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Dialkylcarbamato Complexes of Transition Elements. 1. A New Method for the Synthesis of *N*,*N*-Dialkylcarbamato and *N*,*N*-Dialkyldithiocarbamato Complexes of Uranium(IV)

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The reaction of anhydrous UCl_4 with R_2NH and CO_2 gives the *N*,*N*-dialkylcarbamato derivatives of uranium(IV), $U(O_2CNR_2)_4$, predominantly. Evidence is presented that the reaction probably takes place via the preliminary fast formation of $NH_2R_2^+NR_2CO_2^-$. Infrared spectral data suggest that monomeric $U(O_2CNEt_2)_4$ has probably bidentate carbamato groups in poorly donating solvents and the study of its reactivity has indicated that it may be regarded as a useful intermediate for the preparation of uranium(IV) compounds. Similarly, the reacting system UCl_4–Et_2NH–CS_2 gives tetrakis(*N*,*N*-diethyldithiocarbamato)uranium(IV), most probably via the preliminary fast formation of $NH_2Et_2^+NEt_2CS_2^-$. Reactions of $U(X_2CNEt_2)_4$ (X = O, S) with dioxygen give the corresponding carbamato and dithiocarbamato derivatives of dioxouranium(VI), $UO_2(X_2CNEt_2)_2$.

Introduction

Very few binary carbamato complexes of transition elements are known in the literature. Insertion of CO_2 in the Ti–N bond of tetrakis(dimethylamido)titanium(IV) was reported[1] to yield the corresponding carbamato derivative of titanium(IV). A recent paper[2] has indicated that CO_2 activation by $W(NMe_2)_6$ yields the mixed complex $W(NMe_2)_3(O_2CNMe_2)_3$ and carbamato complexes of early transition elements have been reported.[3] CO_2 insertion in the M–N bond of $M(NR_2)_4$ (M = Th, U; R = Me, Et) to obtain $M(O_2CNR_2)_4$, which were characterized mainly spectroscopically, was also reported.[4] We now wish to publish our own results, i.e., a simplified method for the preparation of $U(O_2CNEt_2)_4$, some mechanistic insight into the new reaction, and a study of the reactivity of $U(X_2CNEt_2)_4$ (X = O, S).

Experimental Section

Due to the sensitivity of the uranium(IV) derivatives to oxygen and moisture, all the manipulations were carried out under an atmosphere of prepurified nitrogen or carbon dioxide. Reagents and solvents were dried before use.

Preparation of $U(O_2CNEt_2)_4$. A solution of $NHEt_2$ (2.46 g, 33.6 mmol) in carefully dried benzene (30 mL) was treated with CO_2 at room temperature for about 40 min. Anhydrous UCl_4 (1.60 g, 4.21 mmol) was then added and the colorless $Et_2NH_2^+Cl^-$ promptly began to precipitate. The reaction mixture was stirred for about 12 h. The green solution was separated from the colorless solid by filtration. The solution was concentrated to small volume under reduced pressure and the uranium complex was precipitated by addition of heptane, filtered, and dried in vacuo (53% yield).

The tetracarbamato complex is a light green solid, very soluble in aromatic hydrocarbons, chloroform, tetrahydrofuran, and pyridine and sparingly soluble in saturated hydrocarbons. It is decomposed by dilute (20%) sulfuric acid evolving CO_2 quantitatively.

Anal. Calcd for $C_{20}H_{40}N_4O_8U$: C, 34.19; H, 5.74; N, 7.97; U, 33.88; CO_2, 25.06; mol wt, 702.6. Found: C, 33.79; H, 5.31; N, 7.49; U, 33.2; CO_2, 24.17; mol wt (for a 0.032 *m* solution by cryoscopy in benzene), 712. Magnetic susceptibility data: $\chi_U^{cor} = 3457 \times 10^{-6}$ cgsu (diamagnetic correction = -304×10^{-6} cgsu); $\mu_{eff} = 2.85\ \mu_B$. Infrared spectrum (Nujol and polychlorofluoroethylene mulls): 2980 (m), 2940 (m), 2880 (w), 1220 (m–s), 1100 (m–s), 1090 (m–s), 1070 (m–w), 1020 (br, w), 975 (m–w), 935 (w), 825 (w), 785 (m–s), 775 (sh), 645 (w), 625 (m), 605 (m–w), 510 (w) cm^{-1}. For the region between 1700 and 1250 cm^{-1}, see Table I.

The compound is attacked by oxygen (vide infra) and appears to be indefinitely stable under dry N_2 or Ar in the solid state.

Preparation of $U(O_2CNMe_2)_4$. Dimethylamine (1.5 g, 33.2 mmol) and successively carbon dioxide were introduced into a flask containing 200 mL of toluene. After about 12 h, UCl_4 (1.64 g, 4.32 mmol) was added to the resulting clear solution. The mixture was stirred for about 7 h and an additional 2.2 g of the amine (48.8 mmol) was added under CO_2. The total reaction time was about 36 h. The reaction mixture was filtered, the green solution was concentrated under reduced pressure, and heptane was added. The carbamato complex obtained by filtration and drying in vacuo was contaminated by some chlorine-containing substance. It was then treated again with dimethylamine and CO_2 in toluene for 24 h. The product (12.5% yield) finally isolated was analytically pure. Anal. Calcd for $C_{12}H_{24}N_4O_8U$: C, 24.41; H, 4.10; N, 9.49; CO_2, 29.82. Found: C, 24.44; H, 3.70; N, 9.01; CO_2, 29.18.

The compound has similar properties to the ethyl analogue.

Reaction of $U(O_2CNEt_2)_4$ with Acetic acid. A toluene (100 mL) solution of the diethylcarbamate was obtained as previously described starting from UCl_4 (2.03 g, 5.34 mmol). The crude solution, after filtration of $NH_2Et_2^+Cl^-$, was treated with acetic acid (15.7 g, 0.26 mmol) at room temperature for 24 h. Carbon dioxide evolution was observed and the light green precipitate of the acetate was filtered, washed with toluene, dried in vacuo (56.5% yield), and analyzed without further purification. Anal. Calcd for $C_8H_{12}O_8U$: C, 20.26; H, 2.55; U, 50.19. Found: C, 19.74; H, 2.42; U, 50.26. The infrared spectrum of the compound (Nujol and polychlorofluoroethylene mulls) has strong bands at 1540 (split, $\nu_{as}(COO)$) and 1430 (split, $\nu_s(COO)$) cm^{-1} and also bands at 1350 (m–w), 1050 (w–m), 1040 (m), 1025 (s), 955 (s), 940 (w), 920 (br, w), 800 (br, w), 670 (s), 640 (s), 615 (m), 605 (m), 550 (br, w), 495 (m–s), and 470 (w–m) cm^{-1}. The spectrum is similar to that of anhydrous iron(II) acetate.[5]

Reaction of $U(O_2CNEt_2)_4$ with Dioxygen. The tetracarbamato complex (0.705 g, 1.00 mmol) in 100 mL of heptane was treated with dioxygen for 3 days. The yellow precipitate was filtered, dried in vacuo, and recrystallized by dissolution in toluene at room temperature and precipitation with heptane (42% yield). The compound, identified analytically and spectroscopically as bis(diethylcarbamato)dioxouranium(VI), $UO_2(O_2CNEt_2)_2$, is very soluble in aromatic hydrocarbons.

Anal. Calcd for $C_{10}H_{20}N_2O_6U$: C, 23.91; H, 4.01; N, 5.58. Found: C, 23.21; H, 3.99; N, 5.37. Infrared spectrum (Nujol): 1510 (s), 1320 (s), 1210 (m), 1160 (w), 1100 (m), 1085 (m), 1070 (m), 1045 (sh), 1020 (sh), 975 (m), 935 (w), 915 (sh), 898 (s), 855 (m), 825 (w), 800 (m–s), 630 (m–s), 605 (sh), 490 (m) cm^{-1}.

Preparation of $U(S_2CNEt_2)_4$. Method A. Anhydrous UCl_4 (3.87 g, 10.2 mmol) and diethylamine (5.95 g, 81.3 mmol) were introduced in a flask containing toluene (280 mL). This mixture was immediately treated with carbon disulfide (3.10 g, 40.7 mmol), the exothermic reaction soon began, and the golden yellow complex started to precipitate. After 12 h, the reaction mixture was filtered, the precipitate was washed with toluene, and the solution was concentrated under reduced pressure. The precipitate of the uranium complex was redissolved by heating the suspension to about 70 °C and the recrystallized compound was filtered and dried in vacuo. Some additional dithiocarbamate was recovered from the mother liquor by addition of heptane (42.5% total yield). Anal. Calcd for $C_{20}H_{40}N_4S_8U$: C, 28.90; H, 4.85; N, 6.74; S, 30.86; U, 28.64; mol wt, 831.1. Found: C, 29.20; H, 4.70; N, 6.51; S, 30.75; U, 28.50; mol wt, 820 (cryoscopy in benzene, 0.038 *m* solution).

Method B. Colorless diethylammonium diethyldithiocarbamate, $NH_2Et_2^+Et_2NCS_2^-$, was prepared in toluene from $NHEt_2$ and CS_2 (2:1). Anal. Calcd for $C_9H_{22}N_2S_2$: C, 48.60; H, 9.97; N, 12.59; S, 28.83. Found: C, 48.44; H, 9.60; N, 12.41; S, 28.39. It has infrared

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Table I. Infrared Spectra of $U(O_2CNEt_2)_4$ in the 1700–1250-cm^{-1} Region[a]

Solvent	ν, cm^{-1}						
Tetrachloroethylene		1510 s	1460 m	1440 m	1380 w	1320 m–s	(–)
Chloroform		1510 s	1460 m	1440 m	1380 w	1320 m–s	1260 m
Tetrahydrofuran	1700 w	(–)	(–)	(–)	(–)	1320 m–s	(–)
Pyridine	1690 w	(–)	(–)	(–)	1380 w	1320 m–s	(–)

[a] 0.1-mm cell. Bands obscured by solvent absorption are indicated by (–).

bands (Nujol mull) at 1302 (m), 1260 (s), 1210 (s), 1160 (w), 1125 (m–s), 1095 (w), 1075 (m), 1065 (m–s), 1060 (m), 1020 (w), 995 (sh), 985 (s), 912 (m–s), 880 (w), 840 (m), 770 (m), 570 (w), 510 (w), and 490 (w) cm^{-1}.

Uranium tetrachloride (0.44 g, 1.16 mmol) suspended in 50 mL of toluene was treated with $NH_2Et_2^+Et_2NCS_2^-$ (1.05 g, 4.72 mmol). After 36 h of stirring the colorless precipitate of $NH_2Et_2^+Cl^-$ was filtered off and the solution of the uranium carbamate was concentrated under reduced pressure. A 42.2% yield of the complex was obtained by dissolving the precipitate again at about 70 °C and by recrystallization in the refrigerator.

Tetrakis(diethyldithiocarbamato)uranium(IV) shows the following infrared bands (Nujol and polychlorofluoroethylene mulls): 2980 (m), 2940 (m–w), 2870 (w), 1490 (s), 1460 (m–w), 1450 (m–w), 1430 (s), 1420 (s–m), 1380 (m–w), 1355 (s–m), 1301 (m), 1292 (m), 1275 (sh), 1268 (s), 1202 (s), 1143 (s), 1090 (m), 1082 (sh), 1074 (m–s), 1060 (m), 1020 (w), 995 (m), 982 (sh), 912 (m), 840 (m), 795 (w, br), 780 (w), 770 (w), 610 (w), 570 (w), 560 (w) cm^{-1}.

Reaction of $U(S_2CNEt_2)_4$ with dioxygen. The dithiocarbamate (0.38 g, 0.46 mmol) dissolved in 20 mL of toluene was treated with dry dioxygen for about 12 h. The red-brown precipitate was filtered and recrystallized by dissolution in tetrahydrofuran and reprecipitation with heptane. It was finally dried in vacuo at room temperature (45.7% yield). This was characterized analytically and spectroscopically as the tetrahydrofuran adduct of bis(diethyldithiocarbamato)dioxouranium(VI), $UO_2(S_2CNEt_2)_2 \cdot 1.5THF$.

Anal. Calcd for $C_{16}H_{32}N_2O_{3.5}S_4U$: C, 28.48; H, 4.78; S, 19.01. Found: C, 28.23; H, 4.72; S, 19.15. The compound has the typical very intense IR band of the uranyl group at 910 cm^{-1} and those of the dithiocarbamato group at 1275 (s), 1210 (s), and 1147 (s) cm^{-1}. A control gas volumetric experiment at 23.5 °C in toluene as solvent has shown that 0.5185 g of the complex (0.62 mmol) absorbed 0.64 mmol of O_2, corresponding to a O_2:U ratio of 1.03 (theoretical value 1.0).

Results and Discussion

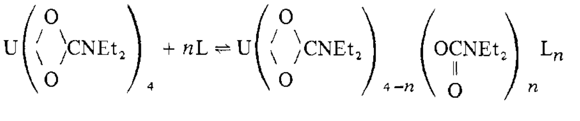
The present paper shows that it is possible to prepare binary dialkylcarbamato complexes of uranium(IV) starting from UCl_4, the dialkylamine, and CO_2. This is a considerable improvement with respect to the known procedure[4] which requires the preliminary synthesis of tetrakis(dialkylamido)uranium(IV), $U(NR_2)_4$. Strictly anhydrous solvents are required in order to minimize the formation of a secondary product, of formula $U_4O_2(O_2CNEt_2)_{12}$, which has been also fully characterized.[6] Its separation from the main product is facilitated by its higher solubility in aliphatic hydrocarbons. The reaction leading to $U(O_2CNEt_2)_4$ was carried out preferentially in toluene, which is an excellent solvent for the carbamato complex and does not substantially solubilize $NH_2R_2^+Cl^-$. The formation of the tetracarbamato complex probably occurs via the preliminary fast formation in situ of the dialkylammonium carbamate:

$$2R_2NH + CO_2 \rightarrow NH_2R_2^+NR_2CO_2^- \qquad (1)$$

$$4NH_2R_2^+NR_2CO_2^- + UCl_4 \rightarrow 4NH_2R_2^+Cl^- + U(O_2CNR_2)_4 \qquad (2)$$

This mechanistic suggestion is based on the following experimental observations: (i) by gas volumetric measurements it has been shown that at 20.2 °C CO_2 is adsorbed by $NHEt_2$ in toluene in a molar ratio of CO_2:$NHEt_2$ = 0.56, thus suggesting that the resulting *solution* contains diethylammonium carbamate predominantly, together with small amounts of diethylcarbamic acid; (ii) subsequent reaction with UCl_4 gives rise to some CO_2 evolution and the final observable CO_2:U molar ratio is 3.6 (theoretical value 4); (iii) the synthesis of $U(O_2CNEt)_4$ can be carried out either by reacting UCl_4 with preformed diethylammonium diethylcarbamate or by treating the UCl_4–amine mixture with CO_2, with no important difference in the yields; on the other hand, the corresponding methyl derivative $U(O_2CNMe_2)_4$ can be successfully obtained only if the strongly exothermic formation of the carbamate precedes the addition of UCl_4; (iv) attempts to prepare the dialkylamido complexes by treating UCl_4 with excess amine in toluene have failed. The last result strongly supports the reaction path shown in eq 2 and suggests that CO_2 insertion in U–NR_2 bonds is not the predominant path in the formation of carbamates.

The dialkylcarbamato complexes of uranium(IV) are monomeric in benzene and they do not show any tendency at room temperature to lose CO_2 in solution or in the solid state, forming the corresponding dialkylamido compounds. The diethylcarbamato complex has a strong infrared absorption at 1510 cm^{-1} ($CHCl_3$ or tetrachloroethylene solutions) which is attributable[3] to the C–N stretching vibration. However, as it is indicated in Table I, the spectra in donor solvents such as tetrahydrofuran and pyridine show an additional vibration at about 1700 cm^{-1}, which may be attributed[2,7] to the C–O stretching vibration of a monodentate carbamato group. We therefore suggest that in donor solvents such as those indicated in Table I, equilibria of the type



$$\mathrm{U}\left(\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\!>\!\mathrm{CNEt_2}\right)_4 + n\mathrm{L} \rightleftharpoons \mathrm{U}\left(\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\!>\!\mathrm{CNEt_2}\right)_{4-n}\left(\overset{\displaystyle \mathrm{OCNEt_2}}{\underset{\displaystyle \mathrm{O}}{\|}}\right)_n \mathrm{L}_n \qquad (3)$$

are established. The equilibrium is probably largely at its left even under these conditions, since the C–O stretching vibrations of monodentate carbamato groups are strong.[2,8] On the other hand, Nujol and polychlorotrifluoroethylene spectra of our carbamato complexes have one main vibration only at about 1500 cm^{-1} suggestive of bidentate carbamato groups. This together with the observed negligible solubility in heptane, the remarkably elevated solubility in aromatic hydrocarbons, and the monomeric molecular weight found in benzene for the diethylcarbamato complex all suggest that the latter is a polymeric substance in the solid state, undergoing a structural change in solution as a consequence of a specific inteaction with aromatic hydrocarbons.

The diethylcarbamato complex of uranium(IV) reacts readily with proton active containing substances, with displacement of the coordinated carbamato group and CO_2 evolution, presumably via electrophilic attack. Reaction with acetic acid leads to the formation of $U(O_2CMe)_4$:

$$U(O_2CNEt_2)_4 + 4MeCOOH \rightarrow 4CO_2 + 4NHEt_2 + U(O_2CMe)_4 \qquad (4)$$

Owing to the low solubility of the acetate in aromatic hydrocarbons, the two-step reaction to give the soluble carbamato complex and its further reaction with acetic acid appears to be the best available method for the preparation of the acetato complex.[9] Other reactions of the same type with substances containing active protons are now under investigation and their results together with their preparative relevance will be reported in a forthcoming paper.

Dioxygen reacts with $U(O_2CNEt_2)_4$ in heptane to give the new compound $UO_2(O_2CNEt_2)_2$, showing the typical[10] band of the uranyl group at about 900 cm^{-1}. No attempts were made to establish the nature of the organic products arising from the displacement of the two diethylcarbamato groups.

The one-step reaction of metal halides with R_2NH-CS_2 for the synthesis of dialkyldithiocarbamato complexes has been employed with arsenic,[11] antimony,[11] and tin[12] but it does not appear to have been successfully used with transition d or f elements. The reaction of UCl_4 with $NH_2R_2^+NR_2CS_2^-$ in donor solvents (alcohols, acetone, or acetate esters) was described,[13] but no dialkyldithiocarbamato complexes of uranium(IV) were isolated.

We find that in hydrocarbon solvents the $UCl_4-Et_2NH-CS_2$ system leads to dialkyldithiocarbamato derivatives of uranium(IV) (method A). In toluene as solvent the reaction is believed to be a substitution reaction of the chlorine ligands of UCl_4 by the $NEt_2CS_2^-$ anion formed in the preliminary fast reaction of Et_2NH with CS_2:

$$2Et_2NH + CS_2 \rightarrow NH_2Et_2^+NEt_2CS_2^- \qquad (5)$$

$$4NH_2Et_2^+NEt_2CS_2^- + UCl_4 \rightarrow 4NH_2Et_2^+Cl^- + U(S_2CNEt_2)_4 \qquad (6)$$

The strongly exothermic reaction (5) was followed spectroscopically in toluene and the C–S stretching vibration of CS_2 at 2160 cm^{-1} was found to disappear a few minutes after the mixing of the reagents and was replaced by the typical bands of the dithiocarbamato group at 1300, 1260, 1210, 1125, 990, 840, and 570 cm^{-1}.

The alternative method of preparation from preformed diethylammonium diethyldithiocarbamate and UCl_4 (method B) gave comparable yields of $U(S_2CNEt_2)_4$.

In conclusion, we can say that both the $R_2NH-CO_2-UCl_4$ and the $R_2NH-CS_2-UCl_4$ systems probably react in the same way, and we do not find any evidence of $M-NR_2$ groups being formed and inserting CX_2 ($X = O, S$).

When using method A, in view of the formation of the stable and soluble $NH_2Et_2^+NEt_2CS_2^-$, is it essential not to exceed the stoichiometric quantities of the reagents, in order to avoid contamination of the uranium complex.

Cryoscopic molecular weight measurements (not yet reported in the literature[14-16]) confirm the monomeric nature of $U(S_2CNEt_2)_4$ in solution at the freezing temperature of benzene. The monomeric structure of the compound in the solid state has been established.[17,18] The infrared spectra of the product obtained by the present procedure are in general agreement with those reported in the literature,[15,16] except for a band of medium intensity at 680 cm^{-1} reported in ref 16, which is not present in our spectra.

Dry dioxygen in toluene oxidizes $U(S_2CNEt_2)_4$ at room temperature and, after recrystallization from tetrahydrofuran, the reaction product was characterized as the THF adduct, $UO_2(S_2CNEt_2)_2\cdot1.5THF$. The absorption of dioxygen was found to be almost exactly 1 mol per uranium. The presence of coordinated tetrahydrofuran was evident by two bands at 1010 and 860 cm^{-1}, attributable[19] to the asymmetric and symmetric C–O stretching vibrations, respectively.

It is interesting to note that the uranyl complex of the nitrato[20] ligand $UO_2(NO_3)_2\cdot2H_2O$ has a hexagonal bipyramidal arrangement of the donor atoms around the eight-coordinate uranium. The same probably applies to the case of the THF adduct, although the well-known lability of this ligand may explain the intermediate stoichiometry. The bis(diethyldithiocarbamato) complexes of dioxouranium(VI) of formula $UO_2(S_2CNEt_2)_2L$ ($L = OPPh_3, OAsPh_3$) were found[21] to contain heptacoordinate uranium.

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Registry No. $U(O_2CNEt_2)_4$(complex form), 53029-68-8; $U(O_2CNMe_2)_4$(complex form), 53029-67-7; $U(O_2CMe)_4$(complex form), 64938-86-9; $UO_2(O_2CNEt_2)_2$, 64938-87-0; $U(S_2CNEt_2)_4$, 12320-69-3; $UO_2(S_2CNEt_2)_2\cdot2THF$, 64913-39-9; $NHEt_2$, 109-89-7; UCl_4, 10026-10-5; CO_2, 124-38-9; $NHMe_2$, 124-40-3; CS_2, 75-15-0; U, 7440-61-1; $U(O_2CMe)_4$(salt form), 3053-46-1; $U(O_2CNMe_2)_4$(salt form), 64900-52-3; $U(O_2CNEt_2)_4$(salt form), 64900-51-2.

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