

## Preparation and Properties of Some Amine Complexes of Uranium Tetrachloride and Uranyl Chloride

MARGUERITE A. WASSEF AND NAGWA H. ESMAIL

*Chemistry Department, University College for Women, Ain Shams University, Cairo Egypt  
Asma Fahmi Street, Heliopolis, Cairo, Egypt*

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**Summary:** Some complex compounds of uranium tetrachloride and uranyl chloride of the types  $UCl_4$ ,  $2NR_3$ ;  $UO_2Cl_2$ ,  $2NR_3$ ,  $(NR_3H)_2UCl_6$  and  $(NR_3H)_2UO_2Cl_4$  have been prepared where  $NR_3=PrNH_2$ ,  $Et_2NH$ ,  $Et_3N$  and  $C_5H_5N$ . The pyridine complexes have been reported previously [1-3], and have been prepared for comparative purposes. Molecular weights and conductivity measurements of solutions of these complexes were carried out and the results are reported.

### Introduction

Divalent radical  $[O=U=O]^{2+}$  forms stable salts with Lewis Bases [4]. Both anionic and cationic complexes of uranyl ion are known with halide ions the complex species,  $UO_2X^+$ ,  $UO_2X_3^-$  and  $UO_2X_4^{2-}$  are reported [5]. Literature includes references for the preparations and properties of both uranium (IV) [6-11] and uranium (VI) with a variety of Lewis bases [12-15].

### Results and Discussion

#### Molecular weights

The compounds  $UCl_4$ ,  $2NR_3$  and  $UO_2Cl_2$ ,  $2NR_3$  are soluble in ethanol, but cannot be recovered from solution because of decomposition, so no measurements were made on these compounds. The salts  $(pyH)_2UCl_6$  and  $(pyH)_2UO_2Cl_4$  are slightly soluble in ethanol, and their molecular weights were determined at one concentration only.

The plot of lowering of vapour pressure,  $\Delta R$  (measured in arbitrary units), against concentration  $C$  (mole/L.) for benzil in ethanol gives a straight line which passes through the origin. The plot of  $\Delta R$  against  $C$  for the other compounds is also linear, but in some cases there is an intercept on the  $\Delta R$  axis, attributed to hydrolysis caused by traces of water in the solvent Table 1 gives the slopes of these lines together with the factor  $F$  which compares the slope with that for benzil, and which is equal to the number of particles produced by each molecule of solute.

Uranyl chloride has a factor  $F$  which is equal to unity within the limits of experimental error, suggesting that the compound behaves as a monomeric

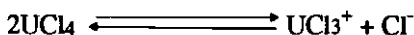
Table 1: Molecular weights

Compounds	$\Delta RC$	F
Benzil	320	1
$UCl_4$	657	2.05
$UO_2Cl_2$	318	1
$(EtNH_3)_2UCl_6$	929	2.9
$(Et_2NH)_2UCl_6$	904	2.8
$(Et_3NH)_2UCl_6$	945	2.9
$(Et_3NH)_2UCl_4$	873	2.7
$(Et_2NH)_2UO_2Cl_4$	818	2.6
$(Et_3NH)_2UO_2Cl_4$	945	
$(PyH)_2UCl_6$	930	2.95
$(PyH)_2UO_2Cl_4$	850	2.7

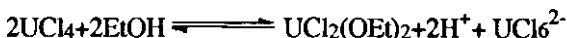
species in solution. This would be consistent with a monomeric species or with ionization producing no net increase in the number of particles according to:



For uranium tetrachloride the factor is 2, which could be simply explained as



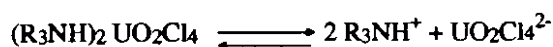
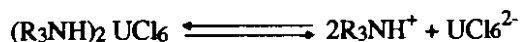
But as it is reported that uranyl tetrachloride is easily solvolysed in ethanol [18] so dissociation and solvolysis of the following type would account for the observed factor.



The formation of  $UO_2Cl_4^{2-}$  and  $UCl_6^{2-}$  anions in case of the  $UO_2Cl_2$  and  $UCl_4$  solutions in ethanol are consistent with the reported complexes.

(LH)<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub> and (LH)<sub>2</sub>UCl<sub>6</sub> obtained by the action of organic ligands on uranyl chloride and uranium tetrachloride respectively [14].

The factors for the hexachlorouranates (IV) and tetrachlorodioxouranates (F = 2.7 - 2.95) are consistent with the simple dissociation into ions.



### Conductivities

(Table 2) gives the molar conductivities at infinite dilution  $\Omega_o$ , these values can give an indication of the number and types of ions in solution [19].

Table 2: Molar conductivities  $\Omega_o$  (ohm<sup>-1</sup>cm<sup>2</sup>)

Compounds	nitrobenzene	in ethanol
(EtNH <sub>3</sub> ) <sub>2</sub> UCl <sub>6</sub>	66	254
(Et <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> UCl <sub>6</sub>	64	250
(Et <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> UCl <sub>6</sub>	68	256
(PyH) <sub>2</sub> UCl <sub>6</sub>	62	248
(EtNH <sub>3</sub> ) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>		117
(Et <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>		151
(Et <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>		133
(PyH) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>		144
UO <sub>2</sub> Cl <sub>2</sub>		35
UCl <sub>4</sub>		170
Et <sub>3</sub> NHCl		49

The molar conductivities of the hexachlorouranates (IV) in nitrobenzene ( $\Omega_o$  62-68) are consistent with the expected mode of ionization.



The molar conductivity of triethyl-ammonium chloride in ethanol has the value expected for a 1:1 electrolyte. The hexachlorouranates ( $\Omega_o$  250-256) are high, suggesting that the molar conductivity of [UCl<sub>6</sub>]<sup>2-</sup> is about 205. Similar high value for the ionic conductivity of [ThCl<sub>6</sub>]<sup>2-</sup>, is reported [20].

The value for the molar conductivity of uranium tetrachloride is consistent with its solvolysis in ethanol. The value for the tetrachlorodioxouranates (IV) ( $\Omega_o$  117-151) suggests that the molar conductivity of [UO<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> is about 185. This value is in consistent with simple dissociation into UO<sub>2</sub>Cl<sup>+</sup>, Cl<sup>-</sup> ions.

The values of the specific conductivities for some amine complexes are given (Table 3) and show that all are non-electrolytes in nitrobenzene.

Table 3: Specific conductivities  $\kappa$ , for some amine complexes in nitrobenzene

UO <sub>2</sub> Cl <sub>2</sub> . 2PrnNH <sub>2</sub>	sat.	0.03
UO <sub>2</sub> Cl <sub>2</sub> . 2Et <sub>2</sub> NH	sat.	0.02
UO <sub>2</sub> Cl <sub>2</sub> . 2Et <sub>3</sub> N	sat.	0.04
UO <sub>2</sub> Cl <sub>2</sub> . 2Py	sat.	0.03

### Experimental

#### Materials

All solvents were dried carefully by conventional methods [16], and were stored in bottles or columns containing molecular sieves. Amines were distilled from barium oxide and phosphorus pentoxide. Reactions carried out in solvents containing traces of moisture give unsatisfactory results. Anhydrous uranium tetrachloride was prepared from uranium trioxide and hexachloropropene [17]. Hydrated uranyl chloride was purchased from B.D.H; this material has a water content of up to 10% by weight and is difficult to dehydrate [18]. Heating in vacuum causes the loss of hydrogen chloride. Distillation of a suspension in benzene did not appear to remove the water. Distillation of an ethanol-benzene solution gave a product whose composition approximated to that of chloroethoxy-dioxouranium (VI), UO<sub>2</sub>CIOEt.

The method adopted for dehydration was to heat the hydrated material in a stream of hydrogen chloride, the temperature being raised to 350 °C over a period of 4 hours and maintained at this level for 2 hours. The yellow product obtained thus was anhydrous uranyl chloride (Found: Cl, 21.2; H, 69.4. Calc. for UO<sub>2</sub>Cl<sub>2</sub>, Cl, 20.8; U, 69.8%).

#### Molecular weights

A merckrolab vapour pressure osmometer model 301 A fitted with a 65 °C probe was used with ethanol as solvent. The instrument was calibrated with benzil, for which the relation between the measured variable  $\Delta R$  and the concentration was found to be linear over the range 0-0.1 mole/L. Absolute ethanol, dried by distillation from magnesium ethoxide, was used for all measurements. Its water

content, was less than 20 p.p.m. or  $10^{-3}$  mole/L., which is low compared with the concentration of uranium compounds.

### Conductivities

Conductivities were measured using Backman Electronic Switchgear bridge model RA-2A with balance indicator. The cell constant, measured by using KCl solutions, was  $0.105 \text{ cm}^{-1}$ . Experiments were carried out in an atmosphere of nitrogen.

Saturated solutions of the addition compounds in nitrobenzene were prepared by adding the solute (Ca 0.1 g), to the solvent (40 ml.) in the conductivity cell, and shaking until the conductance rose no further. The weight of solute in solution was about 1 mg. and could not easily be measured. The addition compounds are slightly soluble and this is confirmed by using arsenazo III as indicator.

### Preparation of the compounds $\text{UO}_2\text{Cl}_2 \cdot 2\text{NR}_3$

Reactions between *i*-propylamine and anhydrous uranyl chloride in ethyl acetate solution in the mole ratio of 2:1, gave a yellow precipitate which was separated by decantation, washed with ethyl acetate and benzene, and dried under reduced pressure at room temperature. The compound was identified as uranyl chloride-bis(*i*-pro-pylamine). (Found: Cl 15.2, U; 51.6,  $\text{C}_6\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2\text{U}$  requires Cl, 15.5; U; 51.9%).

Similar reactions between uranyl chloride and other amines gave the corresponding complex compounds. Analytical data and yields are given in (Table 4).

### Preparation of the compounds $(\text{NR}_3\text{H})_2 \text{UCl}_6$

The preparation of bis(diethylammonium) hexachlorouranate (IV) and bis(pyridinium) hexachlorouranate (IV) was performed by the addition of a solution of amine hydrochloride in chloroform to a suspension of uranium tetrachloride in the same medium. The hexachlorouranates of ethylamine, *i*-propylamine, and triethylamine could not be prepared from chloroform solution, presumably because of the lower solubilities of these amine hydrochlorides.

A solution of uranium tetrachloride in methanol was added to *i*-propylamine hydrochloride in methanol. The solution was evaporated to dryness under reduced pressure at room temperature, and the residue dissolved in ethyl acetate. This solution was evaporated to dryness, and the residue was extracted with benzene. The pale green residue obtained was dried under reduced pressure at room temperature. The product was recrystallized from ethanol and identified as bis(*i*-propylammonium) hexachlorouranate-(IV), decomp.  $193^\circ \text{C}$ . (Found: C, 12.1; H, 3.6; Cl, 37.0; N, 4.7; U, 41.3,  $\text{C}_6\text{H}_{20}\text{Cl}_6\text{N}_2\text{U}$  requires: C, 12.6; H, 3.5; Cl, 37.2; N, 4.9; U, 41.6%).

Table 4: Analytical Results

Compound	Yield (%)		C	H	Cl %	N	U	Formula
1. $\text{UO}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{NH}$	83	Found	19.2	4.9	14.8	5.4	48.3	$\text{C}_8\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_2\text{U}$
		Required	19.7	4.6	14.6	5.7	48.9	
2. $\text{UO}_2\text{Cl}_2 \cdot 2\text{Et}_3\text{NH}$	77	Found	26.1	5.8	13.3	5.2	43.2	$\text{C}_{12}\text{H}_{32}\text{Cl}_2\text{N}_2\text{O}_2\text{U}$
		Required	26.5	5.6	13.0	5.1	43.8	
3. $\text{UO}_2\text{Cl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$	75	Found	24.1	2.3	14.0	5.2	47.8	$\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2\text{U}$
		Required	24.0	2.0	14.2	5.6	47.6	
4. $[\text{EtNH}_3]_2\text{UCl}_6$	86	Found	9.1	3.3	39.0	5.0	43.6	$\text{C}_4\text{H}_{16}\text{Cl}_6\text{N}_2\text{U}$
		Required	8.9	3.0	39.2	5.2	43.9	
5. $[\text{Et}_3\text{NH}]_2\text{UCl}_6$	88	Found	22.4	5.1	32.3	4.6	36.5	$\text{C}_{12}\text{H}_{32}\text{Cl}_6\text{N}_2\text{U}$
		Required	22.0	4.9	32.5	4.3	36.3	
6. $[\text{Et}_3\text{NH}]_2\text{UO}_2\text{Cl}_4$	92	Found	23.3	5.0	22.8	4.3	39.3	$\text{C}_{12}\text{H}_{32}\text{Cl}_4\text{N}_2\text{O}_2\text{U}$
		Required	23.0	5.2	23.0	4.5	38.7	
7. $[\text{Et}_2\text{NH}]_2\text{UO}_2\text{Cl}_4$	85	Found	17.4	4.0	25.0	5.1	42.8	$\text{C}_8\text{H}_{24}\text{Cl}_4\text{N}_2\text{O}_2\text{U}$
		Required	17.1	4.3	25.4	5.0	42.5	
8. $(\text{EtNH}_3)_2\text{UO}_2\text{Cl}_4$	88	Found	9.3	3.3	28.0	5.4	47.6	$\text{C}_4\text{H}_{16}\text{Cl}_4\text{N}_2\text{O}_2\text{U}$
		Required	9.5	3.2	28.1	5.6	47.3	

Similar reactions between uranyl chloride and other amine hydrochlorides in methanol gave a pale yellow precipitate which after drying and recrystallization gave the corresponding tetrachlorodioxouranate (VI). Analytical data and yields are given in Table 4.

### References

1. J. J. Katz, E. Rabinowitch, *The Chemistry of Uraniium. The Elements, Its Binary and Related Compounds*. Dover, New York (1961).
2. R. Rascann, *Ann. Sci. Univ.* **16**, 461 (1931).
3. A. Rosenheim, M. Kelmy, *Z. Anorg. Allgem. Chem.*, **31**, 206 (1932).
4. N. V. Sidgwich, *The Chemical Elements and Their Compounds*, Oxford, Clarendor Press, (1950).
5. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Second revised and augmented edition, Interscience, New York (1972).
6. P. Gans, B. C. Smith, *J. Chem. Soc.*, 4172 (1964).
7. K. W. Bagnall, A. M. Dean, T. Markin, P. S. Robinson, A. M. Stewart, *J. Chem. Soc.*, 1611 (1961).
8. K. W. Bagnall, D. Brown, P. J. Jones, P. S. Rabinson, *J. Chem. Soc.*, 2531 (1964).
9. P. Gans, Thesis, London University (1964).
10. P. Gans, B. C. Smith, *J. Chem. Soc.*, 4177 (1964).
11. K. W. Bagnall, D. Brown, P. J. Jones, *J. Chem. Soc.*, 741 (1966).
12. F. Frere, *J. Amer. Soc.*, **55**, 4362 (1933).
13. W. W. Wendlandt, *Analyt. Chem.*, **28**, 494 (1956).
14. M. A. Wassef, *J. Coord. Chem.*, **12**, 97 (1982).
15. M. A. Wassef, Proc. International Union Conference on Pure and Applied Chemistry, Sofia, Bulgharia (1989).
16. A.W. Weissberger, E. S. Proskouer, *Organic Solvents Physical Properties and Methods of Purification*, Interscience, Second edition (1965).
17. J. A. Hermann, J. F. Suttle, *Inorg. Synth.*, **5**, 143 (1975).
18. D. C. Bradley, R. N. Kapoor, B. C. Smith, *J. Inorg. Nuclear Chem.*, 863 (1962).
19. B. E. Conuray, *Electrochemical Data*, Elsevier, (1952).
20. M. A. Wassef, Ph. D. Thesis, London University, (1967).