COMPOUNDS OF URANYL CHLORIDE WITH MONOAMINES

(LATE) SARJU PRASAD & L. P. PANDEY*

College of Science, Banaras Hindu University, Varanasi

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Compounds of uranyl chloride with monoamines were prepared in non-aqueous solvents. Their properties have been studied and structure discussed.

Some amines of uranium were prepared and studied by Rauscanu[1] in aqueous media. A number of ammoniates of hexavalent and tetravalent uranium were prepared[2] by the action of liquid ammonia on $U(VI)$ and $U(IV)$ chlorides. The compound $3,m\text{-}MeC_6H_3(NH_2)_2.\ UO_2(NO_3)_2$ was precipitated[3] by the action of ethereal solution of $UO_2(NO_3)_2$ on amine. Reaction of uranyl nitrate and acetate with aliphatic amines e.g., methyl, dimethyl, diethyl, ethanol, etc. were studied by Dragulescu & Julean[4] potentiometrically and conductometrically and formation of the complex $(AmH)_2\,0\cdot4\ UO_2$ concluded. It was observed[5] that among the solid compounds $UO_2Cl_2\ 4\ N_2H_4$, $UO_2Cl_2\ 3NH_3$, $UO_2Cl_2\ 2\text{-}3RNH_2$ ($R{=}Me$, Et, Pr, $isoPr$, Bu, $isoBu$, $tertBu$) only ammoniates were stable above 200°C.

The present investigation was undertaken with a view to studying the formation of the compounds of uranyl chloride with monoamines in non-aqueous media.

EXPERIMENTAL PROCEDURE

Uranyl chloride was prepared by passing pure oxygen over uranium tetrachloride at 300-350°C which was prepared by the action of chlorine on intimate mixture of carbon and UO_3 at red heat. A solution of uranyl chloride in ethyl acetate was used in all the experiments.

The other chemicals used were of Merck's or B.D.H. 'extrapure' quality. The organic solvents used were dehydrated and redistilled.

In all the cases a moderately strong ethereal solution of the amine was added to UO_2Cl_2 in ethylacetate with constant shaking till the precipitation was complete and the amine was in slight excess. In carrying out these reactions great care was taken to exclude water since the reaction products are easily hydrolysed. The precipitate was filtered, washed with ether till free of the base and dried over anhydrous calcium chloride. In case both the reactants were in ethylacetate or ether the yield was not good.

ANALYTICAL PROCEDURE

The compound was evaporated subsequently with conc. H_2SO_4 and HNO_3 till all the carbon was oxidised. The solution was extracted with water and ammonium diuranate was precipitated by ammonia, which on ignition yielded U_3O_8. Chlorine was estimated by

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*Now at the Defence Science Laboratory, Metcalfe House, Delhi-6.

TABLE 1

COMPOUNDS OF URANYL CHLORIDE WITH MONOAMINES

Amines	Compounds formed	Colour	Melting point (°C)	% Uranium		% Chlorine		% Organic matter	
				Found	Calculated	Found	Calculated	Found	Calculated
α-Naphthylamine	$UO_2Cl_2.2C_{10}H_7NH_2$	Light Violet	A300	37·82	37·93	11·28	11·32	$C = 38·32$ $H = 2·798$ $N = 4·328$	38·24 2·869 4·463
β-Naphthylamine	$UO_2Cl_2.2C_{10}H_7NH_2$	Grey	200	37·79	37·93	11·23	11·32	$N = 4·386$	4·463
o-Phenetidine	$UO_2Cl_2.2C_6H_4OC_2H_5NH_2$	Grey	—	38·78	38·70	11·48	11·54	$C = 31·28$ $H = 3·621$ N = 4·496	31·22 3·577 4·553
m-Phenetidine	$UO_2Cl_2.2C_6H_4OC_2H_5NH_2$	Brown	221	38·84	38·70	11·37	11·54	$N = 4·613$	4·553
p-Phenetidine	$UO_2Cl_2.2C_6H_4OC_2H_5NH_2$	Yellowish Brown	205	38·52	38·70	11·44	11·54	$N = 4·612$	4·553
Toluidine	$UO_2Cl_22C_6H_4CH_3NH_2$	Dark Grey	118D	42·29	42·86	12·67	12·78	$N = 5·101$	5·043
m-Toluidine	$UO_2Cl_2.2C_6H_4CH_3NH_2$	Dirty Yellow	215D	43·12	42·86	12·74	12·78	$C = 30·33$ $H = 3·218$ $N = 5·082$	30·26 3·242 5·043
p-Toluidine	$UO_2Cl_2.2C_6H_4CH_3NH_2$	Greenish Yellow	214	43·08	42·86	12·68	12·78	$N = 5·069$	5·043
o-Anisidine	$UO_2Cl_2.2C_6H_4OCH_3NH_2$	Black	197	41·23	40·53	12·12	12·09	$N = 4·792$	4·768
m-Anisidine	$UO_2Cl_2. 2C_6H_4OCH_3NH_2$	Black	105	41·17	40·53	12·20	12·09	$N = 4·795$	4·768
3 : 4 Xylidine	$UO_2Cl_2.2C_6H_3(CH_3)_2\ NH_2$	Yellow	190D	40·99	40·83	12·61	12·18	$N = 4·779$	4·803
m-Nitroaniline	$UO_2Cl_2.2C_6H_4NO_2NH_2$	Rust	115	38·98	38·56	11·41	11·49	$N = 4·512$	4·536

A= Above D = Decomposed

Pyriya and Schiff's method. Nitrogen was estimated by Kjeldahl's method and percentage of organic matter calculated. Carbon and hydrogen were estimated by microanalytical methods in a few cases.

General Properties

All the compounds are coloured and fairly stable in dry atmosphere at the room temperature but begin to decompose when they come in contact with moisture. The compounds are mainly insoluble in common organic solvents like benzene, ether, alcohol, acetone and dioxane. Complexes with α-naphthylamine, 3 : 4 xylindine, *m*-phenetidine, *m*-anisidine and *m*-nitroaniline are soluble in alcohol.

The aqueous extract of the compounds gives the test for chlorine showing thereby that either chlorine is in an ionisable state or the compounds decompose. They are decomposed readily when treated with strong acids or alkalies.

DISCUSSION

The plausible explanation for the formation of these compounds may be given as due to coordination, in which ligands donate the loan pair of electrons to the central uranium atom. In view of the fact that uranium exhibits coordination numbers six and eight both, the two possibilities of the structure of these complexes can be discussed.

Coordination Number Six

In this representation (Fig. 1) two chlorine atoms are out of central sphere of attraction forming a six coordinated positive complexion of the type $d^5 s$.

Coordination Number Eight

In this representation (Fig. 2) two chlorine atoms are in the central sphere of attraction, thus forming a neutral complex of the type $d^5\ sp^2$.

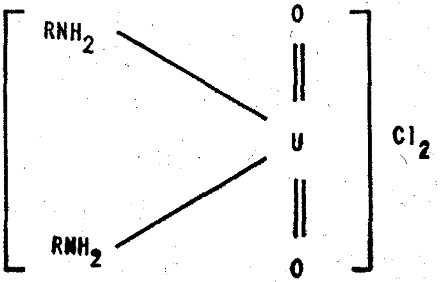

Fig. 1

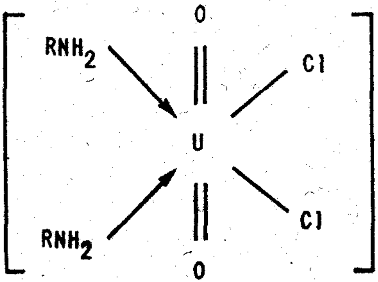

Fig. 2

Since the experimental evidences are not sufficient as to strictly adhere to any particular representation, structures may be represented with the coordination number eight which is more prevalent in uranium.

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