Preparation and characterization of potassium, rubidium and ammonium tetrachlorouranate(III) trihydrates

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Abstract

The synthesis and characterization of a new series of hydrated uranium(III) complex chlorides of the general formula $M^{I}UCl_{4} \cdot 3H_{2}O$ ($M^{I} \equiv K$, Rb or NH₄) are reported. The compounds crystallize in the monoclinic system. Unit cell parameters were determined from X-ray powder diffraction data. The magnetic susceptibilities of the complex chlorides were measured by the Faraday method in the 4.2–300 K range. The compounds exhibit Curie–Weiss paramagnetism in the 100–300 K range, with the derived effective magnetic moments ranging from $3.57\mu_{B}$ to $3.71\mu_{B}$. Solid state electronic and IR spectra were recorded in the 4000–30 000 and 80–4000 cm⁻¹ ranges, respectively and discussed. Non-static high vacuum thermal dehydrations enabled us to obtain the anhydrous compounds KUCl₄, RbUCl₄ and UCl₃.

1. Introduction

In previous papers, the synthesis and characterization of a series of red-purple complex chlorides with the composition $M^{I}UCl_{4} \cdot 4H_{2}O$ (where $M^{I} \equiv K$, Rb or NH₄) [1], as well as of a brown-green compound with an incorrectly assumed formula CsUCl₄·4H₂O [2], have been reported. Crystal structure determinations revealed [3] that the caesium compound is truly a trihydrate, *i.e.* CsUCl₄·3H₂O. Recently, we succeeded also in the preparation of the other members of the series of the general formula $M^{I}UCl_{4} \cdot 3H_{2}O$ (where $M^{I} \equiv K$, Rb or NH_4). Prior to this, the synthesis of a similar series of red-purple pentahydrates as well as of two olive-green complexes with an uncertain degree of hydration has been reported by Bullock and coworkers [4]. On the basis of our preparative method, we could not confirm the existence of the ammonium, potassium and rubidium tetrachlorouranate(III) pentahydrates. The two olive-green complexes, *i.e.* $NH_4UCl_4 \cdot xH_2O$ and RbUCl₄·xH₂O, most probably correspond to the trihydrates reported in this paper, but no physicochemical data of the first complex are available for comparison. One should also note that, besides some expected similarities, the compounds of all the series are reported to exhibit marked differences.

2. Experimental procedure

2.1. Synthesis

For the preparation of $NH_4UCl_4 \cdot 3H_2O$ or Rb-UCl_4 \cdot 3H_2O, a solution consisting of 50 cm³ acetonitrile, 5 cm³ propionic acid and 0.05 cm³ water was mixed for a few hours with 4.3 g UCl₄ and an excess of NH₄Cl or RbCl respectively. After filtering and adding 0.5 cm³ water, the solution was reduced under anaerobic conditions by shaking with a 2.4% liquid zinc amalgam. The greenish-brown, fine crystalline precipitate formed during the reduction was filtered off, washed under an inert atmosphere with a degassed 100:0.8 solution of acetonitrile and water, dried *in vacuo* and stored under nitrogen in sealed tubes at temperatures below 15 °C.

The preparation of $KUCl_4 \cdot 3H_2O$ was performed under somewhat different conditions. In this case, the solution to be reduced consists of 3g UCl₄, an excess of KCl, 50 cm³ CH₃CN, 1 cm³ propionic acid and 0.05 cm³ water. After filtering, 0.25 cm³ of water also was added. The very fine crystalline, greyish-green precipitate was washed with a 100:0.15 solution of acetonitrile and water, dried *in vacuo* and stored as described above.

The synthesis was carried out in an all-glass apparatus with provisions for precipitation, filtration, washing and drying under anaerobic conditions [5]. All reagents used were of analytical grade.

2.2. Analytical data

Analysis calculated for $KUCl_4 \cdot 3H_2O$: K, 8.27; U, 50.32; Cl, 29.98; H₂O, 11.43. Found: K, 8.65; U, 49.87; Cl, 29.65; H₂O, 11.68. Calculated for RbUCl₄ · 3H₂O: Rb, 16.46; U, 45.83; Cl, 27.31; H₂O, 10.41. Found: Rb,

16.70; U, 45.42; Cl, 27.44; H₂O, 10.84. Calculated for $NH_4UCl_4 \cdot 3H_2O$: N, 3.10; H, 2.23; U, 52.67; Cl, 31.38. Found: N, 3.26; H, 1.90; U, 52.29; Cl, 31.61.

2.3. Physical measurements

The X-ray powder diffraction analyses were carried out at the Institute of Low Temperature and Structure Research in Wrocław on a Stoe automated X-ray powder diffractometer using Cu K α_1 radiation. The unit cell parameters were obtained by least-squares refinement of about all 25–55 observed reflections.

The magnetic susceptibilities were measured by the conventional Faraday method on polycrystalline samples in the 4.2–300 K range with a field of 6 kOe. The values of the magnetic susceptibilities were corrected for diamagnetic increments.

Solid state electronic spectra of the compounds were recorded on a Cary–Varian 2300 spectrophotometer in the 4000–30 000 cm⁻¹ absorption range. To obtain the spectrum, a well-ground mixture of the appropriate compound with a few drops of chlorinated naphthalene (index of refraction 1.635) was placed between two quartz windows, approximately 1 cm in diameter, pressed to get a transparent layer and put into the cell compartment of the spectrophotometer.

The IR spectra were recorded on Perkin-Elmer 180 and 789 spectrophotometers using KBr pellets as well as nujol mulls and polyethylene plates.

3. Results and discussion

3.1. Characterization of the compounds

Depending on the size of the crystals, $NH_4UCl_4 \cdot 3H_2O$ and RbUCl₄·3H₂O precipitate from the solutions in the form of green, greenish-brown or brown, fine crystalline solids. KUCl₄·3H₂O precipitates as a green and somewhat finer crystalline solid. The complexes are hygroscopic and oxygen sensitive. When exposed to air they change their colour first to a reddish colour (most probably due to the formation of the tetrahydrates) and next to pale green. The compounds are easily soluble in numerous polar organic and inorganic solvents with the formation of more or less unstable solutions. Concentrated hydrochloric acid gives intensely coloured red-purple solutions characteristic of the $[UCl_n]^{3-n}$ species. The potassium and rubidium hydrates can be converted into the anhydrous salts at a non-static vacuum of 10^{-5} to 10^{-6} kPa and temperatures increasing slowly from 20 to 300 °C. Under the same conditions, the ammonium tetrachlorouranate(III) trihydrate turns into anhydrous uranium trichloride.

3.2. X-ray powder diffraction analysis

The X-ray powder diffraction patterns could be indexed on the basis of a monoclinic cell. In Table 1 the lattice constants of the monoclinic cell $(a, b, c \text{ and } \beta)$, the cell volume (V), the number of formular units (Z) and the calculated densities (d_{calc}) are listed. The unit cell parameters were obtained by least-squares refinements of all the observed (25-55) reflections. The observed and calculated d spacings together with the observed relative intensities are available on request from the authors.

3.3. IR spectra

IR investigations show that the compounds possess all the characteristic frequencies of co-ordinated water as well as of the $\nu(U-Cl)$, $\nu((U-Cl-U))$ and $\delta(Cl-U-Cl)$ stretching and bending modes (Table 2). The description of the bands follows those reported earlier [1] for the ammonium, potassium and rubidium tetrachlorouranate(III) tetrahydrates. Some well-resolved bands observed at 103 cm⁻¹ and below correspond probably to a lattice mode. In the IR spectrum of NH₄UCl₄·3H₂O, one may note also the typical frequencies of the NH₄ group.

3.4. Magnetic susceptibilities

The magnetic susceptibilities of the compounds have been measured in the 4.2-300 K range. A linear relationship of $1/\chi_{\rm M}$ vs. T was observed at temperatures higher than 75, 150 and 100 K for the ammonium, potassium and rubidium tetrachlorouranates(III) trihydrates respectively. At lower temperatures the plots curve below the Curie–Weiss line, approaching zero. The paramagnetic constants from the Curie–Weiss law $\chi'_{\rm M} = C/(T - \theta)$ and the effective moments $\mu_{\rm eff} =$ $2.84C^{1/2}\mu_{\rm B}$ are summarized in Table 3. The derived magnetic moments are very close to those obtained for the tetrahydrates [1] as well as to the 'free ion' value [9], indicating a relatively small crystal-field splitting of the ⁴I_{9/2} ground level.

3.5. Electronic spectra

The solid state electronic spectra of the tetrachlorouranates(III) trihydrates (Figs. 1–3) exhibit no essential differences and are similar to those reported for UCl₃·7H₂O [6] and the U³⁺ aquo-ion [7, 8]. One may note only relatively small changes in the band intensities for some of the observed $5f^3 \rightarrow 5f^3$ transitions. However, as compared with the spectra of the tetrachlorouranates(III) tetrahydrates [1], one does not observe the strong and broad Laporte-allowed $5f^3 \rightarrow 5d^26d^1$ transitions in the visible absorption range, *i.e.* between 16 000 and 21 000 cm⁻¹. The appearance of these bands in this range has been attributed to the formation of inner sphere complexes [8] with some of the ura-

Compound	a (Å)	ь (Å)	с (Å)	β (deg)	Z (mol per cell)	V (Å ³)	d_{calc} (g cm ⁻³)
NHJUCL+3H2O	13.7693	8.8990	7.8643	95.65	4	956.95	3.12
KUCL·3H ₂ O	6.9373	7.2658	9.5209	96.71	2	476.62	3.30
RbUCl ₄ ·3H ₂ O	8.8986	6.9738	8.0517	100.84	2	490.75	3.51

TABLE 1. Unit cell data of the compounds

TABLE 2. IR absorption bands of the compounds

Assignment	Frequencies (cm ⁻¹)					
	NH₄UCl₄•3H₂O	KUCl₄•3H₂O	RbUCl₄•3H₂O			
Rocking U-OH ₂	_ 615 sh 590 s	- 635 s 575 s	650 615 600			
Wagging U-OH ₂	470 s	480	485			
ν (U-OH) stretching mode	385 290 sh	425 280 sh	380 285 sh			
ν (U-Cl) stretching mode	266 s 232	260 s 238 202	255 s 220 190			
ν (U-Cl-U) stretching or lattice mode	172	169 125	151 157			
$\delta(Cl-U-Cl)$ bending mode	147 128	144 125	132 127 121 118			
Stretching and bending modes of co-ordinated water $(1550-1650 \text{ cm}^{-1})$	1585 1600 	 1600 	1565 1580 1605 3470			
(3100–3600 cm ⁻¹)	 3340 3410	3170 3215 3360 3420	3180 3210 3350 3420 3470			
$\nu_{4}(NH_{4}) \\ \nu_{2}(NH_{4}) \\ \nu_{4} + \nu_{6}(NH_{4}) \\ 2\nu_{4} - \nu_{5}(NH_{4}) \\ \nu_{1}(NH_{4}) \\ \nu_{3}(NH_{4})$	1404 vs 1670 1770 2710 3040 3160 vs					

s = strong; sh = shoulder; vs = very strong.

TABLE 3. Magnetic susceptibility data

Compound	$\chi_{dia} imes 10^6$ (emu mol ⁻¹)	Range (K)	θ (K)	$C \\ (emu K \\ mol^{-1})$	$\mu_{ ext{eff}}\ (\mu_{ ext{B}})$
NH.UCL+3H-O	- 163 6	75-300	- 54	1 7073	3.71
KUCl ₄ ·3H ₂ O	- 165.2	150-300	-80	1.7033	3.70
RbUCl₄ · 3H ₂ O	- 172.2	100300	- 64	1.5766	3.57

nium-ligand bond lengths of a markedly more covalent character [9]. In agreement with this statement are the results of the recently investigated crystal structure of $CsUCl_4 \cdot 3H_2O$ [3]. The coordination polyhedron consists of six chloride ions forming a trigonal prism, and the three water molecules capping the three tetrangular faces. The received U^{3+} - Cl^- distances of 2.894 to 3.067 Å are somewhat larger than those in the other investigated uranium(III) chlorocomplexes [9] and seem to



Fig. 1. Absorption spectrum of NH₄UCl₄·3H₂O.



Fig. 3. Absorption spectrum of RbUCl₄·3H₂O.

be responsible for the appearance of the $5f^3 \longrightarrow 5f^36d^1$ bands at higher wavenumbers.

3.6. Supplementary material

The observed and calculated d spacings as well as the observed relative intensities and other experimental details are available on request from the authors.



Fig. 2. Absorption spectrum of KUCl₄·3H₂O.

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References

- 1 J. Drożdżyński, J. Less-Common Met., 138 (1988) 271.
- 2 M. Karbowiak and J. Drożdżyński, J. Less-Common Met., 163 (1990) 159.
- 3 K. Krämer, G. Meyer, M. Karbowiak and J. Drożdżyński, J. Less-Common Met., 175 (1991) 347.
- 4 R. Barnard, J. I. Bullock, B. J. Gellatly and L. F. Larkworthy, J. Chem. Soc., Dalton Trans., 18 (1972) 1932.
- 5 J. Drożdżyński, Inorg. Chim. Acta, 32 (1979) L83.
- 6 J. Drożdżyński, Inorg. Chim. Acta, 109 (1985) 79.
- 7 J. Drożdżyński, J. Inorg. Nucl. Chem., 40 (1978) 319.
- 8 M. Shiloh and Y. Marcus, Isr. J. Chem., 3 (1965) 123.
- 9 J. Drożdżyński, in A. J. Freeman and C. Keller (eds.), Handbook on the Physics and Chemistry of the Actinides, Vol. 6, North-Holland, Amsterdam, 1991, p. 281.