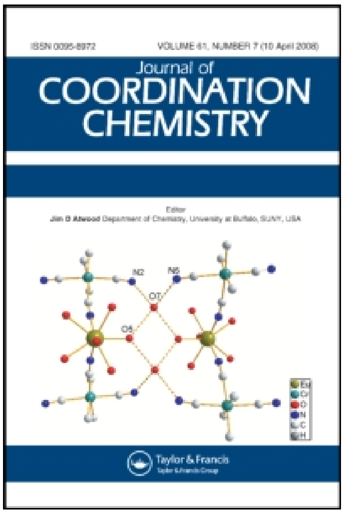

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THE BEHAVIOUR OF FORMYLPHENOL DERIVATIVE COMPLEXES OF URANYL ION IN ALCOHOLIC MEDIA

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The reaction of 2,6-diformyl-4-methylphenol, H(MDA), with boiling ethanol yields the acetalated species 2-diethylacetal-4-methyl-6-formylphenol, H(EAC). Consequently the dioxouranium(VI) complexes $[UO_2(EAC)_2]$ and $[(C_2H_5O)_2CH–OC_6H_2CH_3–HC{=}N(CH_2)]_2XUO_2$ {X=NH, $[UO_2(NEAC)]$; X=S, $[UO_2(SEAC)]$} have been isolated. When condensation is carried out in boiling methanol, the complex $[(CH_3O)_2CH–OC_6H_2CH_3–HC{=}N(CH_2)_2]_2NHUO_2$, $[UO_2(NMAC)]$, is obtained. The compounds bearing the NH group in the chain undergo substitution of one of the acetal groups with the formyl group, yielding the species $[Y_2CH–OC_6H_2CH_3–HC{=}N(CH_2)_2–NH–N(CH_2)_2{=}CH–CH_3C_6H_2O–CHO]\ UO_2$ (Y=OEt and OMe). Ligands and complexes have been characterized by infrared, ^1H and ^{13}C nmr spectroscopy and by thermogravimetric measurements.

Keywords: Formylphenol, uranyl, acetals, complexes, Schiff base

INTRODUCTION

Syntheses of diformylphenol derivatives and of their complexes with metal ions are often performed in alcoholic media. Recently we pointed out the importance of the solvent in such systems,[1–4] due to reaction with formyl groups to give acetalated species.[5] In particular we observed that the dialdehydes 2,6-diformyl-4-chlorophenol, H(DIAL), and 2,6-diformyl-4-methylphenol, H(MDA), react easily with methanol to give the corresponding acetals 2-dimethylacetal-4-chloro-6-formylphenol, H(ALAC), and 2-dimethylacetal-4-methyl-6-formylphenol, H(MAC). Accordingly the reaction of uranyl acetate with diformylphenols in methanol could yield either the simple complexes $[UO_2(DIAL)_2(L)]$ and $[UO_2(MDA)_2(L)]$ or the acetalated species $[UO_2(ALAC)_2(L)]$ and $[UO_2(MAC)_2(L)]$ ($L = H_2O$ or MeOH). The reaction of the preformed uranyl complexes containing acetal groups with the diamines $(H_2N–CH_2–CH_2)_2X$ (X=S and NH) gave the Schiff base derivatives $[(CH_3O)_2CH–OC_6H_2Cl–HC{=}N(CH_2)_2]_2XUO_2$, in which the pentadentate dianionic ligand binds equatorially to the uranyl ion. Acetal intermediates should be expected to form in template syntheses of Schiff base complexes. The reaction of praseodymium(III) nitrate with H(MDA) and triethylenetetramine in methanol, to yield a complex containing a macrocyclic fully condensed dianion, has been reported to give a 1:1 complex

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containing the acetalated anion $\{(CH_3O)_2CH{-}OC_6H_2CH_3{-}HC{=}N{-}[(CH_2)_2NH]_2{-}(CH_2)_2NH_2\}^-$.[6,7] In this case acetalation of one of the H(MDA) formyl groups prevented cyclization and resulted in an open intermediate.

Therefore it was thought worthwhile to examine diformylphenol behaviour in various alcoholic media, in order to ascertain the formation of acetalated species and their stability in the presence of metal ions. Accordingly this paper reports a study of the interaction of 2,6-diformyl-4-methylphenol, H(MDA), of 2-dimethylacetal-4-methyl-6-formylphenol, H(MAC), and of their Schiff base derivatives with ethanol, and of related uranyl complexes.

EXPERIMENTAL

Chemicals

Reagents used were bis(2-aminoethyl)sulphide (K and K) and bis(2-aminoethyl)amine (Schuchardt). The ligands 2,6-diformyl-4-methylphenol, H(MDA), and 2-dimethylacetal-4-methyl-6-formylphenol, H(MAC), and the complexes $[UO_2(MDA)_2(MeOH)]$ and $[UO_2(MAC)_2(MeOH)]$ were prepared as reported in ref. 4. Anhydrous methanol and ethanol were obtained by the usual methods.[8] Deuterated solvents were kept over molecular sieves. Moisture-sensitive compounds were handled in a dry box line filled with dinitrogen.

Preparation of the compounds

$[UO_2(SEAC)]$

An ethanolic solution of bis(2-aminoethyl)sulphide (1.0 mmol in 20 cm^3) was added to a suspension of $[UO_2(MAC)_2(MeOH)]$ in the same solvent (1.0 mmol in 50 cm^3). Under reflux (2 h) a deep red solution was obtained, which on cooling gave red crystals. They were filtered, washed with *n*-pentane and dried *in vacuo*. Yield, 65%. Found: C, 43.80; H, 5.26; N, 3.38%. Calcd. for $C_{30}H_{42}N_2O_8SU$: C, 43.47; H, 5.07; N, 3.38%.

$[UO_2(NEAC)]$ and $[UO_2(NEAF)]$

The complex $[UO_2(NEAC)]$ was prepared by refluxing (2 h) an ethanol suspension containing equimolar amounts of $[UO_2(MAC)_2(MeOH)]$ and bis(2-aminoethyl)amine (1.0 mmol; total volume 70 cm^3). The resulting red solution was filtered and left to stand (12 h). A red microcrystalline solid separated slowly, was filtered, washed with *n*-pentane and dried *in vacuo*. Yield, 55%. Found: C, 44.27; H, 5.36; N, 5.17%. Calcd. for $C_{30}H_{43}N_3O_8U$: C, 44.72, H, 5.34; N, 5.22%.

The compound $[UO_2(NEAF)]$ separated when the mother solution of the $[UO_2(NEAC)]$ preparation was left on standing for several days (4-7d). The yellowish orange crystals were filtered, washed with *n*-pentane and dried *in vacuo*. Yield, 25%. Found: C, 42.61; H, 4.51; N, 5.74%. Calcd. for $C_{26}H_{33}N_3O_7U$: C, 42.33; H, 4.47; N, 5.69%.

$[UO_2(NMAC)]$ and $[UO_2(NMAF)]$

The methanolic suspension containing bis(2-aminoethyl)amine (1.0 mmol) and $[UO_2(MAC)_2(MeOH)]$ (1.0 mmol; total volume 60 cm^3) yielded under reflux a red solution.

The solvent was partially removed under a dinitrogen flux until precipitation of a reddish orange solid, which was filtered, washed with *n*-pentane and dried *in vacuo*. The crude product was treated with methylene chloride, in which [UO_2(NMAC)] is soluble. The filtered red solution, treated quickly with *n*-pentane, separated the pure product. Yield, 50%. Found: C, 40.87; H, 4.18; N, 5.40%. Calcd. for $C_{26}H_{35}N_3O_8U$: C, 41.32; H, 4.63; N, 5.56%.

The pure species [UO_2(NMAF)] separated also as an orange solid when the saturated $CDCl_3$ solutions of [UO_2(NMAC)] used for nmr spectra were left standing for *ca* 10 d. Found: C, 40.33; H, 3.98; N, 5.87%. Calcd. for $C_{24}H_{29}N_3O_7U$: C, 40.62; H, 4.09; N. 5.92%.

[UO_2(NMDA)]

An ethanolic solution of bis(2-aminoethyl)amine (1.0 mmol in 20 cm^3) was added to a suspension of [UO_2(MDA)$_2$(MeOH)] in the same solvent (1.0 mmol in 50 cm^3). The mixture was stirred at room temperature for *ca* 12 h. The heterogeneous reaction yielded a yellowish orange solid, which was washed with ethanol by centrifugation and dried *in vacuo*. Found: C, 39.94; H, 3.47; N, 6.33%. Calcd. for $C_{22}H_{23}N_3O_6U$: C, 39.82; H, 3.47; N, 6.33%.

[UO_2(EAC)$_2$]

The compound was obtained, always impure and containing 10–20% of [UO_2(MDA)$_2$(EtOH)], by refluxing a suspension of either [UO_2(MAC)$_2$(MeOH)] or [UO_2(MDA)$_2$(MeOH)] in anhydrous ethanol (1.0 mmol in 50 cm^3) until complete dissolution to form a red solution (5 h). The solvent was completely removed under reduced pressure (room temperature) to yield a glassy red solid, which was characterized by infrared and nmr spectra. Attempts to recrystallize the compound from ethanol/benzene or methylene chloride/*n*-pentane increased decomposition to [UO_2(MDA)$_2$].

H(EAC)

This was obtained (impure, containing H(MDA)) either by refluxing (2 h) a solution of H(MAC) in anhydrous ethanol under dinitrogen or by prolonged heating (55°C, 7d) of an ethanolic solution of H(MDA). In both cases the solvent was removed under reduced pressure to yield a yellowish oil, which appeared to contain, by proton nmr spectra, either H(EAC) and the fully acetalated species 2,6-diethylacetal-4-methylphenol. When kept under reduced pressure the oil slowly gave white crystals of H(EAC), which were dried on filter paper in order to adsorb the oily fraction and were characterized by infrared and nmr measurements.

Measurements

Infrared spectra were obtained using a Perkin-Elmer 580B spectrophotometer (4000–400 cm^{-1}; KBr pellets). ^1H and ^{13}C nmr spectra were obtained with a Jeol FX 90 Q 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, Al_2O_3).

RESULT AND DISCUSSION

As is shown in Figure 1, both H(MDA) and H(MAC) react with ethanol to form the species 2-diethylacetal-4-methyl-6-formylphenol, H(EAC). Accordingly the uranyl complexes [$UO_2(L)_2(MeOH)$] (L=MDA and MAC) alter to the diethylacetal derivatives in refluxing ethanol. Owing to their facile decomposition, the compounds H(EAC) and [$UO_2(EAC)_2$] were obtained by taking to dryness the appropriate ethanol solution under reduced pressure. The solid samples of both compounds were always impure, containing the corresponding diformylated species, and suggesting a low stability for the diethylacetal group. However, good purity samples of the Schiff base uranyl complexes are easily obtained by condensation of the preformed intermediate [$UO_2(MAC)_2(MeOH)$] with the appropriate diamine in refluxing ethanol. Successive fractions of [UO_2(SEAC)] separated with time from the reaction solution on cooling, whereas the mother solutions of the [UO_2(NEAC)] preparation gave over a few days the less soluble mixed species [UO_2(NEAF)], in which one of the diethylacetal groups is replaced by one formyl group. A parallel behaviour is observed in the synthesis of [UO_2(NMAC)], the crude condensation product containing the corresponding mixed complex [UO_2(NMAF)], easily removed by dichloromethane/*n*-pentane recrystallization. The complexes containing the sulphur atom in the chain seem to be less effected by hydrolysis and decomposition of the acetal groups. The formation of acetalated species is very slow when condensation is performed at room temperature. In fact the reaction of [$UO_2(MDA)_2(MeOH)$] with bis(2-aminoethyl)amine in ethanol at room temperature yields the corresponding non-acetalated Schiff base complex [UO_2(NMDA)].[9]

The infrared spectra of H(EAC) and of the related uranyl complexes (Table I) show two intense broad bands in the 1000–1120 cm^{-1} region, assigned to OEt group stretching. Moreover, the strong H(EAC) absorption at 1669 cm^{-1} is due to the

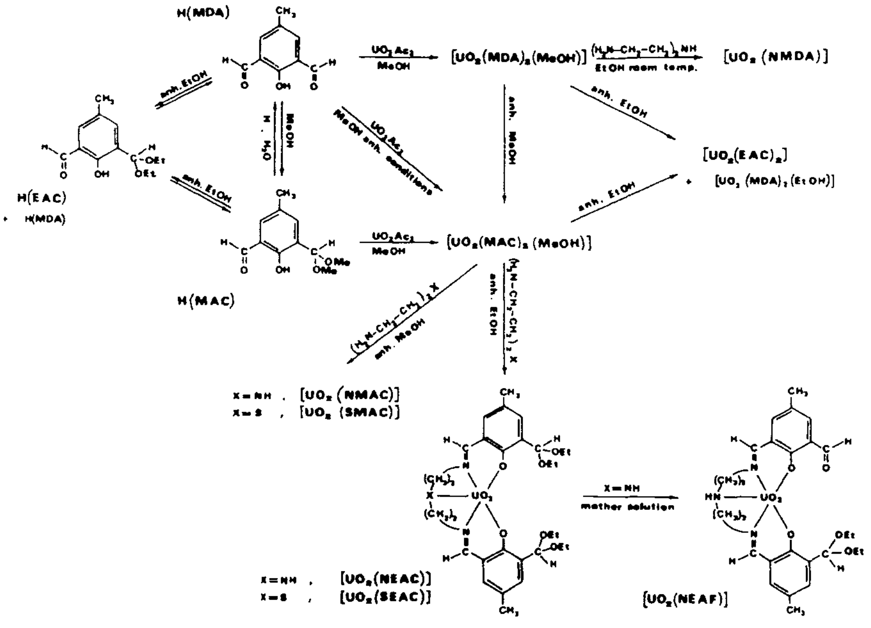

FIGURE 1 Reaction scheme for the complexes.

TABLE I
Infrared data (cm^{-1}) for ligands and complexes

Compound	ν(C−O)	ν(C=N)	ν(C=C)	$\nu(OCH_3)$	$\nu(OCH_2CH_3)$	ν(OUO)	ν(NH)
H(EAC)	1669 vs		1607 s		1120 vs 1061 vs 1010 w		
$[UO_2(EAC)_2]$	1626 vs 1611 vs		1549 vs		1119 s 1042 s 972 w	917 s	
$[UO_2(SEAC)]$		1627 vs	1562 s		1121 s 1065 vs 1012 w	888 s	
$[UO_2(NEAC)]$		1627 vs	1562 s		1108 m 1068 s 1000 w	881 s	3215 m
$[UO_2(NEAF)]$	1673 s	1627 vs	1558 s		1102 m 1069 w 1047 m 1001 w	901 vs	3215 m
$[UO_2(NMAC)]$		1629 vs	1562 s	1115 s 1071 s 1050 m		893 vs	3219 m
$[UO_2(NMAF)]$	1673 s	1627 vs	1560 s	1112 m 1070 w 1048 m		895 vs	3223 m
$[UO_2(NMDA)]$	1677 s	1630 vs	1556 s			898 s	3240 m

stretching of the hydrogen bonded carbonyl group. The corresponding band is present in H(MDA) at 1670 cm^{-1}, the free carbonyl stretching band being observed at higher energy (1685 cm^{-1}).[4] The fully acetalated Schiff base complexes present beyond 1600 cm^{-1} the ν(C=N) absorption at *ca* 1627 cm^{-1}, whereas in either $[UO_2(NMDA)]$ or in the mixed Schiff base complexes containing one formyl group the carbonyl group stretch is around 1675 cm^{-1}. The complexes having a nitrogen atom as a fifth donor show a ν(N–H) absorption at *ca* 3220 cm^{-1}. The uranyl group band, at 917 cm^{-1} in $[UO_2(EAC)_2]$, shifts to lower energy in the Schiff base complexes, as previously observed for dimethylacetal analogues.[3,4]

The thermal degradation of $[UO_2(NMDA)]$ takes place in the 300–560°C temperature interval, the weight loss in the single decomposition step being 56.7% (calculated value for UO_3 as final product 56.9%). The thermograms of $[UO_2(NEAC)]$ and $[UO_2(NEAF)]$ (Figure 2) suggest that the initial degradation process involves the acetal moiety. The first $[UO_2(NEAF)]$ decomposition step (230–280°C) corresponds to a 11.0% weight loss, against a calculated value of 10.0% for the release of the OEt_2 fragment. The second step (290–590°C) concerns the degradaton of the $[UO_2(NMDA)]$ intermediate, the corresponding weight loss being 62.1% (61.2% calculated for UO_3 as final product). The thermal behaviour of $[UO_2(NEAC)]$ parallels that of $[UO_2(NEAF)]$, except for the release of the two OEt_2 fragments in two close successive steps (215–278°C). Only one step was observed for $[UO_2(SEAC)]$ (release of 2 OEt_2 in the 200–245°C interval), which seems to have no tendency to form mixed formyl-acetal intermediates.

The ^1H and ^{13}C nmr spectra of H(EAC) and complexes were generally carried out in deuterated dimethylsulfoxide, in which the Schiff base complexes are also soluble.

TABLE II

^{1}H nmr data (d_6-DMSO; ppm; T *ca* 27°C) for ligands and complexes

Compound	$CH_{(form)}$	$HC=N$	$CH^{a}_{(ring)}$	$CH_{(acet)}$	CH_3	$O-CH_2-CH_3$	$O-CH_2-\mathbf{CH_3}$	$C=NCH_2$	XCH_2	NH
H(EAC)	10.01		7.37, 7.10	5.71	2.29	3.5*br*	1.14			10.8^{b}
	$^{c}9.86$		$7.62, 7.30^{c}$	5.78^{c}	2.34^{c}	$3.70, 3.62^{c}$	1.25^{c}			11.02^{b}
$[UO_2(EAC)_2]$	10.55		7.67, 7.55	6.33	2.36	3.52	1.08			
	10.43^{c}		$7.93, 7.48^{c}$	6.49^{c}	2.42^{c}	$3.6br^{c}$	1.26^{c}			
$[UO_2(SEAC)]$		9.68	7.60, 7.41	6.52	2.39	3.70, 3.66	1.14	4.72^{d}	3.82^{d}	
$[UO_2(NEAC)]$		9.50	7.56, 7.36	6.57	2.35	3.7br	1.15, 1.12	4.6br	4.1, 3.4br	6.8
$[UO_2(NEAF)]$	11.26	9.55	7.55, 7.37	6.41	2.36	3.74, 3.57	1.18, 1.04	4.6br	4.1, 3.5br	7.0
			$7.80, 7.76^{c}$							
$[UO_2[NMAC)]$		9.50	7.54, 7.37	6.46	2.35	$3.42, 3.37^{f}$		4.6br	4.1, 3.5br	6.8
		9.04^{c}	$7.75, 7.14^{c}$	6.63^{c}	2.44^{c}	$3.66, 3.49^{f,c}$		$4.1br^{c}$	^{g}	
$[UO_2(NMAF)]$	11.26	9.51	7.53, 7.38	6.46	2.35	3.42, 3.37		4.6br	4.0, 3.5br	7.0
			$7.77, 7.75^{e}$							
$[UO_2(NMDA)]$	11.03	9.62	7.80, 7.76		2.36			4.7br	4.2, 3.5br	7.2

$^{a}J \approx 2$Hz. ^{b}OH. ^{c}In $CDCl_3$. $^{d}J = 5.3$ Hz. ^{e}Formyl ring protons. $^{f}OCH_3$. ^{g}Superimposed on the OCH_3 signals.

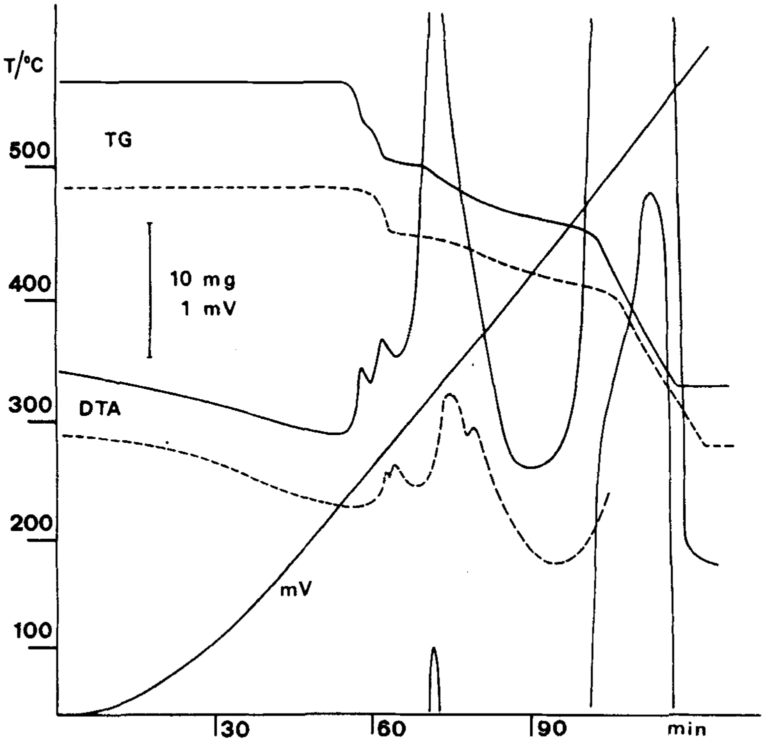

FIGURE 2 Thermogravimetric curves for [UO_2(NEAC)] (34.26 mg; full lines) and [UO_2(NEAF)] (31.09 mg; dotted lines).

In the proton nmr spectra of H(EAC) the CH formyl and acetal singlets are observed at *ca* 10.0 ppm and 5.7 ppm, respectively, whereas the ring protons give rise to doublets owing to reciprocal coupling. The amount of H(MDA), present as an impurity in H(EAC) samples, can be estimated by the integrated areas of the related formyl and phenolato proton signals, those of H(MDA) being of order of 0.3 ppm downfield[4] with respect to the H(EAC) ones. Accordingly the presence of singlets[4] at 7.91 ppm (ring CH) and 10.76 ppm (formyl CH) allows traces of [$UO_2(MDA)_2$(EtOH)] in [$UO_2(EAC)_2$] samples to be detected. As expected, the formyl proton signal is absent in the spectra of [UO_2(SEAC)] and [UO_2(NEAC)], whereas the CH (acetal) proton signal is absent in [UO_2(NMDA)], all complexes showing the nitrilo proton resonance at *ca* 9.6 ppm. The proton nmr spectra suggest that the mixed species [UO_2(NEAF)] and [UO_2(NMAF)] contain two distinct rings, the one bearing the acetal group showing the signals at 7.55 and 7.40 ppm and the other bearing the formyl group giving rise to two very close doublets in the 7.75–7.80 ppm range. Along with the CH acetal signal at 6.4 ppm, the mixed species give a formyl proton singlet at 11.26 ppm, downfield with respect to the corresponding resonance in [UO_2(NMDA)] (11.03 ppm). In all compounds the ring methyl proton singlet is at *ca* 2.4 ppm, whereas the methylene OEt protons give rise generally to broad or doubled signals, suggesting some asymmetry in the diethylacetal moiey. With respect to the methylene chain groups, the proton signal of the CH_2 group bound to the nitrilo group is found at *ca* 4.6 ppm. In [UO_2(SEAC)] the S—CH_2 protons give one signal at 3.82 ppm, whereas the d_6-DMSO spectra of all complexes bearing nitrogen as a chain heteroatom contain

TABLE III

^{13}C nmr data (d_6 − DMSO; ppm; T *ca* 27°C) for ligands and complexes

Compound	$C\mathrm{H}_{(\mathrm{form})}$	$\mathrm{H}C=\mathrm{N}$	$C\mathrm{H}_{(\mathrm{acet})}$	$C\mathrm{H}_3$	$\mathrm{O}-C\mathrm{H}_2-\mathrm{CH}_3$	$\mathrm{O}-\mathrm{CH}_2-C\mathrm{H}_3$	$\mathrm{C}=\mathrm{N}C\mathrm{H}_2$	$\mathrm{X}(C\mathrm{H}_2)$	$C-1$
H(EAC)	196.2		96.2	20.2	61.6	15.0			155.7
$[UO_2(EAC)_2]$[a]	195.6		96.7	19.8	61.4	15.2			168.8
	197.2[b]		97.3	20.2	62.4	15.2			168.7
$[UO_2(SEAC)]$		170.2	96.5	19.7	60.7, 60.5	15.5	62.5	34.6	163.5
$[UO_2(NEAC)]$		169.2	96.5	19.7	60.7, 60.4	15.2	62.2	52.4	164.4
$[UO_2(NEAF)]$	189.9	169.2[c]	96.8	19.7	61.3, 61.2	15.3, 15.2	62.5	52.4	164.0
		170.3[c]		19.4			62.8		168.7[c]
$[UO_2(NMAC)]$	[b]	169.1	98.9	20.2	54.3, 53.3[d]		62.8	52.5	165.4
$[UO_2(NMDA)]$	189.2	169.7[c]		19.3			62.7	52.3	168.7[c]

[a] Weak EtOH signals at 18.5 and 56.0 are observed. [b] In $CDCl_3$. [c] Tentative assignment. [d] OCH_3.

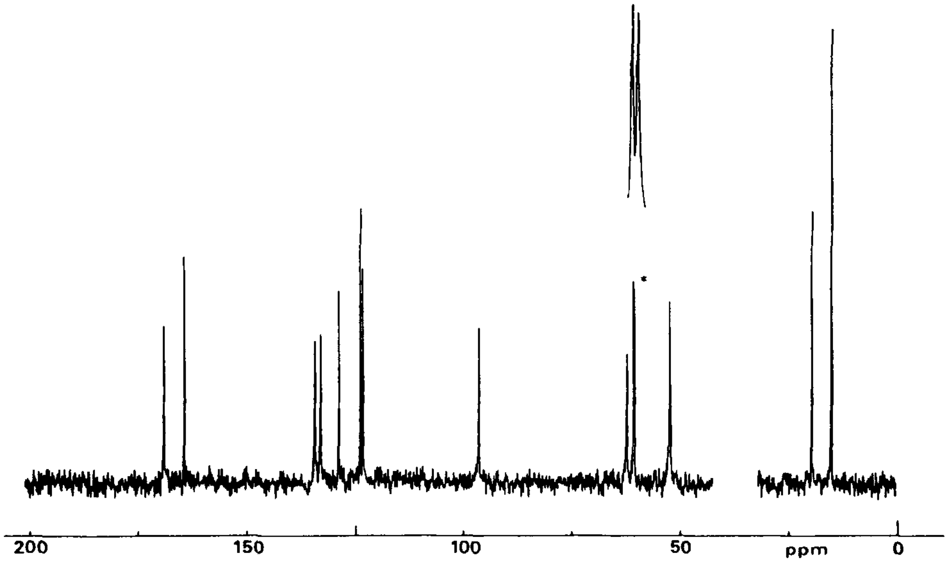

FIGURE 3 ^{13}C nmr spectrum of $[UO_2(NEAC)]$ with protons completely decoupled (solvent d_6 – DMSO).

two broad signals of equal intensity at 4.1 and 3.5 ppm due to the protons of the methylene group bound to the central nitrogen atom. This effect is not observed in the $CDCl_3$ spectrum of $[UO_2(NMAC)]$ because the signals are obscured by the strong OCH_3 resonances, as previously seen for the analogous $[UO_2(NAC)]$ complex, in which the ring methyl is replaced by a chlorine atom.[3] The NH proton gives rise to a broad triplet at *ca* 7.0 ppm.

The ^{13}C nmr spectra (Table III) confirm the complex configurations and shown the CH acetal carbon signal at *ca* 97 ppm and the nitrilo carbon resonance at *ca* 170 ppm. Among the ring carbon atoms, the phenolato C_1 signal shifts downfield *ca* 10 ppm on complexation, whereas the ring CH_3 carbon resonance is at *ca* 20 ppm. All Schiff base complexes show two close signals for the α-carbon atoms of the acetal group, whereas two methyl carbon signals are observed for $[UO_2(NEAF)]$, at 15.3 and 15.2 ppm. Moreover the mixed complex shows two distinct signals for the nitrilo carbon atoms, for the phenolato C–O, for the ring CH_3 and for the nitrilo methylene groups, due to the different substituents, either acetal or formyl, in the ligand rings. As is shown in Figure 3, the ^{13}C nmr spectrum of $[UO_2(NEAC)]$ shows only one signal for the $HN(CH_2)_2$ carbon atoms, and the resonances in the 123–135 ppm range and that at 164.4 ppm belong to the six non-equivalent ring carbon atoms.

As a general remark, either crude or recrystallized samples obtained by reaction of diformylphenols in alcohols should be tested by nmr, infrared spectra being sometimes ambiguous. As an example, the infrared spectrum of $[UO_2(NEAF)]$ could suggest a mixture of $[UO_2(NEAC)]$ and $[UO_2(NMDA)]$, whereas the nmr spectra allow the identification of the mixed species and the exclusion of the possibility of formation of hemiacetals. Moreover, nmr spectra allow the observation of total alkoxy exchange when H(MAC) derivatives are reacted in ethanol. In principle both H(MDA) formyl groups could react with alcohols to give fully acetalated species. Such a reaction should require the presence of dehydrating substances, as observed in salicylaldehyde acetalation.[5,10,11] When salicylaldehyde is refluxed in anhydrous methanol (4 h) and the solution evaporated to dryness under reduced pressure, an oily residue is obtained whose ^1H nmr spectrum in deuterated DMSO suggests partial formation of the dimethylacetal derivative [65%; CH(formyl), 9.43 ppm; CH(acetal), 5.55 ppm; OCH_3, 3.25 ppm]. The fully acetalated H(MDA) derivatives should be unstable under the experimental conditions used by us, one carbonyl group being stabilized by hydrogen bonding with the phenolic OH group, as shown in the x-ray crystal structure of H(ALAC).[2]

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