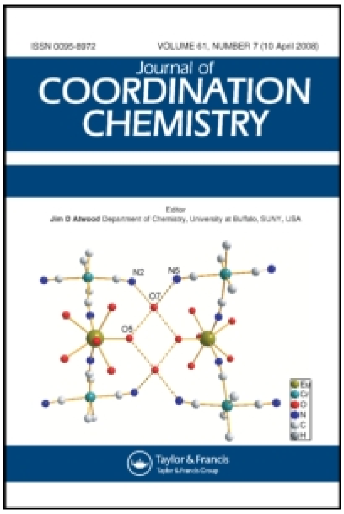

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DIOXOURANIUM(VI) COMPLEXES WITH 2,6-DIFORMYL-4-CHLOROPHENOL

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The ligand H(DIAL) reacts with uranyl acetate to form the complexes $[UO_2(DIAL)_2.H_2O]$, and $[VO_2(DIAL)_2.MeOH]$. Vhermal degradation of the adducts yields two different $[UO_2(DIAL)_2]$ species as intermediates. The compounds have been characterized by infrared and ^1H nmr spectroscopy and by thermogravimetric measurement.

Keywords: Uranium, diformylphenols, complexes, synthesis, adducts

INTRODUCTION

In recent years particular attention has been devoted to compartmental Schiff bases which are able to coordinate one or two metal ions. Such ligands have been generally obtained by condensation of α,ω-diamines with ketophenols and keto-acids.[1-3] An interesting series of Schiff bases has been obtained by reaction of 2,6-diformyl-4-chlorophenol, H(DIAL), with NH_2-$(CH_2)_2$-X-$(CH_2)_2$-NH_2 (where X = NH and S), and some complexes with copper(II), nickel(II) and dioxouranium(VI) have been already reported.[4,5] These complexes were generally prepared by addition of the appropriate amine to a solution containing H(DIAL) and metal salt. We then thought it of interest to investigate the nature of reaction intermediates which can influence the stereochemistry of condensation.

Accordingly, this paper reports a study of the interaction of $UO_2(Ac)_2$ and H(DIAL) in various media.

EXPERIMENTAL

Chemicals

Reagents used were uranyl acetate tetrahydrate (Fluka) and 2,6-diformyl-4-chlorophenol H(DIAL), prepared and purified as given in references 6 and 7. Anhydrous methanol (C. Erba) was prepared by the usual methods.[8] Deuterated solvents (C. Erba) were kept over molecular sieves.

Preparation of the complexes

$[UO_2(DIAL)_2.MeOH]$

A solution of uranyl acetate (0.5 mmol) in anhydrous methanol was added to a solution

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of H(DIAL) (1.0 mmol) in the same solvent (room temperature). A red solid separated immediately, and this was filtered, washed with anhydrous methanol and dried in air. Found: C, 30.3; H, 1.5; Cl, 10.3%. Calcd. for $C_{17}H_{12}Cl_2O_9U$: C, 30.5; H, 1.8; Cl, 10.6%. When dried *in vacuo* at room temperature the compound gradually releases MeOH to give [UO_2(DIAL)$_2$] (B).

[UO_2(DIAL)$_2$.H_2O]

The reaction of uranyl acetate (0.6 mmol) with H(DIAL) (1.2 mmol) in ethanol (*ca* 30 cm^3) yielded a yellowish brown solution. The solvent was partly removed under reduced pressure until the solution volume was *ca* 10 cm^3. Addition of *ca* 10 cm^3 of H_2O yielded the orange compound, which was filtered, washed with small fractions of H_2O-ethanol (1:1 in volume) and dried *in vacuo*. Found: C, 29.9; H, 1.5; Cl, 10.6%. Calcd. for $C_{16}H_{10}Cl_2O_9U$: C, 29.3; H, 1.5; Cl, 10.8%. The compound could be also obtained by treating either [UO_2(DIAL)$_2$.MeOH] or [UO_2(DIAL)$_2$ (A) with H_2O-MeOH (1:1 in volume).

[UO_2(DIAL)$_2$], (B)

This was obtained from [UO_2(DIAL)$_2$.MeOH] either by heating (*ca* 0.1 g) in the thermoanalyzer up to 125°C or by gentle heating (*ca* 60°C) *in vacuo*. Found: C, 30.0; H, 1.2; Cl, 11.0%. Calcd. for $C_{16}H_8Cl_2O_8U$: C, 30.1; H, 1.3; Cl, 11.1%. The anhydrous species (B) transforms easily into (A) if kept under diethylether.

[UO_2(DIAL)$_2$], (A)

This was prepared by thermal decomposition of [UO_2(DIAL)$_2$.H_2O] in air (*ca* 175°C). The same species is formed by washing either [UO_2(DIAL)$_2$.MeOH] or [UO_2(DIAL)$_2$] (B) with diethylether. Found: C, 30.0; H, 1.3; Cl, 11.1%. When kept under H_2O-MeOH (1:1 in volume) the anhydrous (A) species changes to the monohydrate compound.

All the complexes are insoluble in most common solvents but easily soluble in dimethylformamide and dimethylsulfoxide (DMSO).

Measurements

Infrared spectra were obtained using a Perkin Elmen 580 B spectrophotometer (4000-400 cm^{-1}; KBr pellets). ^1H nmr spectra were obtained with a Varian FT 80A spectrometer. Thermogravimetric data (TG and DTA) in air were obtained using a Netzsch STA-429 thermoanalytical instrument (air flux rate, 250 cm^3 min^{-1}; heating rate, 5°C min^{-1}; reference material, neutral Al_2O_3).

RESULT AND DISCUSSION

As is shown in Figure 1, the nature of the compounds isolated by reaction of uranyl acetate and H(DIAL) depends on the solvent. When the reaction is carried out in anhydrous methanol the complex [UO_2(DIAL)$_2$.MeOH] is obtained, whereas in the mixed medium ethanol-H_2O (1:1 by volume) the aqua adduct [UO_2(DIAL)$_2$.H_2O] is isolated. Thermal degradation of both adducts in air yields the anhydrous species UO_2(DIAL)$_2$ in two forms, which have different infrared spectra. The thermograms of [UO_2(DIAL)$_2$.MeOH] (Figure 2a) show the endothermal process to be due to release of the solvent molecule (T, 104°C; weight loss, 4.8%; calcd. weight loss for 1 MeOH, 4.8%) with formation of [UO_2(DIAL)$_2$] (B) which is stable up to 270°C and subsequently

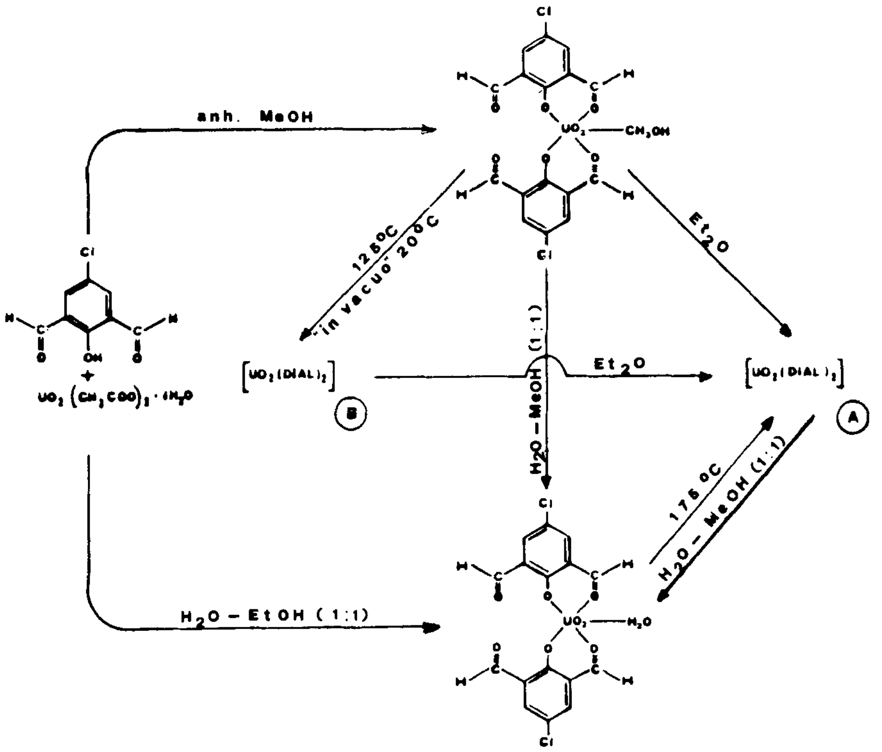

FIGURE 1 Reaction scheme for the complexes.

decomposes (270-450°C temperature interval; weight loss, 53.9%). The complex $[UO_2(DIAL)_2.H_2O]$ has analogous thermal behaviour (Figure 2b), with a dehydration step (T, 170°C; weight loss, 2.7%; calcd. weight loss for 1 H_2O, 2.7%) yielding the species $[UO_2(DIAL)_2]$ (A) and a subsequent decomposition step in the 300-450°C temperature interval (weight loss, 56.4%). The pyrolysis products of uranyl complexes with organic

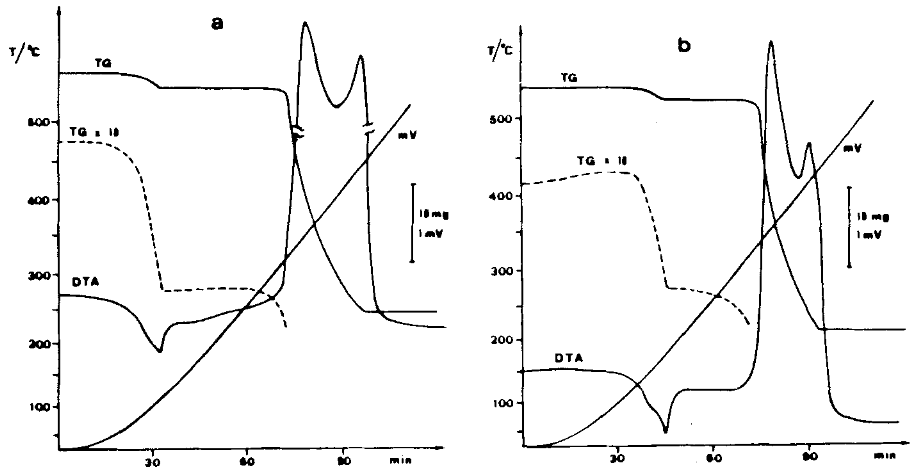

FIGURE 2 Thermograms of $[UO_2(DIAL)_2.MeOH]$ (a, 52.9 mg) and $[UO_2(DIAL)_2.H_2O]$ (c, 51.0 mg).

TABLE I

Infrared (cm^{-1}) and ^{1}H nmr (ppm; T, *ca* 25°C) data.

	Infrared			^{1}H nmr[a]			
	ν(C–O)	ν(C=C)	ν(OUO)	C–H(ring)	C–H(ald)	O–H	other
H(DIAL)	1688 vs 1669 s	1584 m		7.94 [b]7.93 [c]8.01	10.11 10.14 10.16	11.40 11.42 11.50	
[$UO_2(DIAL)_2.CH_3OH$]	1677 m 1627 vs	1539 s	915 m	8.12	10.82		3.39(CH_3) 3.10(OH)[d]
[$UO_2(DIAL)_2.H_2O$]	1676 m 1677 w 1653 m 1635 s	1534 s	923 s	8.08	10.72		2.69(H_2O)
[$UO_2(DIAL)_2$] (B)	1699 m 1683 w 1655 s 1626 vs	1535 s 1527 s	925 m	8.08	10.72		
[$UO_2(DIAL)_2$] (A)	1672 s 1652 vs 1619 vs	1527 vs	924 s	8.10	10.73		

[a]In $CDCl_3$ containing a 10% (by volume) of d_6-DMSO. [b]In $CDCl_3$. [c]In d_6-DMSO. [d]Broad signal.

species as acetate,[9] and formate[10] and glycolate,[11] are generally UO_3 and U_3O_8, whereas the thermograms of these complexes indicate a prevalent formation of UO_2. In fact the calculated weight loss values for UO_2 as final product are 54.8% (MeOH adduct) and 56.0% (H_2O adduct) against the corresponding values 52.5% and 53.6% for formation of UO_3. The thermogravimetric curves of $[UO_2(DIAL)_2]$ (B), prepared from $[UO_2(DIAL)_2.MeOH]$ under reduced pressure at room temperature, show a unique step (320-450°C) with a weight loss of 57.5% against a calculated value for UO_2 as final product of 57.6%. The MeOH and H_2O adducts also have different stability at room temperature. In fact, the MeOH adduct easily releases the solvent molecule either *in vacuo*, yielding $[UO_2(DIAL)_2]$ (B) or under diethylether, yielding $[UO_2(DIAL)_2]$ (A), whereas the H_2O adduct is unchanged under analogous conditions. The presence of free carbonyl groups in both adducts should play an important role in solvent release, because they could replace the H_2O and MeOH molecules giving polymeric species. The formation of labile ethanol adducts has also been observed in uranyl complexes containing uncoordinated thioketo-groups.[12]

The significant infrared absorptions of ligand and complexes are reported in Table I. H(DIAL) has two strong bands at 1688 and 1669 cm^{-1}, due to vibrations of the free C=O group and of the C=O group bonded to hydroxyl by an intramolecular hydrogen bond, respectively. The absorption of the hydrogen bonded aldehyde was found at 1670 cm^{-1} in *o*-formylphenol[13] or in 2-formyl-4-chloro-6-eimetylacetalphenol H(ALAC).[7] The higher energy absorption (1676 cm^{-1}) in the adducts (Figures 3a and 3b) should be of the uncoordinated carbonyl groups, whereas the one around 1630 cm^{-1} should be due to the chelate carbonyl groups, with a contribution of the H_2O bending mode. The uncoordinated carbonyl frequencies are at lower frequencies in the

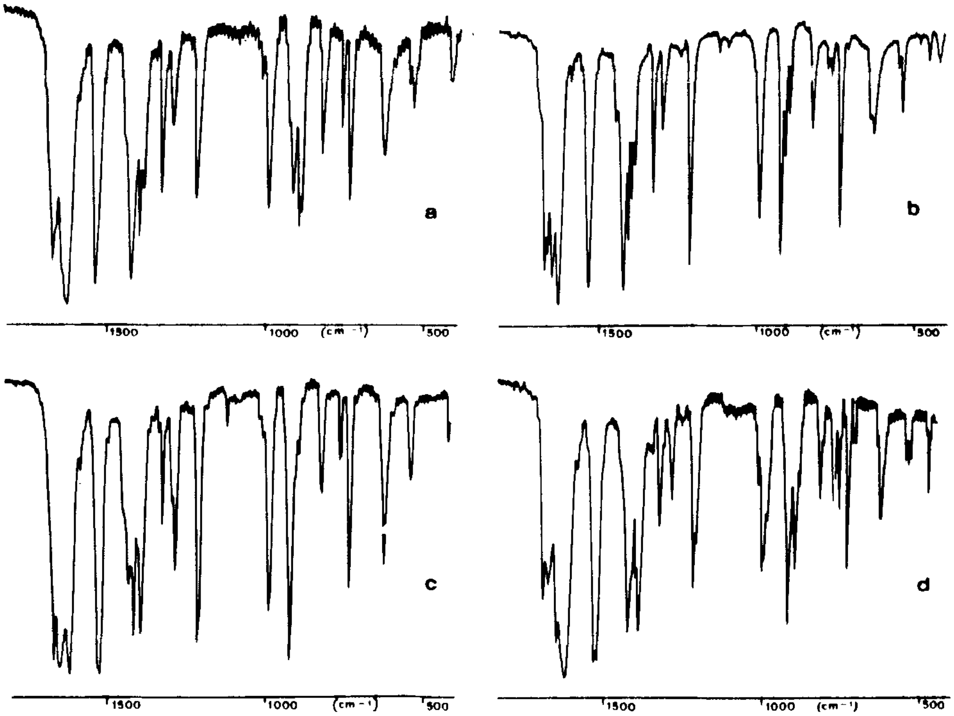

FIGURE 3 Infrared spectra of a): $[UO_2(DIAL)_2.MeOH]$; b): $[UO_2(DIAL)_2.H_2O]$; c): $[UO_2(DIAL)_2]$ (A); d): $[UO_2(DIAL)_2]$ (B).

adducts with respect to the corresponding band in H(DIAL), probably due to intermolecular hydrogen bonds with the H_2O and MeOH molecules. The crystal structure of $[UO_2(ALAC)_2.H_2O]$ shows that the two ligands are symmetric with respect to a twofold axis through the uranium and H_2O oxygen atoms. Moreover the H_2O hydrogens bridge the oxygen atoms of two different acetal groups of a neighbouring molecule.[7] The three bands observed in $[UO_2(DIAL)_2]$ (A) beyond 1600 cm^{-1} (Figure 3c) should be due to either chelating or bridging carbonyl groups, whereas in the anhydrous species (B) the absorption at 1699 cm^{-1} (Figure 3d) could indicate incomplete polymerization. $[UO_2(DIAL)_2]$ (B) should be an intermediate species which, when washed with diethylether, transforms easily into the stable anhydrous form (A). In accordance with the spectra of various *o*-hydroxyaril-carbonyl complexes,[14] the absorption around 1550 cm^{-1} is assigned as $\nu(C{=}C)$, whose splitting in form (B) suggests two different situations in the ligand molecules. The asymmetric stretching mode of the uranyl group can be unambiguously assigned in the complexes (*ca* 924 cm^{-1}) except for $[UO_2(DIAL)_2.MeOH]$, which shows a medium intensity band at 915 cm^{-1} and a doublet at 894 and 885 cm^{-1}. In the anhydrous species (B) one absorption at 903 cm^{-1} is observed, whereas in (A) no band is present in the 880-910 cm^{-1} range. On this basis we assign the absorption at 915 cm^{-1} to the uranyl group stretching frequency in the methanol adduct.

Since the complexes are insoluble in neat chloroform, ^1H nmr measurements were carried out in $CDCl_3$ containing 10% by volume of deuterated DMSO (Table I). The spectrum of H(DIAL) (Figure 4) consists of a sharp singlet for each group of equivalent protons and do not give different signals for the protons of the free or hydrogen bonded carbonyl group. In fact at room temperature intermolecular proton exchange leads to averaging of the signal of the OH proton forming the hydrogen bond. Similar behaviour was observed for the analogous compound 2,6-diformylphenol[15] at room temperature, whereas at −95°C two formyl protons signals were present, the upfield one at 10.0 ppm (belonging to the hydrogen bonded group) and the latter at 10.5 ppm (belonging to the free formyl group). Sharp averaged signals are observed in the spectra of the complexes too. Whereas the ring proton signal affords a small shift, the formyl

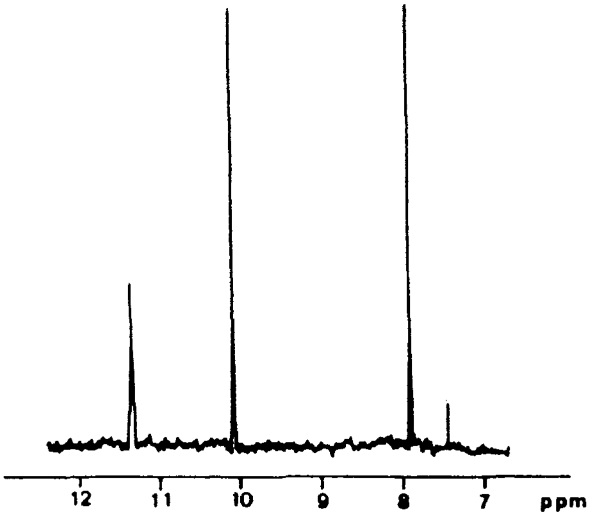

FIGURE 4 ^1H nmr spectrum of H(DIAL) in $CDCl_3$.

proton resonance is downfield (*ca* 0.6 ppm) with respect to the corresponding resonance in H(DIAL). Because the analytical data for the complexes, the ^1H nmr spectra refer to the absence of solvent molecules in the $[UO_2(DIAL)_2]$ species and permit an estimation, by integration, of the amount of MeOH and H_2O in the corresponding adducts. The MeOH and H_2O signals are typical of free species; in fact the strongly coordinating DMSO replaces the weakly bonded solvent molecules in the uranyl coordination sphere.

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