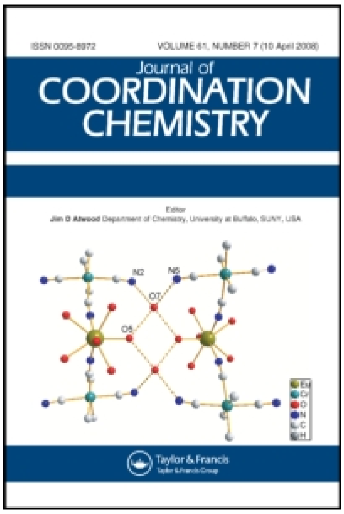

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Complexing Behaviour of Schiff Bases Derived from 3-Acetyl-4-Hydroxy-6-Methyl-2H-Pyran-2-One

Dolores Fregona[a]; Giuseppina Faraglia[a]; Sergio Sitran[b]
[a] Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università, Padova, Italy [b] Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., corso Stati Uniti, Padova, Italy

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COMPLEXING BEHAVIOUR OF SCHIFF BASES DERIVED FROM 3-ACETYL-4-HYDROXY-6-METHYL-2H-PYRAN-2-ONE

DOLORES FREGONA, GIUSEPPINA FARAGLIA

Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università, via Loredan 4, 35100 Padova, Italy

and SERGIO SITRAN*

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., corso Stati Uniti, 35020 Padova, Italy

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By reaction of 3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one (HDh, dehydroacetic acid) with H_2NR (R = Me, *n*Pr or *n*Bu) and $HN(CH_2CH_2NH_2)_2$ the related Schiff bases HDHR and H_2Dh_2T were obtained. All ligands react with uranyl nitrate yielding 1 : 2 adducts. In the uranyl acetate–HDhR systems adduct formation and ligand deprotonation should occur, depending on solvent, reaction time and hydration, whereas H_2Dh_2T undergoes total deprotonation in the presence of uranyl acetate to give $[UO_2(Dh_2T)]$. Ligands and complexes have been characterized by ir and nmr (^1H and ^{13}C) spectroscopy and, in some cases, by thermogravimetric measurements. The action of the amines on the preformed $[UO_2(Dh)_2]$ complex is discussed.

Keywords: Dehydroacetic acid, Schiff bases, uranyl complexes, nmr, synthesis

INTRODUCTION

Recently we have reported lanthanide complexes with Schiff base condensation precursors. In particular, 2,6-diformyl-4-methylphenol (HMDA) and 3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one (HDh, dehydroacetic acid) complexes, of general formula $[Ln(MDA)_3]$ and $[Ln(Dh)_3(L)]$ (L = H_2O or MeOH), were synthesized.[1,2] Moreover, the reaction of lanthanide acetates with either HMDA or HDh yielded the mixed species $[Ln(MDA)_2(O_2CMe)]$ (Ln = La or Ce) and $[Ln(Dh)_2(O_2CMe)(L)_n]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy; L = H_2O or MeOH; n = 1 or 2).[3] Template syntheses of lanthanide Schiff base complexes were attempted by reacting either HMDA or HDh with primary mono- and diamines in the presence of metal salts. In most cases mixtures were obtained, and whose proton nmr spectra suggested the formation of polymeric species through bridging ligands. The product nature seemed also to depend on the anion, the behaviour of lanthanide nitrates being clearly different from that of lanthanide acetates towards the same ligand–amine system. When HDh and primary amines were used, the products contained either dehydroacetato or the related base, the condensation process being partial. We thought it of interest to study the complexing behaviour of HDh and its Schiff bases towards a simpler metal centre, the uranyl ion, which forces the ligand to coordinate

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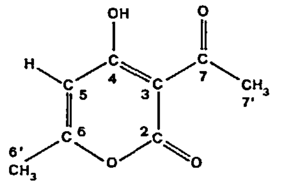
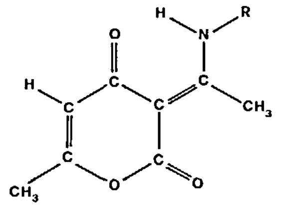
* Author for correspondence.

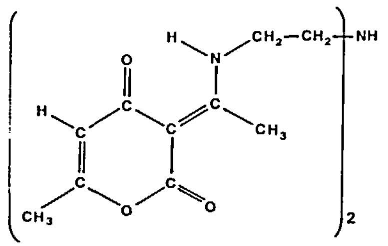
in the equatorial plane of the linear UO_2^{2+} fragment. Previously we performed a detailed study of uranyl complexes with Schiff bases derived from HMDA, with particular attention to the importance of the alcoholic reaction medium on the condensation products.[4,5]

This paper reports the interaction of uranyl acetate and uranyl nitrate with either HDh or Schiff bases obtained by reacting HDh with RNH_2 (R = Me, *n*Pr or *n*Bu) and bis(2-aminoethyl)amine.



HDh





R = CH_3 HDhM
R = CH_2-CH_2-CH_3 HDhP
R = CH_2-CH_2-CH_2-CH_3 HDhB

H_2Dh_2T

EXPERIMENTAL

Chemicals

Dehydroacetic acid ($C_8H_8O_4$, HDh, Fluka), bis(2-aminoethyl)amine (Schuchardt), 1-propanamine and 1-butanamine (Janssen) were used as supplied. Aqueous methanamine (35%) was a C. Erba product. Anhydrous uranyl acetate was prepared by heating the dihydrate salt in a thermobalance crucible to the end of the dehydration endotherm (*ca* 130°C).

Preparation of the Ligands

As a general method, ligands were prepared by condensation of HDh with the appropriate amine in alcoholic medium. In particular, HDhM was obtained by adding aqueous $MeNH_2$ (20 mmol) to an ethanol solution of HDh (20 mmol in 40 cm^3). The resulting yellow solution was evaporated to dryness, to yield a yellow solid, m.p. 119–120°C. The solid could not be purified by sublimation *in vacuo* because the compound easily releases $MeNH_2$ on heating, the sublimed solid being HDh. The reaction of 1-propanamine and HDh at molar ratio of 1 : 1 in ethanol (20 mmol in 40 cm^3) proceeded slowly to form a yellow solution. After refluxing (2h), the solvent was removed to the point of incipient precipitation. The yellow HDhP solid obtained was filtered, washed with *n*-pentane and dried *in vacuo*, m.p. 68–69°C. The ligand HDhB was prepared in ethanol analogously. By evaporating the yellow solution to dryness, a deep yellow oil was obtained, and which was dried by gentle heating under reduced pressure. Sample purity was checked by proton nmr spectroscopy. By reaction of HDh (20 mmol) and bis(2-aminoethyl)amine in methanol (10 mmol in 30 cm^3), the beige solid HDhT separated. It was filtered, washed with a few drops of methanol and dried *in vacuo*, m.p. 142–3°C.

Preparation of the Complexes

By reaction of dihydrated uranyl acetate (0.45 mmol) and HDh in methanol (0.90 mmol in 25 cm^3) a yellow solid separated within 15 min, and which was filtered, washed with methanol and dried *in vacuo* at room temperature. Elemental analyses and thermogravimetric measurements of samples from different preparations supported the formation of either $[UO_2(Dh)_2(H_2O)]$ or $[UO_2(Dh)_2(H_2O)_{1+x}(MeOH)_{1-x}]$ $(x \leqslant 1)$. The weakly bound methanol was easily released either on standing at room temperature (*ca* one month) or by moderate heating *in vacuo*. Anhydrous $[UO_2(Dh)_2]$ was prepared by heating the solvated species in a thermobalance crucible to *ca* 190°C. When anhydrous $[UO_2(Dh)_2]$ was dissolved in dimethyl sulphoxide, a deep yellow solution formed initially, and from which gradually separated the dark yellow $[UO_2(Dh)_2(Me_2SO)]$ complex. The solid was filtered, washed with dichloromethane and *n*-pentane and dried *in vacuo*.

The complex $[UO_2(HDhM)_2(NO_3)_2]$ was prepared by adding solid $UO_2(NO_3)_2 \cdot 4.2H_2O$ (0.4 mmol) to a HDhM solution in methanol (0.8 mmol in 5 cm^3). The amber coloured solution gave with time a pale yellow solid, which was filtered and dried *in vacuo* at room temperature. The yellow HDhP and HDhB analogues were obtained under similar conditions. The reaction of uranyl nitrate with H_2Dh_2T (molar ratio 1 : 1) was heterogeneous (stirring, 2h), owing to the scarce solubility of the ligand. Despite the equimolar amount of H_2Dh_2T, which contains two dehydroacetato moieties, the 1 : 2 pale yellow adduct $[UO_2(H_2Dh_2T)_2](NO_3)_2$ was formed, and which was filtered, washed with methanol and dried *in vacuo*.

Reaction of dihydrated uranyl acetate with H_2Dh_2T in methanol (molar ratio 1 : 1; 0.7 mmol in 10 cm^3) gave the complex $[UO_2(Dh_2T)]$ in quantitative yield. The bright yellow solid was washed with methanol and dried *in vacuo*. The nature of the products obtained by reaction of uranyl acetate with HDhR depended on reaction time, solution concentration and water content of the reaction medium. $[UO_2(HDhM)(O_2CMe)_2]$ was prepared by reaction of equimolar amounts of anhydrous uranyl acetate and HDhM in dichloromethane (0.8 mmol in 7 cm^3). Slow dissolution of the salt caused immediate precipitation of the yellow solid which was dried *in vacuo*. At higher molar ratios, either in dichloromethane or in anhydrous methanol, yellow solutions were obtained which, evaporated nearly to dryness, gave mixtures which contained coordinated acetato and dehydroacetato ions along with free or coordinated HDhM. The amount of dehydroacetato species increased if the starting solutions were left standing overnight. The uranyl acetate–HDhB 1 : 1 or 1 : 2 complexes could not be isolated because of their low melting temperatures. Adduct formation was inferred from nmr spectra of the oils obtained by reaction of anhydrous uranyl acetate (0.4 mmol) and HDhB at the appropriate molar ratio in the minimum amount of anhydrous methanol (1.5 cm^3). The orange red solutions, evaporated to dryness under reduced pressure as quickly as possible, yielded deep orange glassy oils which could not be recrystallized from various solvent mixtures.

They were dissolved in successive amounts of dichloromethane and each fraction was evaporated to dryness in an nmr tube. The nmr spectra of oily samples in deuterated chloroform supported formation of $[UO_2(HDhB)_n(O_2CMe)_2]$ (n = 1 or 2). The 1 : 2 adduct tends to release one ligand molecule in solution, as suggested by nmr spectra at different dilutions. If starting diluted solutions were left standing for several hours, the evaporated residues were mixtures of oils and solids in which ligand, dehydroacetato and free amine were present, whereas residues obtained after standing the solutions for several days yielded, when extracted with dichloromethane/diethylether, yellow solids in which the UO_2^{2+} : Dh : amine molar ratio was nearly 1 : 1 :1. Formation of ligand decomposition products was more facile when hydrated uranyl acetate was used in non-anhydrous solvents.

A parallel investigation of the uranyl acetate–HDhP system supported complexing behaviour similar to that observed for the uranyl acetate–HDhB system.

Measurements

Infrared spectra (4000–400 cm^{-1}; KBr pellets) were obtained using a Perkin Elmer 580B spectrophotometer. Nmr (^1H and ^{13}C) 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, 250 cm^3 min^{-1}; reference material Al_2O_3). Melting points (uncorrected) were measured by a Büchi apparatus.

RESULTS AND DISCUSSION

Dioxouranium bis(dehydroacetate) was prepared by reaction of uranyl acetate dihydrate and dehydroacetic acid in methanol. Depending on dilution and water contents of solutions, the solvated species $[UO_2(Dh)_2(H_2O)]$ or $[UO_2(Dh)_2(H_2O)_{1+x}(MeOH)_{1-x}]$ ($x \leqslant 1$)) were obtained. The sample of Figure 1 contains both water and methanol. The related thermograms present the endotherm due to methanol evolution at 95°C, followed by water release at 195°C. The anhydrous $[UO_2(Dh)_2]$ intermediate decomposes in the 240–410°C temperature interval (exothermic DTA peaks at 325°C and 385°C) with a total weight loss of 57.8% against a calculated value for UO_2 as final product of 58.5%. Anhydrous $[UO_2(Dh)_2]$ dissolves in dimethyl sulphoxide forming an orange solution which slowly separates the dark yellow $[UO_2(Dh)_2(DMSO)]$ adduct (Table I). The species $[UO_2(Dh)_2(H_2O)]$ is scarcely soluble in dimethyl sulphoxide and water–solvent metathesis is incomplete within several days, the solid being a mixture of both solvated species, identified by the different stretching frequencies of the uranyl group near 900 cm^{-1} (Table I). The thermograms of $[UO_2(Dh)_2(DMSO)]$ (Figure 2) do not show any endothermic solvent evolution. Sample degradation starts at 235°C, the weak exotherm at 283°C corresponding to a weight loss of *ca* 14%, higher than that for Me_2SO release (11.4%). Intense pyrolysis causes the exothermic peak at 396°C, the process ending at 450°C with a total weight loss of 59.9% (calculated value for UO_2 as residue, 60.4%). As for the parent lanthanide complexes, the infrared spectra of the uranyl dehydroacetate species (Table I) contain the absorption due to the chelate acetylphenolato group at *ca* 1570 cm^{-1}, whereas the bands at *ca* 1700 and 1487 cm^{-1} are due to ring vibrations. The pyrone carbonyl is uncoordinated, owing to the chelated ligand geometry, and its ν(C=O) band contributes to the broad band at *ca* 1660 cm^{-1}. The proton nmr spectrum (Table II) of hydrated uranyl dehydroacetate in deuterated dimethyl sulphoxide contains the ring signals at 6.37 ppm (CH) and 2.29 ppm (CH_3), nearly unchanged with respect to HDh, whereas the acyl CH_3 singlet undergoes on coordination a downfield shift of the order of 0.45 ppm. The amount of water (3.31 ppm) or of methanol (4.09 and 3.18 ppm) can be estimated from integrated areas of the related signals. Along with the dehydroacetato singlets, the $[UO_2(Dh)_2(Me_2SO)]$ spectrum in deuterated chloroform shows the Me_2SO proton signal at 3.07 ppm, downfield with respect to free Me_2SO (2.5 ppm).

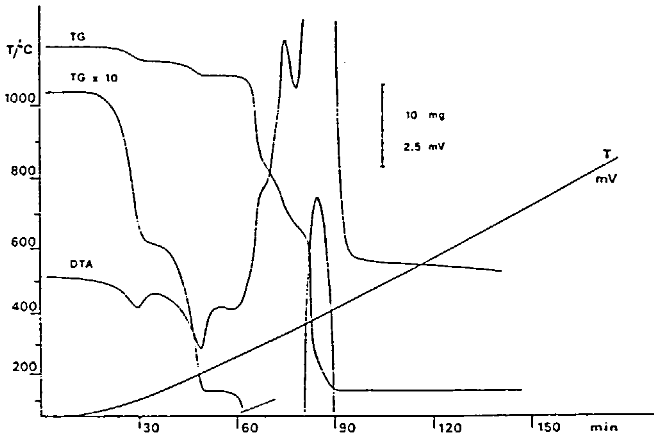


FIGURE 1 Thermograms of $[UO_2(Dh)_2(H_2O)_{1+x}(MeOH)_{1-x}]$ ($x \leq 1$) (74.03 mg).

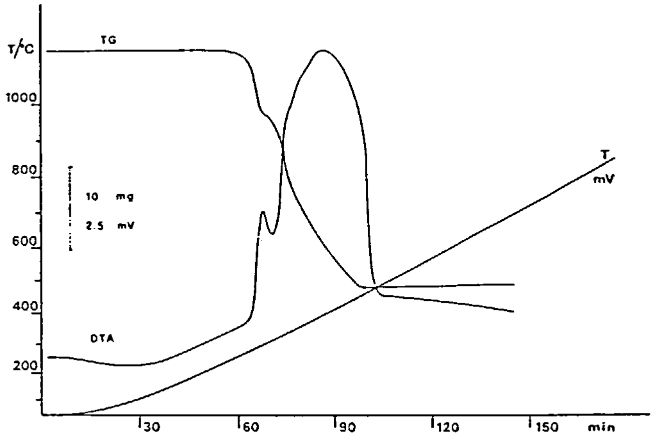


FIGURE 2 Thermograms of $[UO_2(Dh)_2(DMSO)]$ (49.30 mg).

By reacting HDh with primary amines in methanol, the related HDhR Schiff bases have been isolated as yellow solids, except for HDhB, which is a deep yellow oil at room temperature. Condensation occurs at the acyl C=O group, the phenolato proton being transferred to nitrogen. In fact, the HDhR molecules contain two pyrone groups on the ring, as already observed for analogous ligands.[6,7] Accordingly, the OH signal is absent in the HDhR proton nmr spectra (Table II), the

TABLE I
Analytical data (calculated values in parentheses) and selected ir frequencies for ligands and complexes.

					Wavenumber (cm^{-1})		
Compound	Formula	C%	H%	N%	ligand	$\nu_{asym}(NO_2)$	ν(O–U–O)
HDhM	$C_9H_{11}NO_3$	59.5	6.2	7.6	1700s, 1670m, 1610sh,		
		(59.7)	(6.1)	(7.7)	1580s, 1480m		
HDhP	$C_{11}H_{15}NO_3$	63.5	7.4	6.7	1715s, 1669m, 1610s,		
		(63.1)	(7.2)	(6.7)	1589s, 1480m		
HDhB[a]	$C_{12}H_{17}NO_3$				1710s, 1670m, 1610s,		
					1589s, 1486m		
H_2Dh_2T	$C_{20}H_{25}N_3O_6$	60.1	6.3	10.3	1697s, 1665w, 1602s,		
		(59.6)	(6.2)	(10.4)	1581s, 1480m		
$[UO_2(Dh)_2]$	$C_{16}H_{14}O_{10}U$	31.7	2.4		1731m, 1714sh, 1655m,		932s
		(31.8)	(2.3)		1574s, 1484m		
$[UO_2(Dh)_2(Me_2SO)]$	$C_{18}H_{20}O_{11}SU$	31.6	2.6		1724s, 1661m, 1602sh,		919–917s
		(31.7)	(2.9)		1566vs, 1487m		
$[UO_2(HDhM)_2(NO_3)_2]$	$C_{18}H_{22}N_4O_{14}U$	28.4	2.9	7.4	1683s, 1651m,	1540sh,	935s
		(28.6)	(2.9)	(7.4)	1631m, 1457m	1526m	
$[UO_2(HDhP)_2(NO_3)_2]$	$C_{22}H_{30}N_4O_{14}U$	32.4	3.8	6.9	1683s, 1653mw,	1555sh,	941s
		(32.5)	(3.7)	(6.9)	1620m, 1460m	1527m	
$[UO_2(HDhB)_2(NO_3)_2]$	$C_{24}H_{34}N_4O_{14}U$	33.9	4.1	6.7	1691s, 1657m,	1530sbr,	934s
		(34.3)	(4.1)	(6.7)	1612m, 1450m		
$[UO_2(H_2Dh_2T)_2](NO_3)_2$	$C_{40}H_{50}N_8O_{20}U$	40.0	4.2	9.3	1705s, 1668w,	1370vbr,	932m
		(40.0)	(4.2)	(9.3)	1589s, 1484s		917m
$[UO_2(Dh_2T)]$	$C_{20}H_{23}N_3O_8U$	36.0	3.5	6.2	1713s, 1647s,		916–907s
		(35.8)	(3.4)	(6.3)	1577s, 1484s		
$[UO_2(HDhM)(O_2CMe)_2]$	$C_{13}H_{17}NO_9U$	27.1	3.0	2.3	1696m, 1659m, 1628sh,	1532s[b]	930s
		(27.4)	(3.0)	(2.5)	1597m, 1472s		

[a] Liquid at room temperature. [b] Acetate.

resonance at *ca* 14 ppm belonging to the NH proton. The CH resonance appears at *ca* 5.6 ppm, upfield with respect to the corresponding signal in HDh (6.26 ppm) and in 2,6-dimethyl-4H-pyran-4-one (6.01 ppm),[8] whereas opposite slight shifts are observed for ring CH_3 (upfield) and side chain CH_3 (downfield) groups. Among the signals of the amine chain protons, the ones related to the groups in the α position with respect to nitrogen show proton–proton coupling with the NH hydrogen. As an example, the NCH_3 signal at 3.17 ppm in HDhM is a doublet with a coupling constant of 5.1 Hz. Moreover the position of the broad NH signals suggest that this group is involved in hydrogen bonding with one of the nearby carbonyl groups. As expected, the reaction of HDh with bis(2-aminoethyl)amine yielded the ligand H_2Dh_2T, which contains two pyrone rings. Its proton nmr spectrum is similar to those of the HDhR species except for the chain NH resonance, which is observed at *ca* 2 ppm.

TABLE II
^{1}H-nmr data for ligands and complexes ($CDCl_3$; ppm; T, *ca* 27°C).

Compound	NH[a]	CH	CH_3[b]	$CH_{3\,ring}$	NR[c]	other
HDh		6.26	2.54	2.25		16.49(OH)[d]
HDhM	14.0	5.68	2.65	2.12	3.17	
HDhP	14.1	5.62	2.60	2.08	3.40, 1.71, 1.01	
HDhB	14.1	5.65	2.61	2.09	3.54, 1.66, 1.35, 0.93	
H_2Dh_2T	14.1	5.61	2.63	2.10	3.53, 3.00	1.70[e]
H_2Dh_2T[f]	13.7	5.62	2.52	2.04	3.53, 2.80	2.28[e]
$[UO_2(Dh)_2(H_2O)]$[f]		6.37	2.96	2.29		3.31(H_2O)
$[UO_2(Dh)_2(Me_2SO)]$		6.23[d]	3.10	2.29		3.07(Me_2SO)
$[UO_2(HDhM)_2(NO_3)_2]$	13.0	6.23	3.01	2.17	3.31	
$[UO_2(HDhM)_2(NO_3)_2]$[f]	13.5	5.67	2.54	2.05	3.11	
$[UO_2(HDhP)_2(NO_3)_2]$	13.0	6.23	2.99	2.16	3.58, 1.74, 1.01	
$[UO_2(HDhB)_2(NO_3)_2]$	13.0	6.23	3.01	2.16	3.62, 1.65, 1.38, 0.90	
$[UO_2(H_2Dh_2T)_2](NO_3)_2$[f]	13.7	5.67	2.56	2.06	3.71, 3.08	7.1[d,e]
$[UO_2(Dh_2T)]$[f]		6.31	2.61	2.23	4.69, 4.28, 4.06, 3.53	7.26
$[UO_2(HDhM)(O_2CMe)_2]$[f]	13.5	5.69	2.54	2.05	3.11	2.35(O_2CMe)
$[UO_2(HDhP)_2(O_2CMe)_2]$[g]	13.6	6.10	2.74	2.10	3.45, 1.70, 0.98	2.70(O_2CMe)
$[UO_2(HDhB)(O_2CMe)_2]$[g]	13.2	6.45	2.90	2.13	3.51, 1.55, 1.36, 0.86	2.74(O_2CMe)
$[UO_2(HDhB)_2(O_2CMe)_2]$[g]	13.5	6.11	2.66	2.10	3.48, 1.62, 1.38, 0.88	2.76(O_2CMe)

[a] Broad signal which in free ligands depends on concentration. [b] Protons of the acetyl methyl in HDh and derivatives, otherwise the analogous methyl protons in the $-C(NHR)CH_3$ group. [c] Amine chain protons. [d] Broad. [e] Chain NH proton. [f] In deuterated dimethyl sulphoxide. [g] Oils obtained by reaction of uranyl acetate and ligand in the formula stoichiometric ratio (see text).

The absence of an easily ionizable proton in HDhR accounts for the behaviour of this class of ligand as a neutral donor. By reaction with uranyl nitrate in methanol the $[UO_2(HDhR)_2(NO_3)_2]$ complexes were isolated. The adduct infrared spectra do not contain any ligand band in the 1500–1600 cm^{-1} range, the medium intensity band at *ca* 1528 cm^{-1} being due to the $\nu_1$vibration of the nitrato group.[8,9] Infrared spectra do not establish which of the carbonyl groups is bound to the uranyl ion. The absence of strong C=O bands below 1600 cm^{-1} is in favour of coordination through the lactone carbonyl group. The major changes in the complex nmr spectra with respect to free ligands are observerd in the CH and side chain CH_3 resonances, which undergo a downfield shift of 0.6 ppm and 0.4 ppm, respectively, and in the NH signal, which shows an opposite shift of *ca* 1 ppm. The complexes decompose in dimethyl sulphoxide, the nmr spectra in the deuterated solvent being like those of the corresponding free ligand, as shown in Table II for $[UO_2(HDhM)_2(NO_3)_2]$. Despite the presence of two rings, the ligand H_2Dh_2T forms with uranyl nitrate a 1 : 2 adduct even at a 1 : 1 molar ratio. The infrared spectrum supports the presence of ionic nitrato groups. A strong broad absorption is observed at *ca* 1370 cm^{-1}, which masks the free ligand bands at 1404, 1365 and 1335 cm^{-1}. The band shape is similar to the corresponding one in $[Pt(1\text{-propanamine})_4](NO_3)_2$ (*ca* 1360 cm^{-1}), monodentate nitrato groups being ruled out by the absence of the related absorption in the 1500–1515 cm^{-1} range.[10] Since $[UO_2(H_2Dh_2T)_2](NO_3)_2$ is nearly insoluble in deuterated chloroform, the nmr spectrum was measured in deuterated dimethyl sulphoxide (Table II). Notwithstanding the strong donor character of the solvent, coordination of the chain NH is clearly indicated by the broad triplet at 7.1 ppm, along with the downfield shift of the methylene proton signals. The whole spectral pattern of the adduct suggests that the coordination sites in the uranyl group equatorial plane are fulfilled by ligand bites. Probably, each H_2Dh_2T molecule forms a chelate through both the chain nitrogen atom and the oxygen atom (of one of the rings) belonging to the carbonyl group which is not involved in the hydrogen bond with the nearby NH group.

The thermal behaviour of the uranyl nitrate–HDhR adducts resembles that of $[UO_2(HDhB)_2(NO_3)_2]$ (Figure 3), whose decomposition starts at 150°C. The initial degradation process should involve one of the ligand molecules. In fact, the first step weight loss (*ca* 9%) is consistent with evolution of one butanamine molecule (calculated weight loss, 8.7%), as for $[UO_2(HDhP)_2(NO_3)_2]$, which shows a weight loss of a 7.5% against 7.2% calculated for the release of one propanamine. The endothermic peak of Figure 3 at 155°C, probably due to the breaking of the nitrogen bond, is followed by an exothermic peak at 173°C. Similar DTA peaks have been observed in $[UO_2(HDhP)_2(NO_3)_2]$ thermograms at 170°C (endothermic) and 182°C (exothermic), whereas degradation of $[UO_2(HDhM)_2(NO_3)_2]$ begins suddenly at 210°C, possibly due to formation of gaseous methanamine. After the first degradation step, the adduct thermograms follow the trend observed for $[UO_2(HDhB)_2(NO_3)_2]$, which undergoes a gradual weight loss in successive exothermic processes (235°C, 325°C and 495°C). Pyrolysis is complete at 520°C with a total weight loss of 68.0% against a calculated value of 67.9% for UO_2 as final product. The complex $[UO_2(H_2Dh_2T)_2](NO_3)_2$ decomposes in the 170–570°C interval, the presence of ionic nitrato groups causing decrepitation with powder escape from the crucible.

The behaviour of uranyl acetate towards the above reported ligands differs from that of uranyl nitrate in several respects. Interaction of uranyl acetate with H_2Dh_2T in methanol causes ligand deprotonation and consequent precipitation of the $[UO_2(Dh_2T)]$ complex. The infrared spectrum of this species contains a strong absorption at 1647 cm^{-1}, absent in $[UO_2(H_2Dh_2T)](NO_3)_2$, and common to Schiff base uranyl complexes in which the HC=N group is present.[5,11] Electron delocalization in the deprotonated moiety could originate a $CH_3\text{–}C\text{=}N$ group, the ring assuming the original phenolato character of the dehydroacetato ion. The uranyl ion would attain the usual equatorial pentacoordination through the three nitrogen atoms and the phenolato oxygens. The proton nmr spectrum in deuterated dimethyl sulphoxide (Table II) shows the ring CH signal at 6.31 ppm, coordination of chain NH being evidenced by the related proton resonance at 7.26 ppm. Four equally intense signals are observed for methylene protons, suggesting some asymmetry in the chain branches on coordination. The [$UO_2(Dh_2T)$] thermograms are very simple. The complex decomposes gradually in the 300–500°C temperature interval with a weight loss of 59.5% (calculated for UO_2, 59.8%), the related DTA curve showing a broad exotherm with a maximum at 380°C.

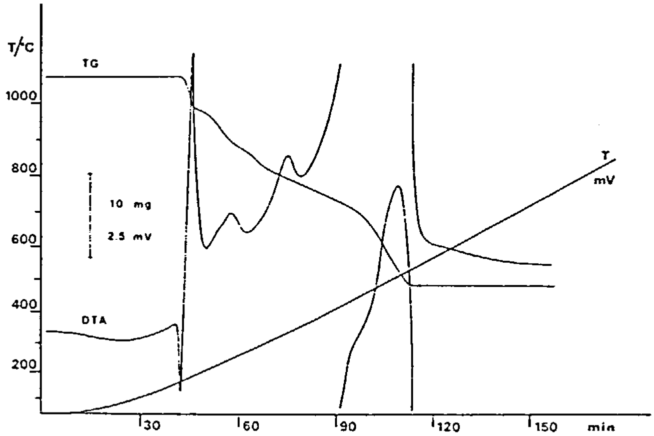


FIGURE 3 Thermograms of [$UO_2(HDhB)_2(NO_3)_2$] (37.46 mg).

The uranyl acetate–HDhR systems yield different products depending on solvent, reaction time and water contents of the solutions. When anhydrous uranyl acetate and HDhM are mixed at a 1 : 1 molar ratio in the minimum amount of dichloromethane, the nearly insoluble [$UO_2(HDhM)(O_2CMe)_2$] adduct is obtained. In diluted dichloromethane solutions or in methanol, ligand deprotonation takes place with time, along with amine release to form uranyl dehydroacetato species. Such behaviour is magnified by using hydrated salt and by allowing solutions to stand for several days. The 1 : 1 uranyl acetate adducts with HDhP and HDhB were isolated as oils by evaporating to dryness equimolar solutions of reagents in dichloromethane. Complex formation was tested by proton nmr spectra, the ligand to acetate ratio being estimated by signal integration. The oils obtained at a ligand to salt molar ratio of 2 : 1 probably contain the corresponding [$UO_2(HDhR)_2(O_2CMe)_2$] adducts; proton nmr spectra are consistent with partial ligand release in chloroform.

The thermal degradation of [$UO_2(HDhM)(O_2CMe)_2$] takes place in the 200–465°C interval with a weight loss of 52.2% (calculated value for UO_2, 52.5%). As for the uranyl nitrate adducts, the initial step involves amine evolution.

Carbon nmr data for ligands and complexes are given in Table III, signal assignments being as reported in ref. 12. The downfield signal in the HDh spectrum belongs to the acyl C=O carbon (204.5 ppm). As expected, this resonance is absent in the Schiff base spectra, the parent carbon signal being observed at *ca* 176 ppm. Moreover, pyrone and CH carbon signals undergo an upfield shift, opposite behaviour being shown by the other ring carbon signals. The resonance of the methyl group bound to the side chain carbonyl is observed in HDh at 29.6 ppm, the corresponding signal in the bases being at *ca* 18 ppm. Small changes are observed in complex spectra with respect to the corresponding free ligands. The presence of acetato groups gives rise to the CO_2 and methyl carbon signals at *ca* 189 ppm and 26 ppm, respectively.

TABLE III

^{13}C-nmr data for ligands and complexes ($CDCl_3$; ppm; T, *ca* 27°C).

Compound	C_7	C_4	C_6	C_2	C_5	C_3	$C_{7'}$	$C_{6'}$	NR	acetato
HDh[a]	204.5	180.3	170.1	160.3	100.9	99.3	29.6	20.0		
HDhM	176.9	184.1	162.4	163.7	107.4	96.5	17.6	19.5	30.4	
HDhP	175.6	184.2	162.2	163.8	107.4	96.3	17.9	19.5	45.7, 22.2, 11.2	
HDhB	175.6	184.2	162.2	163.8	107.4	96.3	17.8	19.6	43.7, 30.8, 19.8, 13.4	
H_2Dh_2T	175.7	183.8	162.0	163.6	107.1	96.2	17.9	19.3	47.2, 43.9	
$[UO_2(HDhM)(O_2CMe)_2]$[a]	176.5	183.1	163.0[b]	162.0[b]	107.1	95.5	17.5	19.1	30.5	188.5, 26.2
$[UO_2(HDhP)_2(O_2CMe)_2]$	176.2	185.3	163.5[b]	164.3[b]	107.6	96.8	18.5	19.7	46.1, 22.1, 11.1	188.9, 26.1
$[UO_2(HDhP)_2(NO_3)_2]$	177.4	185.3	165.4[b]	165.6[b]	107.9	97.3	20.0	19.7	46.9, 22.1, 11.1	
$[UO_2(HDhB)_2(O_2CMe)_2]$	176.3	185.4	164.5[b]	163.8[b]	107.7	96.9	18.6	19.9	44.4, 30.8, 19.9, 13.5	189.2, 26.1
$[UO_2(HDhB)_2(NO_3)_2]$	177.3	185.3	165.6[b]	165.4[b]	107.8	97.2	19.9	19.6	45.0, 30.5, 19.8, 13.3	
$[UO_2(Dh_2T)]$[a]	173.4[b]	180.0[b]	163.9[b]	163.2[b]	105.3	103.2	21.7	19.5	53.6, 51.6	

[a] In deuterated dimethyl sulphoxide. [b] Tentative assignment.

The action of amines on the preformed $[UO_2(Dh)_2]$ complex was examined in methanol. When equimolar amounts of $[UO_2(Dh)_2]$ and bis(2-aminoethyl)amine were reacted (0.4 mmol in 5 cm^3) a yellow solution was obtained, and from which slowly separated a yellow solid whose infrared and analytical data matched for $[UO_2(Dh_2T)]$. The proton nmr spectrum in dimethyl sulphoxide supported this, except for a lower than stoichiometric amount of coordinated chain NH, suggesting that a small amount of triamine condenses with acyl groups bound to different uranium atoms, leaving the central NH uncoordinated. In larger methanol volumes (*ca* 40 cm^3, in order to dissolve $[UO_2(Dh)_2]$ completely), mixtures of partially condensed products were obtained. By adding 1-butanamine to a $[UO_2(Dh)_2]$ suspension in dichloromethane (molar ratio 2 : 1) a yellow solution was obtained, and which was treated with *n*-pentane. The yellow precipitate which formed was a mixture of partly condensed species containing weakly coordinated amine. Similar mixtures were isolated by reaction of $[UO_2(Dh)_2]$ and 1-butanamine at molar ratios of 1 : 2 in alcoholic media. Samples obtained from solutions which were left to stand for several days seemed to contain only one dehydroacetato group for each uranium atom. It is possible that the amine interacts with the lactone group with consequent cleavage of the pyrone ring, as observed in similar systems.[13,14]

In conclusion, Schiff bases derived from dehydroacetic acid can act either as neutral or deprotonated ligands, deprotonation being favoured when α,ω-diamines are used, owing to the possibility of forming chelating moieties. Moreover, the bases derived from monoamines undergo, along with deprotonation, partial breaking at the nitrogen bond to reform the starting compounds. This behaviour is probably caused by interaction of HDhR with acetic acid forming in solution.

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