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# N-Substituted Ethylcarbamate Adducts of Thorium Tetrachloride, Uranium Tetrachloride and Uranyl Nitrate

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*Thorium tetrachloride forms 1:3 complexes with N,N-dimethylethylcarbamate (DMU) and with N-methylethylcarbamate (MU), whereas uranium tetrachloride forms complexes of formula $UCl_4 \cdot 2DMU$ and $UCl_4 \cdot 2MU \cdot THF$ (where THF = tetrahydrofuran) respectively. Uranyl nitrate forms 1:2 complexes with either DMU or MU. The IR spectra show that in all the adducts both the ligands coordinate the metal through the carbonyl oxygen atom. The uranyl complexes exhibit their most usual six-coordination around the central ion realized by two chelated nitrato groups and two monodentate molecules of the organic ligand. In the uranium and thorium tetrachloride adducts with MU the chlorine atoms seem to act as hydrogen bond acceptors with respect to the NH groups of the ligand. $^1H$ nmr spectra are reported and discussed.*

## Introduction

Complexes of uranium and thorium tetrachlorides with ligands such as N-substituted ureas and amides have been investigated extensively[1–3]. Their stoichiometries were found to be dependent chiefly on the bulkiness of the ligands (L). In fact adducts of formula $UCl_4 \cdot 2L$ and $ThCl_4 \cdot 3L$ are obtained when the ligand is tetramethyl-N-urea, while both the tetrachlorides exhibit 1:4 stoichiometry with trimethyl-N-urea. However, on using the less bulky N,N'-dimethylurea, the complexes $UCl_4 \cdot 4L$ and $ThCl_4 \cdot 6L$ can be isolated[2]. An analogous marked influence of the ligand size has been also found in complexes of di-N- and mono-N-substituted amides[3]. It was therefore of interest to investigate the complexing behaviour of uranium(IV) and thorium(IV) chlorides towards ethylcarbamate derivatives $R^1R^2NC(O)OC_2H_5$, structurally similar to the substituted amides.

The complexes of uranyl nitrate with urea and amides are generally of the type $UO_2(NO_3)_2 \cdot 2L$[4–6]; with urea the complex $UO_2(NO_3)_2 \cdot 4L \cdot H_2O$ is also obtained[6,7]. In the complex with ethylcarbamate (urethane, U), $UO_2(NO_3)_2 \cdot 2U$, the uranyl group exhibits a coordination number of six. The X-ray analysis demonstrated that the linear uranyl ion is normal to an irregular hexagon consisting of six oxygen atoms, four from two chelated nitrato groups and two from the carbonyl groups of the ligand molecules[8,9].

The research has been now extended to the complexes with N-substituted urethanes. This paper reports the preparation of the adducts of $UCl_4$, $ThCl_4$ and $UO_2(NO_3)_2$ with the ligands N,N-dimethylethylcarbamate, $(CH_3)_2NC(O)OC_2H_5$ (dimethylurethane, DMU), and N-methylethylcarbamate, $CH_3HNC(O)OC_2H_5$ (methylurethane, MU). The complexes, having formula $UCl_4 \cdot 2DMU$, $UCl_4 \cdot 2MU \cdot THF$, $ThCl_4 \cdot 3L$ and $UO_2(NO_3)_2 \cdot 2L$ (where THF = tetrahydrofuran, L = DMU, MU), have been characterized by elemental analysis and by IR and $^1H$ nmr measurements.

## Experimental

Uranium and thorium tetrachlorides were anhydrous commercial products (K & K Laboratories, Inc.), used as supplied.

Uranyl nitrate hexahydrate was a R.G. product. Dimethylurethane[10] and methylurethane[11] were stored under nitrogen and redistilled before use. Tetrahydrofuran and hexane were distilled from $LiAlH_4$, and successively from Na/K alloy. Benzene was distilled from sodium. Freshly distilled solvents were always used. All the manipulations of $UCl_4$ and $ThCl_4$ and their adducts were carried out in nitrogen filled dry-boxes.

### *Preparation of the $UCl_4$ and $ThCl_4$ Adducts*

A solution of $MCl_4$ (M = U, Th) in tetrahydrofuran (2–3 mmol in 10–20 ml) was treated with an excess of the appropriate ligand (metal to ligand molar ratios varying from 1:3 to 1:6). Hexane was then added dropwise until slight turbidity. The complexes crystallized slowly on cooling at about 5° C (2–7 days). They were filtered, washed with hexane (2 ml) and vacuum dried. An excess of hexane led generally to separation of oils which were very difficult to crystallize. Oils were also obtained by dissolving $MCl_4$ directly in the pure

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

| Compound | M.p. °C | C % | H % | N % | Cl % |
|---|---|---|---|---|---|
| $ThCl_4 \cdot 3DMU$ | 90 | 24.1<br>(24.8) | 5.1<br>(4.5) | 5.5<br>(5.8) | 19.9<br>(19.5) |
| $ThCl_4 \cdot 3MU$ | 56 | 21.0<br>(21.1) | 4.3<br>(4.0) | 6.1<br>(6.1) | 20.5<br>(20.8) |
| $UCl_4 \cdot 2DMU$ | 152 | 19.1<br>(19.6) | 3.8<br>(3.6) | 4.4<br>(4.5) | 23.3<br>(23.1) |
| $UCl_4 \cdot 2MU \cdot THF$ | a | 21.0<br>(21.9) | 4.1<br>(4.0) | 4.3<br>(4.2) | 21.9<br>(21.6) |
| $UO_2(NO_3)_2 \cdot 2DMU$ | 90 | 19.0<br>(19.1) | 3.7<br>(3.5) | 8.7<br>(8.9) | – |
| $UO_2(NO_3)_2 \cdot 2MU$ | 109 | 16.2<br>(15.9) | 3.1<br>(3.0) | 9.3<br>(9.3) | – |

[a] The compound loses tetrahydrofuran (THF) on heating.

TABLE II. Fundamental and Combination Frequencies (cm$^{-1}$) of the Nitrato Groups in the Uranyl Complexes.

| Compound | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_6$ | $\nu_2+\nu_1$ | $\nu_2+\nu_4$ | $\nu_2+\nu_3$ | $\nu_2+\nu_5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $UO_2(NO_3)_2 \cdot 2U$[9] | 1525 | 1028 | 740 | 1290<br>1270 | n.o.[a] | 800 | 2540 | 2300 | 1778 | n.o.[a] |
| $UO_2(NO_3)_2 \cdot 2DMU$ | 1530 | 1010[b]<br>1030 | 745 | 1270[c] | 715sh | 805 | 2540 | 2295 | 1775 | n.o.[a] |
| $UO_2(NO_3)_2 \cdot 2MU$ | 1500[b] | 1040[b]<br>1020 | 742 | 1280[c] | 715sh | 802 | 2545 | 2310 | 1782 | 1740 |

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

TABLE III. Some Stretching Frequencies (cm$^{-1}$) of the Adducts.

| Compound | $\nu$(N–H) | $\nu$(C = O) | $\nu$(U–O)[a] | $\nu$(M–Cl) where M = U, Th |
|---|---|---|---|---|
| $ThCl_4 \cdot 3DMU$ | – | 1640<br>1625 s, br | – | 256 vs, br<br>238 sh |
| $ThCl_4 \cdot 3MU$ | 3330 m, br | 1655 s, br | – | 224[b] s, br |
| $UCl_4 \cdot 2DMU$ | – | 1640<br>1625 s, br | – | 278<br>271 vs, br |
| $UCl_4 \cdot 2MU \cdot THF$[c] | 3325 m, br | 1632 s, br | – | 230[b] s, br |
| $UO_2(NO_3)_2 \cdot 2DMU$ | – | 1635 s, br | 940 s | – |
| $UO_2(NO_3)_2 \cdot 2MU$ | 3405 m, br | 1640 s, br | 940 s | – |

[a] Asymmetric stretching frequency of the uranyl group. [b] Tentative assignment. [c] THF = tetrahydrofuran.

liquid ligands, and by distilling off the excess of ligand under reduced pressure. The thorium adducts are white crystalline solids; the uranium ones form deep green crystals. $UCl_4 \cdot 2MU \cdot THF$ tends to release tetrahydrofuran during the filtration and, when ground, gives sticky powders. In the air the uranium adducts seem to oxidize more easily than the uncomplexed $UCl_4$.

### *Preparation of the $UO_2(NO_3)_2$ Adducts*

$UO_2(NO_3)_2 \cdot 2DMU$ was prepared by dissolving uranyl nitrate hexahydrate in dimethylurethane. The complex, extracted with ethyl ether, precipitated after addition of hexane by cooling. The product was filtered and washed with hexane. $UO_2(NO_3)_2 \cdot 2MU$ crystallized by slow concentration of an ethanol solution con-

TABLE IV. Chemical Shifts (in ppm) of N-methyl and Ester Ethyl Protons of Ligands and Complexes at 27° C (in benzene, except when otherwise stated).

| Compound | Weight[a] | Ester $CH_3$(T)[e] | N–$CH_3$ | Ester $CH_2$(Q)[e] |
|---|---|---|---|---|
| DMU | 108 | 1.02 | 2.56 | 4.02 |
| DMU | 3 | 1.03 | 2.49[b]; 2.57[b] | 4.07 |
| DMU ($CDCl_3$) | 90 | 1.26 | 2.90 | 4.12 |
| $UO_2(NO_3)_2 \cdot 2DMU$ | 28 | 0.94 | 2.35; 2.68 | 4.38 |
| $UO_2(NO_3)_2 \cdot 2DMU$ ($CDCl_3$) | 78 | 1.32 | 3.17; 3.27 | 4.50 |
| $ThCl_4 \cdot 3DMU$ | 25 | 1.14 | 2.22; 3.13 | 4.87 |
| $UCl_4 \cdot 2DMU$[c] | sat. d | −1.22 | −2.47; −2.96 | −2.37 |
| MU | 49 | 1.00 | 2.49(D)[e] | 4.02 |
| $UO_2(NO_3)_2 \cdot 2MU$ | 30 | 1.04[d]; 0.97 | 2.02(D)[d]; 2.38(D) | 4.50[d]; 4.27 |
| $ThCl_4 \cdot 3MU$ | 13 | 1.12 | 2.24(D) | 4.54 |

[a] Weight (mg) of compound added to 0.5 ml of solvent. [b] Broad signals. [c] Negative values are upfield from tetramethylsilane. [d] Stronger signal (70% from integrated area). [e] T = triplet; Q = quartet; D = doublet.

taining uranyl nitrate hexahydrate and the ligand in a stoichiometric amount. The crystals were filtered and washed with ethanol. Both the complexes, obtained as pale yellow crystals, were dried under vacuum over $P_2O_5$.

The compounds are listed in Table I along with the analytical data.

Elemental C, H, N analyses of the moisture-sensitive complexes were performed as reported[12]; chlorides were titrated potentiometrically with $AgNO_3$.

The molecular weights of the uranyl complexes were measured in benzene at 37° C by a Mechrolab Mod. 302 Vapor Pressure Osmometer.

The IR spectra in the region 4000–400 $cm^{-1}$ were recorded on a Perkin–Elmer Mod. 621 Infrared Spectrophotometer, using Nujol mulls between KBr plates. In the region 400–100 $cm^{-1}$ the spectra were run on a Beckman IR 11 Spectrophotometer, using Nujol mulls between polythene plates (Table II and III).

The $^1H$ nmr spectra were recorded on a Brucker Spectrospin HFX-10 90 MHz Spectrometer equipped with a variable temperature device. The solvents used were benzene and *d*-chloroform. The chemical shifts of the *d*-chloroform solutions were measured against tetramethylsilane as an internal standard; for the benzene solutions the solvent signal was used as internal shift reference. The chemical shift values, listed in Table IV, are all given from tetramethylsilane (negative values refer to shifts upfield from TMS).

## Results and Discussion

The complexes of thorium and uranium tetrachloride with the N-substituted urethanes DMU and MU are extremely sensitive to moisture, whereas the uranyl complexes are stable in the air (Table I). Tetrahydrofuran in the complex $UCl_4 \cdot 2MU \cdot THF$ must be coordinated very weakly; in fact the compound tends to release THF also under a nitrogen atmosphere. Tetrahydrofuran, when coordinated, exhibits characteristic IR bands around 870 $cm^{-1}$ and 1050 $cm^{-1}$ [13–15]; in those regions the compound presents broad bands whose intensity varies from sample to sample.

Both the ligands, DMU and MU, like the unsubstituted urethane[8, 9], give with uranyl nitrate complexes having 1:2 stoichiometry. Bidentate nitrato groups are present in these complexes as shown by a comparison with the IR spectra of analogous compounds containing such groups[9, 16, 17] (Table II).

Amides and urethanes are known to bind the uranyl group through the carbonyl oxygen; the ligands DMU and MU appear to behave similarly. As a matter of fact, the C=O bond stretching frequencies of the uranyl complexes (Table III) are considerably lower (60 $cm^{-1}$) than the corresponding ones of the free ligands. The pure liquids MU and DMU absorb at 1700 and 1695 $cm^{-1}$, respectively; the values are lower than the ones observed in vapour phase, owing to intermolecular associations[18].

The value of the U–O (uranyl) asymmetric stretching frequency, 940 $cm^{-1}$ for both adducts, would suggest that N-substituted urethanes are weaker donors than trimethylamine-, triphenylphosphine-, or triphenylarsine-oxide[19–21] and have a donor ability comparable to that of urea[6, 9, 16].

The $\nu$(C=O) values of the uranium(IV) and thorium(IV) adducts (Table III) indicate that also in those complexes the donor site of the ligands is the carbonyl oxygen.

Free N-methylurethane shows in the region 3500–3200 $cm^{-1}$ a broad absorption due to the N–H stretching, whose frequency depends on dipolar interaction with the solvent[18]. This band, at 3405 $cm^{-1}$ for $UO_2(NO_3)_2 \cdot 2MU$, shifts by about 80 $cm^{-1}$ towards lower frequencies in the corresponding $UCl_4$ and $ThCl_4$ adducts, suggesting the existence of hydrogen bonds in the latter compounds. The hydrogen bonding should be very weak in the uranyl complex, in accordance with the structural data of $UO_2(NO_3)_2 \cdot 2U$. The far infrared spectra of the DMU derivatives of the uranium and thorium tetrachlorides (Table III) exhibit strong bands, generally assigned to the M–Cl stretching, in the region expected for complexes of similar stoichiometries (240–280 $cm^{-1}$)[3,22]. The corresponding MU complexes do not show any absorption in this region. The M–Cl absorption should contribute to the relatively strong, broad bands observed in the 230–210 $cm^{-1}$ region, where also a contribution of the M–O bond must be present. The considerably low values of the $\nu$(M–Cl) and $\nu$(N–H) frequencies would suggest for the MU complexes a strong hydrogen bond interaction between N–H groups and chlorine atoms. Strong hydrogen bonds of such a type have been already observed in the complexes $HgCl_2 \cdot 2(H_2NC(S)OC_2H_5)$[23] and $CoBr_2 \cdot 2(C_6H_5HNC(S)OC_2H_5)$[24] by X-ray measurements.

The $^1H$ nmr spectrum of dimethylurethane in $CDCl_3$ at 27° C (Table IV) shows one signal for the N-$CH_3$ protons, suggesting free rotation about the C–N bond[25–27]. The spectrum of DMU in benzene at 27° C and at relatively high concentrations is similar to the one in $CDCl_3$, except that all the resonances are shifted upfield. This behaviour, very similar to that seen for amides[28], indicates that the DMU–benzene interaction increases the double bond character of the N–C bond, the interaction being more effective in dilute solutions, where two N-$CH_3$ resonances are present.

The complex $UO_2(NO_3)_2 \cdot 2DMU$ shows in $CDCl_3$ two sharp 1 : 1 signals for the N-$CH_3$ protons, shifted downfield with respect to the free ligand single signal. The coordination of the carbonyl group to metal leads to hindered rotation about the N–C bond. An analogous effect has been found for the system $SbCl_5$–DMU[29].

In benzene the separation of the N-$CH_3$ signals is larger than in $CDCl_3$ and all the resonances are shifted upfield. Both these effects can be attributed to interactions with the solvent. The N-$CH_3$ signals tend to get closer on increasing the temperature, but are far from coalescence at 70° C, indicating in the adduct a free energy of activation for the hindered internal rotation substantially higher than that in the free ligand. The molecular weight of $UO_2(NO_3)_2 \cdot 2DMU$ in benzene (found: 630; calcd.: 628) and the IR spectrum in the same solvent (absence of the free ligand band at 1705 $cm^{-1}$) indicate that the complex does not dissociate in benzene.

The $^1H$ nmr spectrum of $ThCl_4 \cdot 3DMU$ in benzene is similar to that of the uranyl nitrate adduct except for a larger separation of the N-$CH_3$ signals, slightly affected by temperature. At 27° C this separation is 0.91 ppm with respect to 0.33 ppm for the uranyl adduct. In studying the adducts of N,N-dimethylbenzamides with $MCl_4$ (M = Si, Sn, Ti) and $SbCl_5$, Matsubayashi and Tanaka[30] correlated the N-$CH_3$ signal separations to the electron withdrawing from the carbonyl oxygen, so that a stronger coordination of the carbonyl group to the metal causes a larger chemical shift difference between the N-methyl groups. On this basis thorium tetrachloride should be considered a stronger Lewis acid than uranyl nitrate towards dimethylurethane.

In the spectrum of $UCl_4 \cdot 2DMU$ all the resonances are remarkably shifted upfield, the effect being due to the paramagnetism of uranium(IV)[31]. The most shifted signal refers to the protons near to the ethereal oxygen, as found for the systems $Eu(fod)_3$–dimethylurethane[32] and $Eu(fod)_3$–trimethylcarbamate[33,34].

Methylurethane, like the N-methylamides[28,35], may exist in two isomeric configurations when the rotation about the C–N bond is hindered.

The $^1H$ nmr spectra of MU in $CDCl_3$[36] and in benzene (Table IV) show that the signal of the N-methyl protons consists of a doublet (J = 5 cps); in benzene all the signals are shifted upfield, analogously to DMU. The presence of one signal would suggest either free rotation about the C–N bond or predominance of one of the isomers. By increasing the concentration of MU in benzene, the doublet shifts slightly downfield, whereas the triplet and the quartet remain unchanged.

The spectrum of $UO_2(NO_3)_2 \cdot 2MU$ shows for each type of resonance two signals, the major component amounting to about 70%. By increasing the temperature up to 70° C, the two signals for either the triplet and the quartet tend to coalesce, while the N-$CH_3$ signals broaden and the stronger one migrates downfield. Since the benzene solution of the complex does not contain free ligand (MW, found: 625; calcd.: 600) the two series of signals in the nmr spectrum could be attributed to the presence of the ligand in its two isomeric forms. The shift downfield of both the quartet signals with respect to the corresponding free ligand resonance indicates that both the isomers coordinate the uranium atom. A change of the isomeric ratio from free to complexed ligand has been already found for another uranyl nitrate complex with an asymmetric amide[37]. The isomer ratio of the ligand in benzene solutions of $UO_2(NO_3)_2 \cdot 2MU$ is not affected by changes in concentration and temperature.

The spectrum of $ThCl_4 \cdot 3MU$ shows the $CH_2$ quartet shifted downfield with respect to the free ligand, as generally observed for coordinated urethanes. Unlike the corresponding uranyl nitrate adduct, the thorium complex exhibits one signal for each resonance, suggesting the presence of MU in only one of its isomeric configurations.

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