N-substituted Ethylcarbamate Complexes of Uranyl-Nitrate and Chloride

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With the N-substituted ethylcarbamates $R_2NC(O)$-OC_2H_5 (where $R = C_2H_5$ or C_6H_5) and $RR'NC(O)$-OC_2H_5 (where $R = H$; $R' = C_2H_5$, C_6H_5, $C_6H_5(CH_3)$-CH, and $R = C_2H_5$; $R' = C_6H_5$) uranyl nitrate forms complexes of formula $UO_2(NO_3)_2 \cdot 2Ligand$, whereas with the chloride only $UO_2Cl_2 \cdot 2[C_2H_5NHC(O)OC_2$-$H_5]$ has been isolated. In addition the complexes $UO_2Cl_2 \cdot 2[(CH_3)_2NC(O)OC_2H_5]$ and $UO_2Cl_2 \cdot 3[CH_3$-$NHC(O)OC_2H_5]$ are described. From the IR spectra the ligands appear to coordinate the metal through the carbonyl oxygen atom.

In the nitrato-complexes the anions act as chelate ligands leading to six-coordination in the equatorial plane of the uranyl group. For the 1:2 chloro-complexes in the solid state a chloro-bridged dimeric structure is suggested.

. The IR and ^1H nmr spectral data of the complexes are reported and discussed.

Introduction

In a previous paper [1] we reported preliminary information on the complexes of uranyl nitrate with N-methylethylcarbamate (methylurethane, MU) and N,N-dimethylethylcarbamate (dimethylurethane, DMU). The complexes of formula $UO_2(NO_3)_2 \cdot 2$-Ligand have been found to be undissociated in benzene; their ^1H nmr spectra in this solvent were indicative of hindered rotation around the C–H bond of the coordinated carbamate.
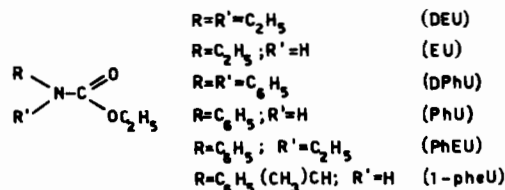
In the case of monosubstituted carbamates hindered rotation leads to the possibility of *cis–trans* isomerism:

and in effect we suggested for the complex UO_2-$(NO_3)_2 \cdot 2MU$ the presence of the ligand coordinated in both its isomeric forms.

The investigation has been now extended to a number of N-substituted carbamates in order to ascertain the influence of substituents different from the methyl group on the properties of the complexes.

The ligands and the respective abbreviations used in the text are as indicated below:

R=R'=C₂H₅	(DEU)
R=C₂H₅ ; R'=H	(EU)
R=R'=C₆H₅	(DPhU)
R=C₆H₅ ; R'=H	(PhU)
R=C₆H₅ ; R'=C₂H₅	(PhEU)
R=C₆H₅(CH₃)CH; R'=H	(1-pheU)

It is known that uranyl nitrate complexes are usually of the type 1:2 [1–3]. However uranyl chloride forms complexes with stoichiometries depending on the ligand bulkiness, as already described for the adducts with ureas and amides [4, 5]. We have therefore studied the complexing ability of uranyl chloride towards the above listed urethanes and in addition towards MU and DMU with the aim to compare the chemical behaviour of the adducts with that of the corresponding nitrates.

Experimental

Uranyl nitrate hexahydrate and uranyl chloride trihydrate were R.G. commercial products used as supplied.

The ligands DMU and MU were as described [1]; EU and DEU (K&K Laboratories Inc.) were dissolved in anhydrous diethyl ether, dried over Na_2SO_4 and distilled under reduced pressure. DPhU, PhU, PhEU and 1-pheU were prepared by reaction of ethylchloroformate with the appropriate amine; their physical properties agree with those in the literature [6–9]. Solvents were distilled under nitrogen: n-hexane and diethyl ether from Na/K alloy, benzene from Na.

Preparation of the Uranyl Nitrate Complexes

Uranyl nitrate hexahydrate (1 mmol) and the ligand (2 mmol) were dissolved in diethyl ether; the water was separated and the ethereal solution evaporated to give yellow oils. The products, which crystallized in about half an hour, were washed with n-hexane and dried over P_2O_5 *in vacuo*.

Preparation of the Uranyl Chloride Complexes

Uranyl chloride trihydrate (1 mmol) was dissolved in benzene containing the ligand (10 mmol); the solution was dried over anhydrous Na_2SO_4 and then benzene removed at reduced pressure. Yellow oils were obtained, washed repeatedly with n-hexane and dried over P_2O_5 *in vacuo*. The compounds solidified in 3–8 days, and were handled in glove-boxes filled with dry nitrogen.

The complexes are listed in Table I along with the analytical data. Elemental analyses, molecular weight measurements in benzene, IR spectra of Nujol mulls (Tables II and III) and ^1H nmr spectra in benzene (Table IV) were as described [1]. IR spectra in benzene were run on a Perkin-Elmer Mod. 457 Grating Spectrophotometer using 0.5 mm KBr cells. Conductivity values of the complexes in nitromethane $(10^{-3}M)$ were measured at 25 °C using an L.K.B. 3216 B type Conductivity Bridge.

Results and Discussion

The uranyl nitrate adducts (Table I) are yellow crystalline solids of general formula $UO_2(NO_3)_2 \cdot$ 2Ligand. Whereas the EU, DEU and 1-pheU derivatives are fairly stable, the complexes with N-phenyl substituted urethanes show a remarkably lower stability: the PhU and DPhU complexes decompose

in a few weeks if stored over a dessicant *in vacuo* and the complex with PhEU decomposes to a green solid in 4–6 hours.

By reacting uranyl chloride trihydrate with the above urethanes, we were able to isolate only the complexes $UO_2Cl_2 \cdot 3MU$, $UO_2Cl_2 \cdot 2DMU$ and UO_2-$Cl_2 \cdot 2EU$ (Table I), the other reactions giving either decomposable products or oils difficult to solidify. The prepared adducts are strongly hygroscopic and quite unstable even if kept *in vacuo*.

The IR spectra of the uranyl nitrate complexes exhibit bands characteristic of bidentate nitrato groups (Table II), as already found for the corresponding MU and DMU adducts. The nitrates (as the chlorides) give a low conductivity in nitromethane. Molecular weight values in benzene (Table I) correspond to the weight formula for the EU, DEU and 1-pheU derivatives, whereas they indicate for the DPhU, PhU and PhEU adducts the presence of free ligand in solution.

From the IR data of the solid compounds the ligands appear to bind the metal through the carbonyl oxygen, the C=O bond stretching frequencies of the complexes (Table III) being considerably lower (80 cm^{-1}) than the corresponding ones of the free ligands. The IR data in benzene are in accordance with the molecular weight experimental values: the complexes of the N-phenyl substituted urethanes exhibit in the region 1750–1600 cm^{-1} (C=O bond

TABLE I. Analytical Data of the Complexes (the calculated values are in parentheses).

Compound	M.p. °C	C%	H%	N%	Cl%	M.W.[a]
$UO_2(NO_3)_2 \cdot 2DPhU$	170 (dec.)	41.8 (41.1)	3.7 (3.4)	6.2 (6.4)	–	470[b] (876)
$UO_2(NO_3)_2 \cdot 2PhU$	120 (dec.)	29.9 (29.8)	3.0 (3.0)	7.7 (7.7)	–	380[b] (724)
$UO_2(NO_3)_2 \cdot 2PhEU$	100	33.9 (33.9)	3.8 (3.8)	7.2 (7.2)	–	350 (780)
$UO_2(NO_3)_2 \cdot 2(1\text{-pheU})$	113	33.9 (33.9)	4.0 (3.8)	7.1 (7.2)	–	760[b] (780)
$UO_2(NO_3)_2 \cdot 2DEU$	80	24.3 (24.6)	4.5 (4.4)	8.1 (8.2)	–	650 (684)
$UO_2(NO_3)_2 \cdot 2EU$	61	18.9 (19.1)	3.5 (3.5)	8.8 (8.9)	–	605 (628)
$UO_2Cl_2 \cdot 2EU$	86	20.8 (20.9)	3.8 (3.8)	4.9 (4.9)	12.2 (12.3)	c
$UO_2Cl_2 \cdot 2DMU$	80[d]	20.4 (20.9)	4.1 (3.8)	4.8 (4.9)	12.2 (12.3)	c
$UO_2Cl_2 \cdot 3MU$	80	21.7 (22.2)	4.2 (4.1)	6.3 (6.4)	10.8 (10.9)	c

[a] In benzene at 37 °C (solutions 10^{-2}–$10^{-3}M$). [b] The solid was dissolved by heating at 50 °C. [c] The measurements were not possible because of decomposition. [d] Dec. without melting.

TABLE II. Fundamental, Combination and Overtone Frequencies (cm^{-1}) of the Nitrato Group.

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	$2\nu_2$	$\nu_2 + \nu_1$	$\nu_2 + \nu_4$	$\nu_2 + \nu_3$	$\nu_2 + \nu_5$
UO$_2$(NO$_3$)$_2$·2DPhU	1528	1028	743[ab]	1280[b]	N.O.[c]	803	2054	2553	2280	1775	1750
UO$_2$(NO$_3$)$_2$·2PhU	1514[ab]	1018[b]	N.O.[c]	1275[b]	720[a]	800	2046	2545	2280	1770	1745
UO$_2$(NO$_3$)$_2$·2PhEU	1528	1025[b] / 1016	741	1268	719	802	2050	2552	2290	1771	1740
UO$_2$(NO$_3$)$_2$·2(1-pheU)	1540[b]	1020 / 1006	742	1280	N.O.[c]	800	2046	2565	2270	1780 / 1770	1748
UO$_2$(NO$_3$)$_2$·2DEU	1520 / 1500	1028[a]	744	1298[a] / 1275	720	809	2055	2547	2290	1772	1746
UO$_2$(NO$_3$)$_2$·2EU	1500	1027[b]	741	1275[b]	N.O.[c]	805	2058	2540	2305	1778	1743

[a]Tentative assignment. [b]The ligand contributes to this absorption. [c]Not observed band.

TABLE III. Some IR Frequencies (cm^{-1}) of the Complexes.

Compound	ν(N–H)[a]	ν(C=O)[b]	ν(C=O)[c]	ν(O–U–O)[d,e]	δ(O–U–O)[f]	ν(U–Cl)
UO$_2$(NO$_3$)$_2$·2DPhU	–	1630	1715[g], 1620	945 / 938		
UO$_2$(NO$_3$)$_2$·2PhU	3328	1662	1740[g], 1640	940 / 932		
UO$_2$(NO$_3$)$_2$·2PhEU	–	1610	1700[g], 1615	930		
UO$_2$(NO$_3$)$_2$·2(1-pheU)	3326	1621	1635	945 / 938		
UO$_2$(NO$_3$)$_2$·2DEU	–	1620	1620 / 1610	935 / 930		
UO$_2$(NO$_3$)$_2$·2EU	3390	1633	1645			
UO$_2$Cl$_2$·2EU	3350 sh / 3320	1660 sh / 1630	1720[g], 1630	945	268	253, 225 br
UO$_2$Cl$_2$·2DMU	–	1625	1700[g], 1630	930	272	250 / 245 sh
UO$_2$Cl$_2$·3MU	3330 / 3280 sh	1630	1725[g], 1640	948 / 938	264	218 br

[a]Medium, broad. [b]Strong, broad. [c]In benzene solution. [d]Asymmetric stretching frequency of the uranyl group. [e]Strong. [f]Deformation frequency of the uranyl group. [g]Free ligand band.

TABLE IV. ^{1}H nmr Data (in ppm) of Ligands and Complexes in Benzene (at 27 °C except when otherwise stated).

Compound	Weight[a]	O–CH$_2$–CH_3	O–CH_2–CH$_3$	N–CH_2–CH$_3$	N–CH$_2$–CH_3	N–CH$_3$
DEU	50	1.01	4.05	3.05[bc]	0.90	–
UO$_2$(NO$_3$)$_2$·2DEU	33	0.93	4.37	2.93–3.30	0.88	–
EU	80	1.00	4.01	3.07	0.91	–
UO$_2$(NO$_3$)$_2$·2EU	35	1.06[d]–0.95	4.55[d]–4.29	2.63[d]–3.06	0.60	–
UO$_2$(NO$_3$)$_2$·2EU (55 °C)	35	1.11[b]	4.60[bd]–4.30[b]	2.70[db]–3.10[b]	0.66	–
UO$_2$Cl$_2$·2EU (5 °C)	sat.d	1.12[d]–1.00	4.66[d]–4.50[b]	2.73[d]–3.31[b]	0.71[d]–0.80	–
UO$_2$Cl$_2$·2EU (40 °C)	sat.d	1.11[b]	4.60[b]	2.79[bd]–3.30[b]	0.76[b]	–
PhEU	52	1.00	4.03	3.60	0.95	–
UO$_2$(NO$_3$)$_2$·2PhEU	36	0.93	4.32	3.70[b]	0.86	–
DMU [1]	108	1.02	4.02	–	–	2.56[b]
UO$_2$(NO$_3$)$_2$·2DMU [1]	28	0.94	4.38	–	–	2.35–2.68
UO$_2$Cl$_2$·2DMU	sat.d[e]	1.05	4.69	–	–	2.16–2.95
MU [1]	49	1.00	4.02	–	–	2.49
UO$_2$(NO$_3$)$_2$·2MU [1]	30	1.04[d]–0.97	4.50[d]–4.27	–	–	2.02[d]–2.38
UO$_2$Cl$_2$·3MU	25	1.08[d]–1.04	4.55[d]–4.30	–	–	2.17[d]–2.53
				N–CH–CH$_3$	N–CH–CH_3	
1-pheU	40	0.97	3.99	4.9[f]	1.15	–
UO$_2$(NO$_3$)$_2$·2(1-pheU)	30[e]	0.89	4.40[b]	[g]	1.01	–

[a]Weight (mg) of compound added to 0.5 ml of solvent. [b]Broad signal. [c]The signal becomes sharp at 70 °C (3.09 ppm). [d]Stronger signal: for UO$_2$(NO$_3$)$_2$·2EU 65%; for UO$_2$Cl$_2$·2EU 72%; for UO$_2$(NO$_3$)$_2$·2MU 70%; for UO$_2$Cl$_2$·3MU 63% from integrated area. [e]The sample was dissolved by heating at 50 °C. [f]Unresolved signal (two protons from integrated area) due also to the N–H resonance. [g]The signal overlaps the O–CH_2–CH$_3$ resonance.

stretching) two distinct absorptions with separations of about 90 cm^{-1}, the higher frequency being due to the free ligand. The presence of free ligand has also been observed for the uranyl chloride complexes, but this is appreciable only for dilute solutions of UO$_2$·Cl$_2$·3MU.

The monosubstituted urethanes present a broad band around 3300 cm^{-1} due to the stretching of the N–H bond. In the complexes UO$_2$Cl$_2$·3MU and UO$_2$·Cl$_2$·2EU the related absorptions have been observed at lower frequencies with respect to the corresponding uranyl nitrate complexes, as previously found for the MU adducts of ThCl$_4$ and UCl$_4$ [1]. In the far IR region UO$_2$Cl$_2$·2DMU exhibits one strong band at 250 cm^{-1} assignable to the U–Cl bond stretching [10, 11]. UO$_2$Cl$_2$·3MU has this band at 218 cm^{-1} [12]: the shift towards lower frequencies of both the N–H and U–Cl absorptions suggests the formation of hydrogen bonds involving the chlorine atoms. The presence of two bands (at 253 cm^{-1} and at 225 cm^{-1}) suggests for UO$_2$Cl$_2$·2EU two different situations for the chlorine atoms. For this complex a dimeric structure similar to the one found for UO$_2$F$_2$·2urea [13], could be assumed with two bridging and two terminal chlorine atoms, the latter being involved in hydrogen bonds with the N–H groups.

The ^{1}H nmr spectra of ligands and complexes in benzene are reported in Table IV. The signals due to

the O–CH$_2$–CH$_3$ protons are for the free ligands near 1 ppm (CH$_3$) and 4 ppm (CH$_2$); on complexation the CH$_2$ resonance shifts downfield, whereas the CH$_3$ resonance remains practically unchanged. Free DEU in benzene at 70 °C shows a quartet at 3.09 ppm assigned to the CH$_2$ protons of the N–CH$_2$–CH$_3$ group; at 27 °C the signal (3.05 ppm) is broad and poorly resolved suggesting non-equivalence of the N-ethyl groups owing to an interaction with the solvent, as observed for DMU. In the adduct UO$_2$(NO$_3$)$_2$·2DEU the presence of two well-separated 1:1 quartets clearly indicates the effect of coordination on the double bond character of the C–N bond. Similarly UO$_2$(NO$_3$)$_2$·2DMU and UO$_2$Cl$_2$·2DMU exhibit two 1:1 singlets ascribed to the N–CH$_3$ protons, whereas the free ligand shows only one signal for this resonance. The larger separation observed for the chloro-complex (0.79 ppm) than that for the nitrato-complex (0.33 ppm) suggests that uranyl chloride is a stronger Lewis acid than uranyl nitrate towards the N,N-dimethylethylcarbamate [14]. The broadening of the N–CH$_3$ signals of the chloro-complex should be ascribed to the existence in solution of free DMU which undergoes exchange with the coordinated ligand [15]. The presence of free ligand in solution has been confirmed by IR measurements (Table III).

Free EU shows a multiplet at 3.07 ppm assigned to the CH$_2$ protons of the N–CH$_2$–CH$_3$ group. The

related uranyl adducts present two multiplets of unequal intensities which indicate two different situations for the coordinated ligand. MU appears to behave similarly in both the uranyl nitrate and chloride adducts. The doubling of the nmr signals for the coordinated MU or EU can be ascribed to the presence of *cis–trans* isomers formed when the rotation around the C–N bond is hindered. The per cent ratios of the isomers in the complexes are reported in Table IV.

The spectra of $UO_2(NO_3)_2 \cdot 2(1\text{-pheU})$, $UO_2(NO_3)_2 \cdot 2PhU$ and $UO_2(NO_3)_2 \cdot 2PhEU$ do not reveal the presence of isomers. The last complex, which is very soluble and dissociated in benzene (as results from Tables I and III), gives only one signal for either the CH_2 or the CH_3 protons (ether) and one unresolved signal for the CH_2 protons (amine), the broadening possibly being due to the presence of free ligand in solution. The complexes $UO_2(NO_3)_2 \cdot 2DPhU$ and $UO_2(NO_3)_2 \cdot 2PhU$ are sparingly soluble in benzene. Their solutions obtained by heating at 50 °C have the $O-CH_2-CH_3$ resonance shifted downfield (0.2–0.4 ppm) with respect to the free ligands whereas dilute solutions prepared at room temperature exhibit a signal nearly corresponding to that of the uncoordinated ligands (about 4 ppm).

From molecular weight, IR and ^1H nmr data there is some evidence that the complexes of uranyl nitrate with N-phenyl substituted ethylcarbamates are unstable in benzene solution because of the tendency to release the ligand. It could be suggested that an arylic ring bonded to the nitrogen lowers the donor ability of the ethylcarbamate owing to the electron-withdrawing from the carbonyl group in an extensive electron delocalized system. All the reported chloro-complexes are unstable in benzene in contrast to their nitrato analogues; the least stable derivative appears to be $UO_2Cl_2 \cdot 2DMU$, whose saturated solution slowly decomposes to give insoluble species and free ligand.

The complexes with ethylcarbamates asymmetrically substituted to the nitrogen atom will be the subject of a successive study based on variable temperature nmr measurements.

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