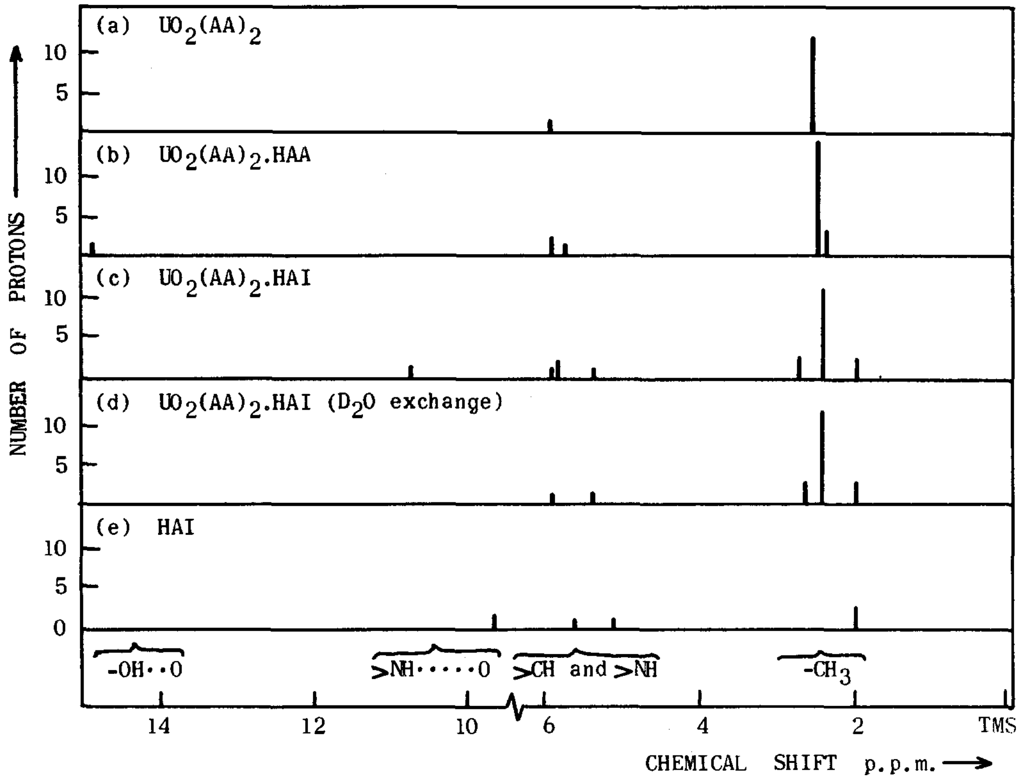
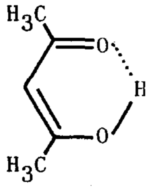
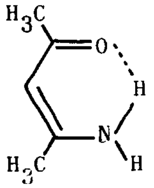


FIGURE 2. P.m.r. spectra of uranyl complexes in deuterochloroform.

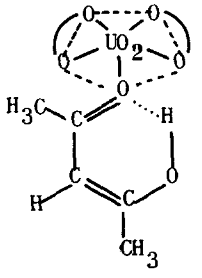
Abbreviations: HAA =

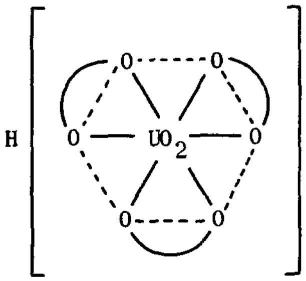


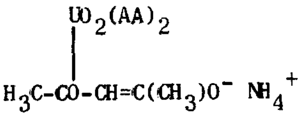
; HAI =



indicating a third, uniquely bonded molecule of acetylacetone. The p.m.r. spectra (Fig. 2a,b) lead to a similar conclusion since the signals arising from the methyl and >CH protons are split and a signal far downfield of TMS is associated with the hydrogen-bonded enolic OH group (it integrates for a single proton and is removed by D_2O exchange). The i.r. spectrum of the adduct in the U=O stretching frequency region exhibits no complexity which could be ascribed to non-linearity of the O=U=O group and the combined evidence suggests that the adduct has the structure (I) analogous to that established (6) by x-ray diffraction for $UO_2(AA)_2.H_2O$.


(I)

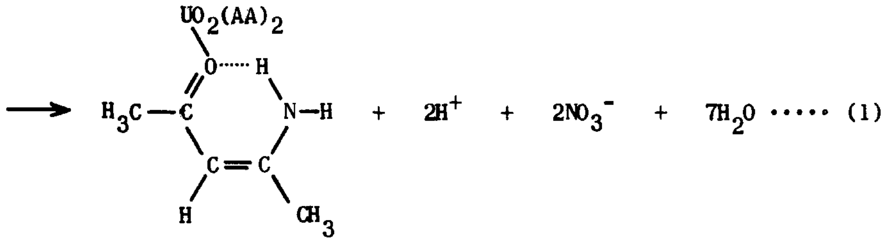

(II)


(III)

$$H_3C\text{-}\underset{\displaystyle |}{\overset{\displaystyle UO_2(AA)_2}{CO}}\text{-}CH{=}C(CH_3)O^- \; NH_4^+$$

Szoke reports (2) the formation of $H[UO_2(AA)_3]$(II) via a two stage synthesis in the first of which ammonia was present for pH control. Since ammonia is known to react with $UO_2(AA)_2$ to form a complex formulated by Hager (5) on the basis of its microanalysis as the ammonium salt (III) we considered it likely that the products of the reactions leading to (II) and (III) are identical. By repeating Hager's synthesis of (III) we obtained a product having an i.r. spectrum identical with that reported by Szoke for (II) including the presence of bands in the N-H stretching region. While the i.r. spectrum of our product (Fig. 1c) could be construed as consistent with the formulation (III), the N-H stretching frequencies are somewhat high for a quaternary ammonium ion. The p.m.r. spectrum (Fig. 2c) on the other hand, confirms that neither (II) nor (III) represents the correct formulation of the product; instead the spectrum is consistent with the β-ketoimine adduct of uranyl acetylacetonate (IV) which probably arises from the reaction:

$$[UO_2(NO_3)_2(H_2O)_2].4H_2O \quad + \quad 3HAA \quad + \quad NH_3$$



(IV)

Thus the spectrum shows the existence of two methyl groups which are in different environments from one another and from the methyl groups in the chelate rings. Furthermore the signal at 10.71 p.p.m. downfield of TMS is ascribed to the hydrogen-bonded N-H proton since it is removed by D_2O exchange, while the spectrum between 5 and 6 p.p.m. indicates the existence of two >CH protons in a similar environment, a third in a unique environment and a free N-H proton. Hager's reported uranium analyses and our own are moreover in better agreement with (IV) than with (III).

The compound formulated in two papers (3, 4) as $UO_2(AA)_2.NH_3$ is almost certainly also correctly formulated as (IV) since it was prepared by Hager's method, analyses were not reported and the published i.r. spectrum conforms to that given by (IV). These considerations lead to the question of whether simple adducts of the type UO_2(β-diketone)$_2$.RNH_2 are capable of being synthesized. All attempts in this laboratory to prepare $UO_2(AA)_2.NH_3$ have failed, (IV) being obtained under a variety of conditions. By contrast, we find that uranyl dibenzoylmethanate yields only the simple adduct $UO_2(DBM)_2.NH_3$. Furthermore, since tertiary aliphatic amines are incapable of forming β-ketoimines, reaction (1) was carried out using *tri*methyl- and triethylamine in place of ammonia. In both cases the simple adducts $UO_2(AA)_2.NR_3$ ($R = CH_3$; C_2H_5) were obtained. Repetition of reaction (1) with a large series of primary and secondary amines which are capable of β-ketoimine formation always yielded products which are the analogues of (IV).

Acknowledgements

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