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Complexes of Uranium(V) Chloride with Oxygen Donor Ligands

MANGAL SINGH*, GURDEV SINGH and RAM CHAND PAUL
Department of Chemistry, Panjab University, Chandigarh-14, India
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Stable uranium(V) chloride complexes of the type $UCl_5 \cdot B$ *and* $UCl_5 \cdot 2B$ *(B = anthrone, benzanthrone, methyleneanthrone, benzalanthrone, benzil) and* $UCl_5 \cdot 3$*dioxane have been isolated from uranium(V) chloride solution in thionyl chloride. Magnetic susceptibilities at temperatures varying from 86° K to 300° K, electron spin resonance, infrared and reflectance spectra of some of the compounds have been studied to throw some light on the nature of these complexes.*

Introduction

Addition complexes of uranium(V) chloride have been reviewed by Selbin *et al.*[1] We have reported the syntheses of new uranium(V) chloride complexes with nitrogen tertiary bases having uranium(V) chloride: base molar ratio of 1:2 and 1:3.[2] Selbin and coworkers[3] have prepared uranium(V) chloride complexes with ligands containing N, P, As, Bi, O, S, Se and Te as donor atoms. Brown *et al.* have isolated the complex, $UCl_5 \cdot 2Ph_3PO$.[4] In the present work we report the syntheses of uranium(V) chloride complexes with oxygen donor ligands such as anthrone, benzanthrone, methyleneanthrone, benzalanthrone, benzil and dioxane. Infrared, electron spin resonance, reflectance spectra and magnetic susceptibilities of these compounds have been studied to characterise these compounds.

Experimental

Materials

Uranium(V) chloride was prepared by refluxing UO_3 or UO_2Cl_2 with thionyl chloride.[5] Anthrone (BDH) was used as such. Benzanthrone (BDH) was recrystallised from carbon tetrachloride and animal charcoal into light yellow needles (m.p. 170° C). Methyleneanthrone and benzalanthrone were prepared and recrystallised as reported in literature.[6,7] Benzil (E. Merck) was used without further purification. Nitrogen gas was passed through dioxane (BDH) for about 3 hours. It was then refluxed with sodium for about 6 hours and then fractionally distilled. Since uranium(V) chloride compounds are highly susceptible to disproportionation by moisture, all manipulations including filtration and drying have been carried out in completely dry atmosphere. Petroleum ether (40–60° C), carbon tetrachloride and benzene were purified and dried by usual methods and petroleum ether and benzene were stored over sodium.

Preparation of Complexes

(i) The $UCl_5 \cdot 1$*Base type complexes*

Benzanthrone, methyleneanthrone, benzalanthrone and benzil were dissolved in ice cooled thionyl chloride and this solution was added to an ice cooled solution of uranium(V) chloride in thionyl chloride in 1:1 stoichiometry. On the addition of dry petroleum ether, reddish brown complex in case of benzil and dark brown complexes in case of benzanthrone, methyleneanthrone and benzalanthrone separated out. These complexes were filtered under strictly anhydrous conditions, washed with dry petroleum ether and dried under vacuum. However, $UCl_5 \cdot$Benzil complex separates out as a viscous liquid and after repeated washing with dry petroleum ether was dried under vacuum. Procedure for $UCl_5 \cdot$Anthrone complex was the same as above except that anthrone was dissolved in dry benzene instead of thionyl chloride.

(ii) The $UCl_5 \cdot 2$*Base type complexes*

Benzanthrone and benzil were dissolved in ice cooled thionyl chloride and this solution was added to an ice cooled solution of uranium(V) chloride in thionyl chloride in a molar ratio of 2:1. On the addition of dry petroleum ether a dark brown solid was separated out in case of benzanthrone. This was filtered, washed with dry petroleum ether and dried under vacuum. In case of benzil the complex remained in viscous form and on drying under vacuum raddish brown solid was obtained. In case of anthrone complex, anthrone was dissolved in benzene and rest of the procedure was the same.

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* Department of Chemistry, Guru Nanak University, Amritsar, India. All correspondence should be sent to this address.

(iii) The $UCl_5 \cdot 3$Dioxane complex

To uranium(V) chloride solution in thionyl chloride cooled in an ice bath an excess of dioxane was added. On the addition of dry petroleum ether a deep yellow solid was separated out. It was washed with dry petroleum ether and dried under vacuum.

The analytical results are given in Table I.

Analytical Methods

For the estimation of the organic ligand in the complex, advantage was taken of the fact that the complexes are decomposed by water into the pure organic ligand which is insoluble and uranium part which disproportionates into U(IV) and U(VI) which are soluble in water. The complex was directly weighed into a sintered glass crucible (1-G-4). It was thoroughly washed with water and filtered when the pure organic ligand was left behind as solid residue. It was dried at 110–120° C and weighed as such. Benzil was estimated similarly but the residue was dried at 80° C. Uranium was estimated from the filtrate volumetrically and gravimetrically as reported in the previous publication.[2] Chlorine was estimated volumetrically by Volhard's method and gravimetrically as silver chloride.

Spectral Measurements

Reflectance and ESR spectra were recorded on the Spectrophotometers already described.[2] Infrared spectra were recorded in nujol mulls on a Perkin–Elmer 337 Grating Infrared Spectrophotometer. The mulls were prepared and pasted in sodium chloride cell in the dry box.

Magnetic Susceptibility Measurements

Magnetic susceptibilities were measured on a Gouy type balance at temperatures varying from 86° K to 300° K^2. Susceptibilities of some of the compounds were measured at room temperature only.

Results and Discussion

All the $UCl_5 \cdot$Base and $UCl_5 \cdot 2$Base complexes are stable only under strictly anhydrous conditions and disproportionate into U(IV) and U(VI) on exposure to even traces of moisture. These complexes are insoluble in common organic solvents such as benzene, carbon tetrachloride, petroleum ether and cyclohexane, and disproportionate into U(IV) and U(VI) in anhydrous polar solvents such as diethyl ether, chloroform, acetonitrile, ethylacetate, dimethylsulphoxide, acetylchloride, benzoylchloride and acetone. On thermal decomposition all these complexes give U_3O_8 as the end product without the formation of any intermediate. Since the analytical methods do not distinguish U(V) from an equimolar mixture of U(IV) and U(VI) formed on disproportionation of U(V), reflectance and ESR spectra of a few compounds have been studied to make this distinction. Begnall *et al.*[8] have reported that in the range of 600–900 mμ uranium(V) shows only one characteristic peak. We have reported the reflectance spectra of uranium(V) chloride complexes with nitrogen donor ligands[2] which show strong absorption band at about 860 mμ showing that complexes are true complexes of uranium(V). In the present paper reflectance spectra of $UCl_5 \cdot$Anthrone, $UCl_5 \cdot$Benzil, $UCl_5 \cdot 3$Dioxane, $UCl_5 \cdot$Benzanthrone and $UCl_5 \cdot 2$Benzanthrone in the region 800–1000 mμ have been studied. The spectra show strong absorption peaks at 845, 860, 860, 940 and 940 mμ respectively.

ESR spectrum of $UCl_5 \cdot$Benzil produces broad signal at 5970 Gauss at 80° K and 'g' value calculated for this compound is 1.12. The ESR spectrum of $UCl_5 \cdot 2$Benzanthrone produces extremely broad signal between 5420–6120 Gauss at 80° K. The 'g' value varies between 1.11 and 1.25. These 'g' values are comparable to the average 'g' values of 1.1 already reported[2,9]

TABLE I. Uranium(V) Chloride Complexes with Oxygen Bases.

Base	Complex	Analytical Results					
		Found			Required		
		Uranium	Chloride	Anthrone	Uranium	Chloride	Anthrone
Anthrone	$UCl_5 \cdot$Anthrone	39.40	29.42	31.80	39.04	29.13	31.50
Benzanthrone	$UCl_5 \cdot$Benzanthrone	36.79	26.95	36.12	36.90	27.49	35.62
Methyleneanthrone	$UCl_5 \cdot$Methyleneanthrone	38.72	28.37	33.08	38.30	28.56	33.15
Benzalanthrone	$UCl_5 \cdot$Benzalanthrone	34.12	25.23	40.71	34.12	25.45	40.42
Benzil	$UCl_5 \cdot$Benzil	37.78	28.25	33.14	38.05	28.38	33.57
Anthrone	$UCl_5 \cdot 2$Anthrone	29.77	21.88	47.24	29.62	22.02	48.28
Benzanthrone	$UCl_5 \cdot 2$Benzanthrone	27.32	20.40	52.37	27.17	20.25	52.58
Benzil	$UCl_5 \cdot 2$Benzil	28.40	21.37	50.15	28.48	21.24	50.25
Dioxane	$UCl_5 \cdot 3$Dioxane	35.34	26.37		35.02	26.12	

TABLE II. Magnetic Susceptibility Data for Uranium(V) Chloride Complexes.[a]

$UCl_5 \cdot$Benzanthrone				$UCl_5 \cdot$2Benzanthrone				$UCl_5 \cdot$Benzil			
T(° K)	$\chi_m \times 10^6$	μ_{eff} (B.M.)	μ_{eff} (B.M.) Θ applied	T(° K)	$\chi_m \times 10^6$	μ_{eff} (B.M.)	μ_{eff} (B.M.) Θ applied	T(° K)	$\chi_m \times 10^6$	μ_{eff} (B.M.)	μ_{eff} (B.M.) Θ applied
89.5	1824	1.14	1.80	87.5	1894	1.15	2.03	87.5	5345	1.93	2.37
96.0	1774	1.17	1.80	97.0	1967	1.23	2.10	96.5	4933	2.19	2.35
107.0	1714	1.21	1.81	107.5	1879	1.27	2.09	107.5	4602	1.99	2.37
119.5	1612	1.24	1.80	119.5	1725	1.28	2.04	120.0	4227	2.01	2.35
134.5	1559	1.29	1.82	136.0	1608	1.32	2.03	135.0	3830	2.03	2.34
150.5	1413	1.30	1.79	153.5	1595	1.40	2.07	153.5	3491	2.07	2.35
176.0	1223	1.31	1.74	177.0	1486	1.45	2.07	176.3	3207	2.12	2.38
207.0	1147	1.38	1.76	208.0	1377	1.51	2.08	208.5	2807	2.16	2.38
249.5	1096	1.48	1.83	251.0	1311	1.62	2.13	250.0	2403	2.19	2.37
294.0	963	1.50	1.81	295.7	1220	1.70	2.17	294.5	2027	2.18	2.34
			$\Theta = -132°$				$\Theta = -184°$				$\Theta = -44°$

[a] $\mu_{eff} = 2.828(\chi_m T)^{1/2}$
μ_{eff}, Θ applied $= 2.828(\chi_m(T-\Theta)^{1/2}$

but are in contrast to 'g' value of about 2 reported in literature.[3] From ESR spectra of uranium(V) chloride complexes it can be suggested that the lone U(V) electron is not completely delocalized into the π antibonding molecular orbitals of these molecules.

The infrared spectra of the anthrones and their complexes with uranium(V) chloride in the region 1700–1500 cm^{-1} show shifts towards lower frequency in the carbonyl stretching frequencies. Thus the carbonyl stretching frequencies in benzanthrone, methyleneanthrone, benzalanthrone and anthrone are lowered from 1650, 1650, 1650, 1654 cm^{-1} in respective anthrones to 1615, 1610, 1580, 1580 and 1585 cm^{-1} in $UCl_5 \cdot$Benzanthrone, $UCl_5 \cdot$2Benzanthrone, $UCl_5 \cdot$Methyleneanthrone, $UCl_5 \cdot$Benzalanthrone and $UCl_5 \cdot$Anthrone respectively. The lowering of the carbonyl stretching frequency shows that oxygen atom of the anthrones coordinates to uranium atom of uranium(V) chloride. The coordination number of uranium in these complexes may be six or seven according to the number of anthrone molecules complexing with uranium(V) chloride.

Magnetic susceptibility data on uranium(V) complexes have been reviewed.[1] Selbin *et al.*[3] have reported the data for some of the uranium(V) chloride complexes with N, P, As, S, Se and Te donors at room temperatures. Magnetic susceptibilities of UCl_5 complexes with nitrogen bases have been reported by Paul *et al.*[2] Magnetic susceptibilities of $UCl_5 \cdot$Benzanthrone, $UCl_5 \cdot$2Benzanthrone and $UCl_5 \cdot$Benzil from 86° K to 300° K (Table II) have been studied. The complexes $UCl_5 \cdot$Benzanthrone and $UCl_5 \cdot$Benzil show Curie–Weiss dependence from 89.5° K to 294° K and 87.5° K to 294.5° K respectively. The complex $UCl_5 \cdot$2Benzanthrone shows Curie–Weiss dependence from 87.5° K to 208° K and shows some temperature independent paramagnetism (TIP) above this temperature. This TIP has generally been observed for compounds which have low values of paramagnetic susceptibility.[10] The Weiss constant for $UCl_5 \cdot$Benzenethrone, $UCl_5 \cdot$2Benzeneanthrone and $UCl_5 \cdot$Benzil are −132°, −184° and −44° and magnetic moments at room temperatures are 1.81, 2.16 and 2.34 B.M. respectively. Due to large values of Θ, these values of magnetic moments are not of much significance. However, the reduced magnetic moments at low temperatures (Table II) indicate metal–metal interaction probably due to magnetic exchange involving chlorine bridging. Magnetic susceptibilities of $UCl_5 \cdot$Anthrone, $UCl_5 \cdot$Methyleneanthrone and $UCl_5 \cdot$3Dioxane have been measured at room temperature only giving μ_{eff} values of 1.91, 2.18 and 1.66 B.M. respectively.

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