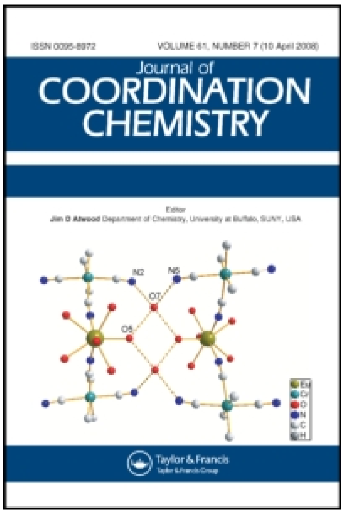

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DIOXOURANIUM(VI) COMPLEXES WITH FORMYLPHENOL DERIVATIVES

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The ligand 2,6-diformyl-4-methylphenol, H(MDA), transforms slowly into 2-dimethylacetal-4-methyl-6-formylphenol, H(MAC), in warm anhydrous methanol. Both ligands react with uranyl acetate to give the adducts $[UO_2(MDA)_2(L)]$ (L=MeOH and EtOH) and $[UO_2(MAC)_2(MeOH)]$, whose thermal degradation yields $[UO_2(MDA)_2]$ as an intermediate. The condensation reaction of $[UO_2(MAC)_2(MeOH)]$ with $(H_2N\text{-}CH_2\text{-}CH_2)_2S$ yields the complex $[(CH_3O)_2CH\text{-}OC_6H_2CH_3\text{-}HC{=}N(CH_2)_2]_2SUO_2$, $[UO_2(SMAC)]$, in which the ligand acts as pentadentate. Ligands and complexes have been characterized by infrared, ^1H and ^{13}C nmr spectroscopy and by thermogravimetric measurements. Their behaviour in MeOH and EtOH solutions is discussed.

INTRODUCTION

Formyl phenols are widely used in the synthesis of multidentate ligands by condensation with polyamines. As a part of a study on template syntheses of dioxouranium(VI) Schiff base complexes,[1–4] we examined the behaviour of formyl phenol precursors in combined reaction with solvent and metal oxoion. We observed that 2,6-diformyl-4-chlorophenol, H(DIAL), transforms easily into 2-dimethylacetal-4-chloro-6-formylphenol, H(ALAC), in refluxing anhydrous methanol.[5] Moreover the complexes $[UO_2(DIAL)_2]$ and $[UO_2(DIAL)_2(L)]$ (L=H_2O and MeOH) form in part $[UO_2(ALAC)_2(H_2O)]$ in methanol.[5,6] In the last compound the uranium atom coordinates four ligand oxygen atoms and one water molecule equatorially, a crystallographic twofold axis passing through the uranium and water oxygen atoms. Because the compound has opportune geometry, it was reacted with the diamines $(H_2N\text{-}CH_2\text{-}CH_2)_2X$ (X=NH and S) to obtain complexes of general formula $[(CH_3O)_2CH\text{-}OC_6H_2Cl\text{-}HC{=}N(CH_2)_2]_2XUO_2$, in which the ligands act as pentadentates.

This paper reports a parallel study of uranyl acetate interactions with 2,6-diformyl-4-methylphenol, H(MDA), and 2-dimethylacetal-4-methyl-6-formylphenol, H(MAC), in anhydrous methanol.

EXPERIMENTAL

Chemicals

Reagents used were uranyl acetate tetrahydrate (Fluka), *p*-cresol (C. Erba), hexamethylenetetramine (C. Erba) and bis(2-aminoethyl)sulphide (K and K). Anhydrous methanol and ethanol were prepared by the usual methods.[8] Deuterated solvents were kept over molecular sieves.

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Preparation of the Compounds

H(MDA). As reported in ref. 9, the solid obtained by grinding hexamethylenetetramine and *p*-cresol (molar ratio 1:1.2) was poured in P_2O_5/H_3PO_4 with stirring (160°C). After addition of H_2O and steam distillation, the crude product was filtered and washed with H_2O. The solid contained unidentified side products (ir: broad absorption at *ca* 1700 cm^{-1}; ^1H nmr: doublets at 5.0 and 3.4 ppm) which were removed by prolonged heating (50°C) under reduced pressure. Yield, 8%. Good purity samples have been obtained by adding 1 M aqueous HCl to a methanol solution of H(MAC). Methanol was removed in a rotavapor to obtain white yellowish needles. M.p. 119–120°C (130–2°C in ref. 9). Found: C, 65.7; H, 5.0%. Calcd. for $C_9H_8O_3$: C, 65.8; H, 4.9%.

H(MAC)

A solution of crude H(MDA) in anhydrous methanol was kept at 55°C for 7 d. The solvent was then removed in a rotavapor to obtain a pale yellow oil which, under reduced pressure, transformed gradually into oily white crystals (12 h, room temperature). A methanol solution of the crude product was treated quickly with abundant H_2O with stirring. The white solid was filtered immediately on a paper filter (which adsorbs the oily fraction) and dried *in vacuo*. Yield, 60%. M.p., 77–8°C. Found: C, 62.7; H, 6.5%. Calcd. for $C_{11}H_{14}O_4$: C, 62.8; H, 6.7%.

[$UO_2(MDA)_2(MeOH)$]

A solution of uranyl acetate (1 mmol) in non-anhydrous methanol was added to a solution of H(MDA) in the same solvent (2 mmol; total volume 20 cm^3; room temperature). A reddish orange solid separated immediately, was washed with methanol by centrifugation and dried *in vacuo* (10 min). Yield, 55%. Found: C, 34.1; H, 2.6%. Calcd. for $C_{19}H_{18}O_9U$: C, 36.3; H, 2.9%. Calcd. for formation of [$UO_2(MDA)_2$] by MeOH release before combustion: C, 34.4; H, 2.2%. When the residual methanolic solution was left standing for some days, [$UO_2(MAC)_2(MeOH)$] separated slowly.

[$UO_2(MDA)_2(EtOH)$]

This was prepared as was the previous complex by carrying out the reaction in anhydrous ethanol (total volume 50 cm^3). Yield, 65%. Found: C, 34.6; H, 2.7%. Calcd. for $C_{20}H_{20}O_9U$: C, 37.4; H, 3.1%. Calcd. for formation of [$UO_2(MDA)_2$] by EtOH release before combustion: C, 33.6; H, 2.2%. It was also the main product in the reaction of uranyl acetate with H(MAC) in non-anhydrous ethanol (molar ratio 1:2).

[$UO_2(MDA)_2$]

This was obtained in quantitative yield when [$UO_2(MDA)_2(MeOH)$] was kept under reduced pressure for a long time (room temperature, 24 h). Moreover it was formed by heating either [$UO_2(MDA)_2(MeOH)$] or [$UO_2(MDA)_2(EtOH)$] in the thermoanalyzer to 120°C and 185°C respectively. Found: C, 36.3; H, 2.6%. Calcd. for $C_{18}H_{14}O_8U$: C, 36.2; H, 2.4%.

[$UO_2(MAC)_2(MeOH)$]

A solution of uranyl acetate (1 mmol) in anhydrous methanol ws added to a solution of H(MAC) in the same solvent (2 mmol; total volume 50 cm^3). After volume reduction to *ca* 15 cm^3 a red solid separated slowly, which was washed with small fractions of cold methanol by centrifugation and dried *in vacuo*. Yield, 60%. Found: C, 38.6; H, 3.9%. Calcd. for $C_{23}H_{30}O_{11}U$: C, 38.8; H, 4.2%. The compound is also obtained when uranyl acetate and H(MDA) are allowed to react in a large volume of anhydrous methanol.

[$UO_2(SMAC)$]

A methanol solution of bis(2-aminoethyl)sulphide (0.5 mmol in 10 cm^3) was added to a [$UO_2(MAC)_2(MeOH)$] suspension in the same solvent (0.5 mmol in 30 cm^3). Under reflux a red solution was obtained which on cooling separated orange crystals of the compound. Yield, 65%. Found: C, 40.2; H, 4.2; N, 3.4%. Calcd. for $C_{26}H_{34}N_2O_8SU$: C, 40.4; H, 4.2; N, 3.4%.

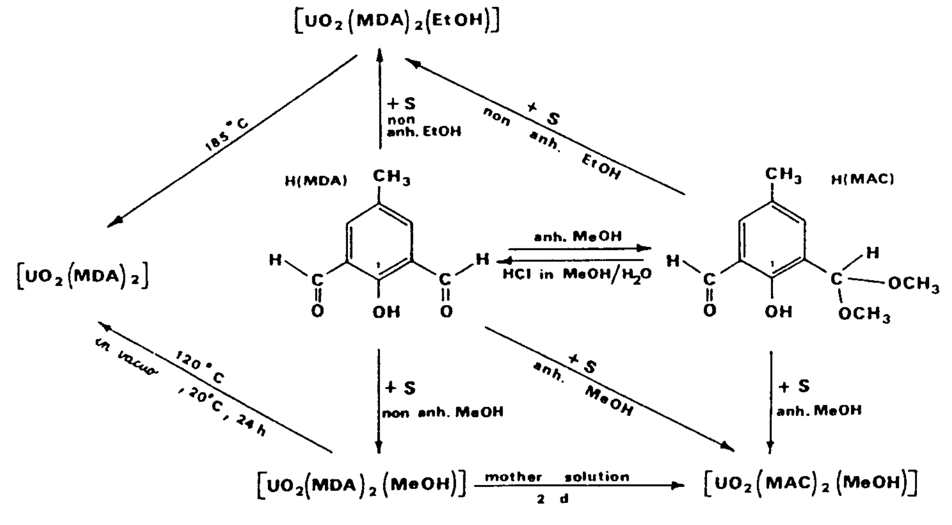
Measurements

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

The preparation of H(MAC) by reaction of H(MDA) with methanol requires anhydrous conditions and moderate heating (55°C). When the reaction is performed in refluxing methanol, as previously seen in the H(DIAL) into H(ALAC) transformation, the species H(MAC) is obtained in a low yield along with probably polymeric oily products and small amounts of H(MDA). Fractional recrystallization does not allow the separation of H(DMA) and H(MAC), owing to their similar solubility in the usual solvents and their insolubility in water. Only one of the H(MDA) formyl groups reacts with methanol, the second one being involved in a hydrogen bond with the phenolic proton. In fact the crystal structure of H(ALAC) shows a contact distance between phenolic hydrogen and formyl oxygen atoms of 1.88 Å.[5]

The infrared spectrum of H(MDA) shows two strong absorptions at 1685 and 1670 cm^{-1}, assigned to the free carbonyl and hydrogen bonded carbonyl groups respectively. As expected, the higher energy band is absent in H(MAC), whose MeO group vibrations are at 1118 and 1049 cm^{-1}. Moreover H(MDA) shows in the 3000 cm^{-1} region only one absorption (2874 cm^{-1}), whereas H(MAC) shows five close bands in the interval 2888–2834 cm^{-1}. The slow transformation of H(MDA) into H(MAC) can be followed by the disappearance of the H(MDA) absorption at 1685 cm^{-1} and the increase of the acetal group bands around 1100 cm^{-1}. As observed for H(DIAL), the ^1H nmr spectrum of H(MDA) is simple and consists of four singlets, one for each group of equivalent protons. Both carbonyl groups give rise to a common CH signal at 10.2 ppm, due to intermolecular OH proton exchange at room temperature. In the spectrum of H(MAC) the CH(acetal) resonance is well upfield (5.6 ppm) with respect to the formyl



S = $UO_2(CH_3COO)_2 \cdot 4H_2O$

FIGURE 1 Reaction scheme for the complexes.

group signal (10.0 ppm). Moreover the ring protons are magnetically non-equivalent, due to the different neighbouring groups. In acid media H(MAC) transforms easily into the corresponding dialdehyde. The reaction can be followed by ^1H nmr measurements of H(MAC) solutions in $CDCl_3$ into which small amounts of gaseous hydrochloric acid are admitted.

The reaction scheme of uranyl acetate with both ligands (Figure 1) points out the influence of the solvent on the reaction product. Anhydrous methanol and long reaction time leads to the formation of $[UO_2(MAC)_2(MeOH)]$, whereas in ethanol both ligands react with the uranyl salt to give $[UO_2(MDA)_2(EtOH)]$. The thermal degradation of $[UO_2(MDA)_2(MeOH)]$ starts at *ca* 50°C (Figure 2) and the first step is due to the release of MeOH (weight loss 4.7% against a calculated value for formation of $[UO_2(MDA)_2]$ of 5.1%); the corresponding endotherm is at 90°C. The decomposition of $[UO_2(MDA)_2]$ starts at 280°C and the process is complete at *ca* 500°C. The experimental weight loss in the second step is 55.7%, against a calculated value for U_3O_8 as final product of 55.3%. The thermal behaviour of $[UO_2(MDA)_2(EtOH)]$ parallels that of the methanol adduct, the ethanol molecule being released in the 60–180°C interval (endothermal peak, 160°C) with a weight loss of 6.9% (calculated value, 7.2%). In the second step the weight loss (230–500°C) is 55.9% against a calculated value to U_3O_8 of 56.3%.

Both methanol and ethanol adducts release slowly the alcohol molecule when kept in air for a long time. The lability of the neutral ligand can explain the analytical data for the adducts (see Experimental Section) which are in accordance with loss of the alcohol molecule before combustion of the samples. As previously seen for $[UO_2(ALAC)_2(H_2O)]$, the first degradation process in $[UO_2(MAC)_2(MeOH)]$ involves the acetal groups (Figure 3). In the 115–260°C temperature interval a weight loss of 17.5% is observed (endothermal peak at 155°C) due to the release of 2 MeO + 2 Me + MeOH (calculated weight loss, 17.2%) to form $[UO_2(MDA)_2]$ as an intermediate.

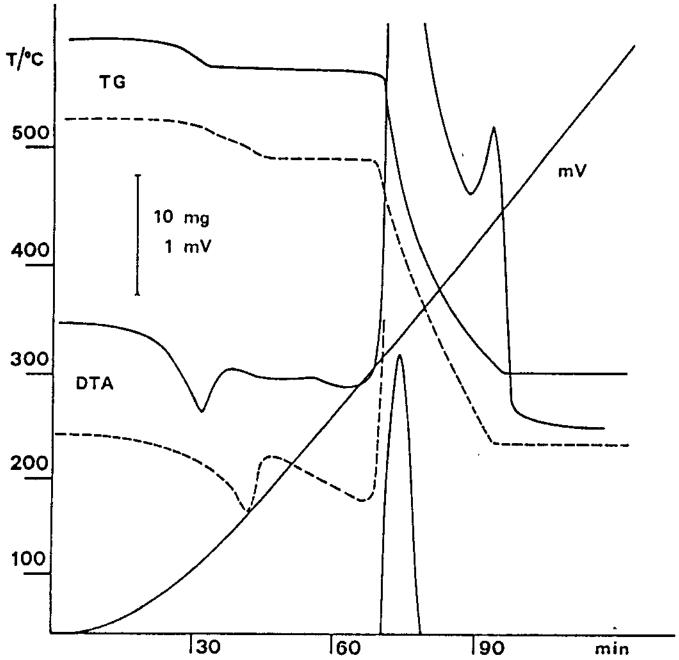


FIGURE 2 Thermograms of $[UO_2(MDA)_2(MeOH)]$ (50.64 mg; full lines) and $[UO_2(MDA)_2(EtOH)]$ (48.87 mg; dotted lines).

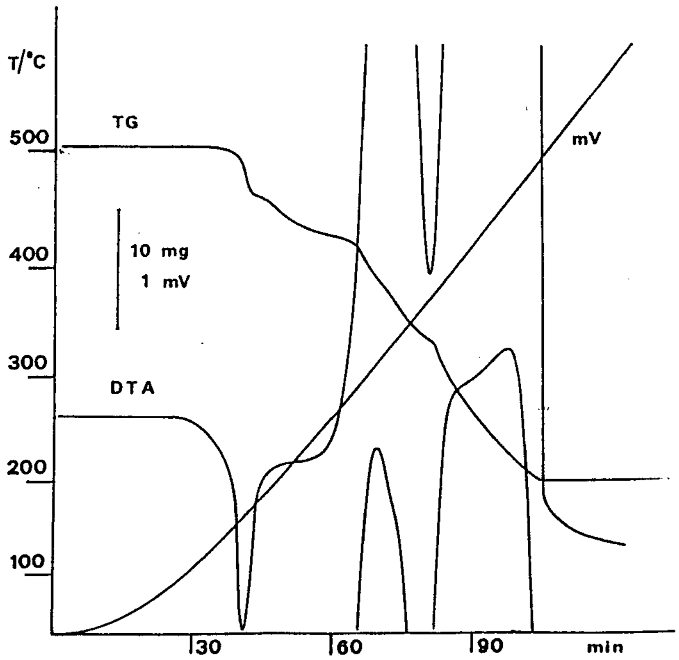


FIGURE 3 Thermograms of $[UO_2(MAC)_2(MeOH)]$ (47.24 mg).

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

Compound	ν(C-O)	ν(C=C)	ν(OCH$_3$)	ν(OUO)
H(MDA)	1685 vs 1670 s	1606 s		
H(MAC)	1659 vs 1627 s	1606 m	1118 vs 1049 vs	
$[UO_2(MDA)_2(MeOH)]$	1662 s 1630 vs 1605 m	1546 s		910 s
$[UO_2(MDA)_2(EtOH)]$	1681 s 1629 vs 1605 s	1542 vs		906 s
$[UO_2(MDA)_2]$	1691 s 1630 vs 1606 s	1542 vs		918 s
$[UO_2(MAC)_2(MeOH)]$	1641 vs 1628 vs	1554 vs	1111 vs 1041 s	914 s
$[UO_2(SMAC)]^a$		1562 s	1118 s 1067 s	893 s

$^a\nu$(C=N), 1626 vs.

TABLE II
^{1}H nmr data (d_6-DMSO; ppm; T *ca* 25°C) for ligands and complexes.

Compound	CH$_{(ring)}$	CH$_{(form)}$	CH$_{(acet)}$	OCH$_3$	CH$_3$	OH	L
H(MDA)	7.87	10.20			2.33	11.39	
	7.75^a	10.20			2.37	11.44	
H(MAC)	7.55, 7.50^b	10.02	5.60	3.30	2.31	10.84	
	7.58, 7.30^{a,b}	9.87	5.66	3.40	2.34	11.08	
$[UO_2(MDA)_2(MeOH)]$	7.88	10.72			2.37		3.16, 4.05^c
$[UO_2(MDA)_2(EtOH)]$	7.91	10.76			2.39		1.07, 3.5, 4.35^d
$[UO_2(MDA)_2]$	7.89	10.72			2.38		
$[UO_2(MAC)_2(MeOH)]$	7.6, 7.5^b	10.55	6.12	3.30	2.35		3.40, 3.24^c
$[UO_2(SMAC)]^e$	7.49, 7.33^b		6.32	3.30–3.23	2.30		

^{a}In CDCl$_3$. ^{b}Broad signals, J *ca* 2.5 Hz. ^{c}MeOH signals. ^{d}EtOH signals. ^{e}SCH$_2$ 3.72 and NCH$_2$ 4.63 ppm (J *ca* 5.3 Hz); H-C=N 9.58 ppm.

The significant infrared absorptions of the complexes are shown in Table I. As expected, the coordinated carbonyl stretching frequency is below the corresponding values in free ligands, the higher energy absorption in the MDA adducts belonging to the free carbonyl group. The uranyl group stretching frequency is as usual around 900 cm^{-1} and in the MAC adduct the acetal MeO stretching bands are unchanged with respect to the free ligand. The ^{1}H nmr spectra (Table II) show that the ring proton signals are scarcely affected by coordination, whereas the resonances of the formyl and acetal CH protons are shifted downfield with respect to the corresponding signals in free ligands. The ^{13}C nmr spectrum of H(MDA) (Table III) shows the formyl carbon resonance at 192 ppm, and four ring carbon signals, the downfield one (161 ppm)

TABLE III

^{13}C nmr data (d_6-DMSO: ppm; T *ca* 25°C) for ligands and complexes.

				Ring				
Compound	OCH_3	$CH_{(form)}$	$CH_{(acet)}$	C-1	C-3, C-5	other	CH_3	L[a]
H(MDA)		192.1		160.2	137.2	129.1,123.1	19.4	
H(MDA)[b]		192.2		161.6	137.8	129.4,122.8	19.9	
H(MAC)	53.4	196.4	98.2	155.9	134.9,132.9	128.2,125.9,121.0	19.7	
H(MAC)[b]	53.8	196.3	98.6	157.1	135.6,133.6	128.7,126.1,120.4	20.3	
$[UO_2(MDA)_2(MeOH)]$		192.4		173.8	137.1	128.3,124.8	19.5	49.8
$[UO_2(MDA)_2(EtOH)]$		192.5		173.8	137.2	128.3,124.8	19.5	56.0,18.5
$[UO_2(MAC)_2(MeOH)]$	53.5	196.0	99.0	169.2	137.2,133.2	130.5,126.2,124.2	19.9	54.1
$[UO_2(DIAL)_2(MeOH)]$		190.8		174.3	133.6	130.2,120.0		53.9
$[UO_2(ALAC)_2(H_2O)]$	53.6	193.6	98.6	170.1	133.7	129.3,127.7,119.1		
$[UO_2(SMAC)]$[c]	52.7		98.2	163.7	134.3,133.2	127.6,125.2,122.9	19.7	

[a] MeOH and EtOH. [b] In $CDCl_3$. [c] SCH_2, 34.6; NCH_2, 62.3; N=CH, 170.2.

belonging to the ring carbon bonded to oxygen (C-1). Because the ring carbon atoms are non-equivalent, six signals are observed in H(MAC), along with the acetal group CH (98 ppm) and OCH_3 (53 ppm) resonances. The spectra of the complexes mirror the general features of the corresponding free ligands, apart from a significant downfield shift of the C-1 ring carbon resonance.

The complex $[UO_2(MAC)_2(MeOH)]$ reacts easily in methanol with the diamine $(H_2N\text{-}CH_2\text{-}CH_2)_2S$ yielding the complex $[(OCH_3)_2CH\text{-}OC_6H_2CH_3\text{-}CH{=}N(CH_2)_2]_2SUO_2$, $[UO_2(SMAC)]$. Its configuration should be similar to that of the parent chloro-derivative,[7] in which the pentadentate ligand binds equatorially to the uranyl ion, the sulphur atom being 1.25 Å out of the coordination plane and the U-S distance being 3.003 Å. Accordingly in the infrared spectrum of the compound the $\nu(C{=}N)$ absorption is at 1626 cm^{-1} and the MeO vibrations occur at 1118 and 1067 cm^{-1} (Table I), whereas the uranyl stretching frequency is below 900 cm^{-1}. The ^1H nmr spectrum of $[UO_2(SMAC)]$ shows the N=CH proton singlet at 9.58 ppm and the SCH_2 proton triplet at 3.72 ppm, upfield with respect to the NCH_2 triplet (4.63 ppm). The acetal group resonances are as in $[UO_2(MAC)_2(MeOH)]$, as are the ring proton signals. As is shown in Figure 4, the ^{13}C nmr spectrum of $[UO_2(SMAC)]$ has two signals at 170.2 and 163.7 ppm, assigned to N=CH and ring C-1 carbon resonances respectively. Along with the six ring carbon signals the spectrum clearly shows the acetal group carbon resonances at 98.2 and 52.7 ppm, and the ethylene group signals at 62.3 and 34.6 ppm. The absence of any formyl carbon signal at *ca* 190 ppm shows that partial hydrolysis of the acetal group does not occur.

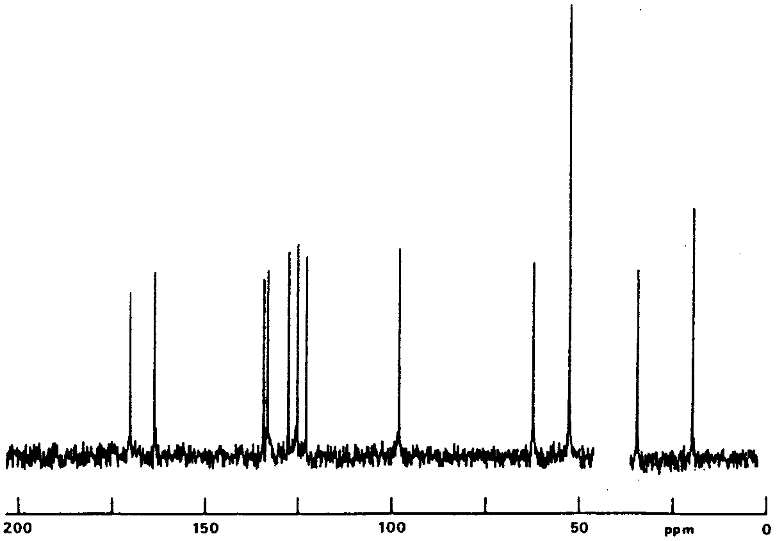


FIGURE 4 ^{13}C nmr spectrum of $[UO_2(SMAC)]$ with protons decoupled (solvent d_6-DMSO).

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