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Anhydrous Uranium(+3) Chloro-Complexes

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A series of anhydrous uranium(+3) chloro-complexes of the M_2UCl_5 type [M = NH_4, K or Rb], have been isolated and characterized by spectral and magnetic measurements. The complexes are hygroscopic but stable to oxidation in dry air. All compounds exhibit antiferromagnetic transitions as well as broad and strong absorption bands in the visible and u.v. regions.

Introduction

The formation of uranium(+3) chloro-complexes in aqueous and anhydrous media has been known for a long time [1–8] and was first postulated by Jørgensen [1]. The first chloro-complexes which have been isolated were two series of hydrated uranium(+3) double chlorides [5] of the types $MUCl_4 \cdot 5H_2O$ [M = K, Rb or NH_4] and $MUCl_4 \cdot xH_2O$ [M = Rb or NH_4]. They were prepared from cold aqueous solutions of uranium(+3) double sulphates [9] as well as from those obtained by electrolytic reduction of uranium(+4) in 1*M* HCl. Attempts to obtain anhydrous double chlorides by thermal decomposition of the hydrated complexes have been unsuccessful [5].

In this paper the synthesis as well as some chemical, magnetic and spectral properties of a new series of anhydrous uranium(+3) chloro-complexes of the type M_2UCl_5 [M = NH_4, K or Rb], are reported.

Experimental

General Procedure for the Preparation of Complexes

The uranium(+3) chloro-complexes were obtained by reduction of the appropriate uranium(+4) chloro-complexes in acetonitrile, with liquid zinc amalgam. In a typical preparation 2–10 g of uranium tetrachloride with a large excess (1–5 g) of dry MCl [M = NH_4, K or Rb] was dissolved under stirring in 100 ml of a 50:1 mixture of anhydrous acetonitrile and propionic acid. After filtration, these solutions were reduced by shaking for 10–20 min with a 2% liquid zinc amalgam. This reduction gave the fine crystalline, violet–purple precipitates of $(NH_4)_2UCl_5$, K_2UCl_5 and Rb_2UCl_5, respectively. After separation from the liquid zinc amalgam, the complexes were filtered, washed thoroughly with acetonitrile and dried under vacuum. All the operations have been performed in an all-glass apparatus [10] under an inert atmosphere. The chloro-complexes obtained were stored in sealed tubes.

The sodium and caesium complexes could not be prepared using the method described above. A brown complex of the formula $LaCl_3 \cdot UCl_3 \cdot xH_2O$ was also separated, but was too unstable to permit characterization.

Reagents

Uranium tetrachloride was prepared from UO_2 by chlorination with CCl_4 vapours, according to the procedure given in Ref. [11]. Acetonitrile was dried over anhydrous Na_2SO_4 and distilled under reduced pressure. Other reagents used were of analytical grade.

Analytical Data

Calc. for $(NH_4)_2UCl_5$: U, 52.73; Cl, 42.14; N, 6.20. Found: U, 52.10; Cl, 41.17; N, 6.05. Calc. for K_2UCl_5: U, 48.23; Cl, 35.92; K, 15.85; Found: U, 47.55; Cl, 35.49; K, 15.10. Calc. for Rb_2UCl_5: U, 40.60; Cl, 30.24; Rb, 29.16. Found: U, 40.53; Cl, 30.35; Rb, 28.81.

Magnetic and Spectral Measurements

Magnetic susceptibilities of polycrystalline samples were measured by the conventional Faraday method at a field of 6 KOe. A variable-temperature liquid helium Dewar was used to enable measurements in the 4–290 °K region. The magnetic data obtained, including diamagnetic corrections, are listed in Table I.

TABLE I. Magnetic susceptibility constants.

Compound	Colour	Temperature range (°K)	μ_{eff} (B.M.)	C^a (emu °K/mol)	θ^a (°K)	T_N^b (°K)
K_2UCl_5	purple	20–130	3.99	1.871	−53.5	13.2
		130–300	3.77	1.602	−33.5	
Rb_2UCl_5	violet–red	10–150	3.57	1.485	−45.5	8.6
		150–300	3.44	1.375	−32.0	
$NH_4\ _2UCl_5$	violet	17–220	3.54	1.545	−37.5	7.8
		220–300	3.47	1.465	−26.0	

[a]Constants from Curie–Weiss law, $\chi'_M = C/(T - \theta)$. [b]Néel temperature.

TABLE II. Energies of the observed maxima in the absorption spectra of the uranium(+3) chloro-complexes.

Level Assignment L'S'J'[a]	K_2UCl_5 (cm^{-1})	Rb_2UCl_5 (cm^{-1})	$(NH_4)_2UCl_5$ (cm^{-1})
$^4I_{9/2}$	–	–	–
$^4I_{11/2}$	4310 w	(4210) vw	4444 w
	(4444)	4310 w	4512 w
	4484 w	(4420) w	4551 w
	(4545)	4494 w	4638 w
	4619 w	(4625) w	4812 w
$^4F_{3/2}$	7246 vw	7146 vw	7564 vw
			7610 vw
$^4I_{13/2}$	(7990)	(7849) w	7952 w
	(8064)	(7911) w	8130 m
	8153 w	(8124) w	8203 m
	8288 w	8210 m	(8333)
	(8354)	8350 m	8389 w
	8554 vw	8658 vw	8561 w
$^2H_{9/2}$	(8984) w	(8960) vw	9033 vw
	(9208)	9276 w	9225 w
$^4F_{5/2}$	9276 w	(9328) w	(9302)
	9328 w	9451 w	9394 w
	9451 w	9624 w	(9451)
	9569 w	(9900) w	9847 w
	9838 w	9980 w	9980 w
	(9910)	10162 vw	(10126)
	9985 m		10162 m
	(10147) vw		
$^4S_{3/2}$	(10799)	(10526) vw	10887 m
	11037 m	10776 w	11031 m
$^4G_{5/2}$	(11098)	11013 sm	11255 m
	11363 w	(11061)	11389 m
$^4I_{15/2}$	(11248)	(11236) w	11834 w
	(11554)	(11363) w	
$^4F_{7/2}$		11547 w	
$^4G_{7/2}$	13157 w	12820 w	13046 vw
	13360 w	13140 w	13210 w
			13396 w
			13495 w
	(14492) m	(14534) w	14631 w
	(14836)	(14792)	14705
	15384 s	(15384) m	14792
	(16129)	(15875)	(15456)
	16736 vs	(16181)	15552 m
	16949 vs	16608 vs	(15772)
	17197	16987 vs	(16000)
	17271	17241 vs	16313 bs
	17574 bvs	17513 vs	(17050)
	18867 vs	(17730)	(17241)
	19607 bvs	18857 s	(17543)
	(20040)	(19084)	17777 bvs
	(21367)	19607	(18033) vs
	(21551)	(20080)	(18726)
	21692 bvs	21645 bvs	(19011)
	28089 bvs		(19267)
			19607 vs
			(20366)
			21881 bvs
			24540 vs
			28409 vs
			(30211)
			(31055)
			31446 bvs
			(31746)

[a]Major component of eigenvector.

In order to obtain the electronic spectra, a mixture of the corresponding uranium(+3) chloro-complex in Halowax* was placed between two quartz windows and pressed to get a clear and uniform film. Absorption spectra of such films were recorded on a Cary 14 spectrophotometer in the 4000–26000 cm^{-1} range [Table II].

Solid state, far-i.r. spectra were obtained on a Perkin-Elmer 180 spectrophotometer, using nujol mulls and polyethylene plates.

Results and Discussion

Chemical Properties

The uranium(+3) chloro-complexes synthesized are well defined violet–purple crystalline powders. All of them are hygroscopic, but stable to oxidation in dry air. They dissolved easily in strong acids with the formation of unstable red or red–green solutions. In concentrated hydrochloric acid the characteristic red-wine unstable uranium(+3) solutions [1–3] were formed. The red–green water solutions of these complexes are easily oxidized to uranium(+4). Unlike other anhydrous uranium(+3) compounds, they give relatively stable red solutions in numerous organic solvents such as methanol, ethanol, formic acid, acetic acid, tributhylphosphate and N-methylformamide. They dissolve also in hexamethylphosphoramide with the separation of MCl [M = K, Rb, and NH_4] [12]. These complexes appear to be the only anhydrous and stable uranium(+3) compounds soluble in organic solvents, besides UI_3 and UBr_3 [13].

Magnetic Susceptibility Measurements

The lower parts of the molar magnetic susceptibility *vs.* temperature plots of the three M_2UCl_5 complexes are given in Fig. 1. All of them display the characteristic maximum arising from antiferromagnetism. The observed Néel temperatures are given in Table I. Above the transition temperatures the inverse susceptibility *vs.* temperature plots of the complexes follow the Curie–Weiss law in two temperature ranges [Table I], separated by a slight but apparent break at 130, 150 and 220 °K, for K_2UCl_5, Rb_2UCl_2 and $(NH_4)_2UCl_5$, respectively.

The effective magnetic moments of the investigated complexes are near the value of 3.70 B.M. This value was calculated [14] for the "free ion" moment and the following relationship: $\mu_{eff} = g_J \cdot \sqrt{J(J+1)}$ B.M. was used, where g_J is the intermediate-coupling Lande splitting factor and has a value of 0.743 for U^{+3}. These values differ markedly from those reported for the hydrated double chlorides [9] and the octahedral Cs_2NaUCl_6 complex [15]. However, they are close to the magnetic moments of the halides [16–17] and $U(HCOO)_3$ [10].

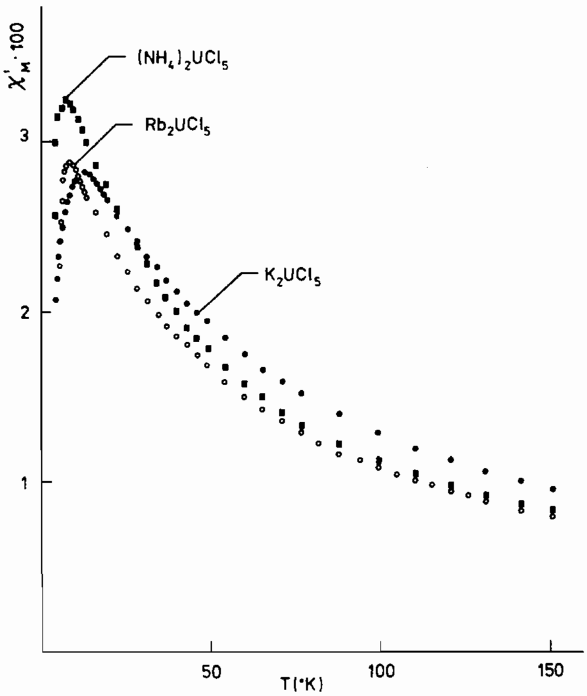

Fig. 1. Molar magnetic susceptibilities of K_2UCl_5 (●), Rb_2UCl_5 (○) and $(NH_4)_2UCl_5$ (■).

Electronic Spectra

The electronic spectra of the investigated complexes are very similar to those of uranium(+3) chloro-complexes in aqueous solutions [1, 3, 5] and in anhydrous media [2, 5–8, 12] as well as to the diffuse reflectance spectra of the red double chlorides [5].

In the observed absorption region one may distinguish two types of transitions [Table II]. The bands of low intensity, centered between 4000–15000 cm^{-1}, are Laporte-forbidden, internal f–f transitions. The energies and relative intensities of these bands are found to be little affected by the change of the environment [8]. Although the f–f bands in this region seem to be typical for uranium(+3), some changes in their intensity pattern and separation may occur. This has been recently observed [12] in the absorption spectrum of Rb_2UCl_5 in hexamethylphosphoramide.

The bands centered in the visible and near-u.v. regions are more likely to change their intensities and energies with varying crystal or ligand fields. In this region broad and very intense bands are observed at 17500–19000 cm^{-1}. The appearance of

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*Halowax = chlorinated naphthalene, index of refraction = 1.635.

TABLE III. Observed maxima in the far-i.r. spectra of the uranium(+3) chloro-complexes.

Compound	Far IR Bands
$(NH_4)_2UCl_5$	140–260 cm^{-1}
K_2UCl_5	140–240 cm^{-1}
Rb_2UCl_5	100–260 cm^{-1}

similar bands has been attributed to the formation of the inner sphere uranium(+3) complexes [3, 6–8] and Laporte-allowed 5f–6d transitions [1, 3, 5–9].

Infrared Spectra

All of the uranium(+3) chloro-complexes show very similar far-i.r. spectra, with one broad band [Table III]. None of the bands are well resolved. Similar far-i.r. spectra have been obtained by Barnard *et al.* [9] for most of the hydrated uranium(+3) double chlorides. The well resolved bands at 230–102 cm^{-1} in the spectrum of the red $RbUCl_4 \cdot 5H_2O$ has been assigned [5] to the uranium–chloride stretching vibrations, by analogy to the i.r. spectra of the americium(+3) chloro-complexes [18]. Kötlisch and Müller [19] have reported that UCl_5-N_3 and $UCl_4(N_3)_2$ exhibit the ν(U–Cl) mode at 347, 320 and 305 cm^{-1}. Hence, one may assume that the bands observed in the spectra of the M_2UCl_5 complexes [Table III] are due to the U–Cl stretching modes. Since these bands are not well resolved, no further information regarding these complexes can be obtained.

Conclusions

The investigated chloro-complexes are, except UBr_3 and UI_3 [13], the only anhydrous and well defined uranium(+3) compounds soluble in organic solvents. Since UBr_3 and UI_3 are less soluble and more sensitive to oxidation, they appear to be most suitable as starting materials for the preparation of new uranium(+3) compounds, especially complex compounds. Furthermore, they may also stimulate interest in the investigations of uranium(+3) solution chemistry and the preparation of corresponding actinide complexes.

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