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Synthesis and characterization of strontium pentachlorouranate(III) and dibarium heptachlorouranate(III)

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Abstract

Uranium(III) chloro complexes of the formulas $SrUCl_5$ and Ba_2UCl_7 were synthesized and characterized by electronic absorption spectra, X-ray powder diffraction and magnetic susceptibility investigations. Ba_2UCl_7 crystallizes in the monoclinic system, $P2_1/c$, with $a=7.20$ Å, $b=15.61$ Å, $c=10.66$ Å, $\beta=91.1°$ and $Z=4$. Magnetic susceptibilities of polycrystalline samples of the compounds were measured on a SQUID magnetometer in the 1.7–300 K range. The inverse magnetic susceptibility versus temperature plots of $SrUCl_5$ and Ba_2UCl_7 follow the Curie–Weiss law above 90 and 105 K, respectively. The following paramagnetic constants from the Curie–Weiss law $C=\chi_M(T-\Theta)$ have been obtained: $C=1.653$ emu·K·mol^{-1}, $\Theta=-127$ K, $\mu_{eff}=2.84\sqrt{c}=3.65$ B.M. (for $SrUCl_5$) and $C=1.310$ emu·K·mol^{-1}, $\Theta=-95$ K, $\mu_{eff}=3.25$ B.M. (for Ba_2UCl_7). Solid state electronic spectra of the compounds have been recorded in the 4000–30 000 cm^{-1} range and are discussed. © 1998 Elsevier Science S.A.

Keywords: Uranium(III) chloro complexes; Synthesis; Magnetic susceptibilities; Electronic absorption spectra; X-ray powder diffraction data

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1. Introduction

This paper presents the preparation, as well as the X-ray powder diffraction, magnetic and spectroscopic characterization, of uranium(III) chloro complexes with the formulas $SrUCl_5$ and Ba_2UCl_7. The compounds were first identified during investigations of the binary fused salt systems $SrCl_2$–UCl_3 and $BaCl_2$–UCl_3 [1]. To the best of our knowledge, no prior information about the properties of these compounds are available. So far also only structural and some luminescence investigations of the isostructural series of compounds Ba_2MCl_7 (M = Gd–Yb, Y) have been reported [2,3]. The purpose of our investigations was the preparation of uranium(III) compounds suitable for doping into single crystals of isostructural lanthanide complex chlorides. Low temperature spectroscopic measurements, crystal-field analysis and upconversion investigations are in progress.

2. Experimental procedure

2.1. Synthesis

The compounds have been prepared by heating together for seven days in graphite coated quartz tubes a well-ground mixture of stoichiometric amounts of vacuum-dried $SrCl_2$ or $BaCl_2$ with UCl_3. The mixtures were heated in a dynamic vacuum of circ. 10^{-6} hPa at 730°C and 670°C, respectively. Uranium trichloride has been prepared by decomposition of $NH_4UCl_4\cdot 4H_2O$ [4]. Crystalline powders of deep olive-green $SrUCl_5$ and deep black-brown Ba_2UCl_7 have been obtained. The products are not resistant to hydrolysis and oxidation and were stored under nitrogen in sealed tubes.

2.2. Physical measurements

The X-ray powder diffraction analysis of the compounds were carried out in the Institute of Low Temperature and Structure Research in Wrocław on a ‘‘Stoe Fast Powder Diffractometer’’ using Cu Kα radiation. The unit cell parameters were obtained by least-squares refinement of all observed reflections.

Absorption spectra of thin films of the complex chlorides were recorded on a Cary 5 NIR-Vis-UV spectrophotometer at 300 K. A well-ground mixture of the compound with some paraffin oil was placed between two quartz windows, approximately 1 cm in diameter, pressed to get a transparent layer, and put into the cell compartment of this spectrophotometer.

Magnetic susceptibilities of polycrystalline samples of the compounds were measured on a MPMS-5 type SQIUD magnetometer in the 1.7–300 K range. Corrections for

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diamagnetism of the constituent atoms were made using Pascal’s constants.

3. Results and discussion

3.1. Characterization of the compounds

The compounds form well crystalline solids. A deep olive-green crystalline powder of $SrUCl_5$ and a deep black-brown powder of Ba_2UCl_7 have been obtained. The products are not resistant to hydrolysis and oxidation. On exposure to air the heptachloride becomes pale brown and then green, whereas the pentachloride first turns red and then green. The compounds are readily soluble in numerous polar organic solvents like methanol, ethanol and formic acid. In water and aqueous solutions they dissolve with decomposition and oxidation to U(IV). In conc. HCl they are soluble with the formation of unstable UCl_n^{3-n} complex anions (where $3<n<6$).

3.2. X-ray powder diffraction analysis

The powder pattern of Ba_2UCl_7 was indexed on the basis of a monoclinic cell with $a=7.20$ Å, $b=15.61$ Å, $c=10.66$ Å, ($\beta=91.1°$ whose $V=1197$ Å^3. There are four molecules per unit cell. The calculated and pyknometrically measured densities are 4.22 and 4.14 g cm^{-3}, respectively. The diffraction data have proved that the compound is isotypic with the series of compounds Ba_2MCl_7 (M= Gd–Yb, Y) [2,3] that has been assigned to the space group $P2_1/c$. Hence, one can assume that the characteristic feature of the crystal structure is isolated polyhedrons of seven-coordinated U^{3+} ions, which has been described as trigonal prisms monocapped on a rectangular prismatic face [2]. Because there are no X-ray data of isostructural lanthanide compounds available, the diffraction pattern obtained from $SrUCl_5$ could not be unambiguously indexed. The observed and calculated d spacings and observed relative intensities for Ba_2MCl_7 are listed in Table 1 whereas the observed d spacings and relative intensities for $SrUCl_5$ are given in Table 2.

Table 2
Observed d spacings and relative intensities for $SrUCl_5$

$d_{obs.}$	I/I_0	$d_{obs.}$	I/I_0
6.534	36.7	2.023	14.6
4.067	90.8	1.932	26.7
3.747	22.8	1.751	11.0
3.601	35.9	1.648	27.4
3.520	32.7	1.605	13.52
3.163	79.7	1.578	10.7
2.911	19.2	1.429	23.5
2.735	36.3	1.347	11.4
2.589	31.0	1.313	8.5
2.479	100	1.254	11.0
2.320	22.4	1.236	9.7
2.151	21.0	1.219	8.2
2.110	45.9		

3.3. Magnetic susceptibilities

The inverse magnetic susceptibility versus temperature plots of $SrUCl_5$ and Ba_2UCl_7 follow the Curie–Weiss law above 90 and 105 K, respectively. The paramagnetic constants derived from the Curie–Weiss law $C=\chi_M(T-\Theta)$ are summarized in Table 3. At lower temperatures the plots curve below the Curie–Weiss line approaching zero (Fig. 1). Such a zero-converging character of the plot is typical for lanthanide and actinide ions exhibiting a Kramers doublet in the ground state [5]. The derived magnetic moments are close to those reported for other anhydrous uranium(III) complex chlorides [6,7].

Table 1
Observed and calculated d spacings and observed and calculated intensities for Ba_2MCl_7

h	k	l	$d_{obs.}$	$d_{calc.}$	I/I_0	h	k	l	$d_{obs.}$	$d_{calc.}$	I/I_0
1	1	0	6.5185	6.5302	21.3	−2	4	1	2.5698	2.5875	9.4
0	2	1	6.2868	6.2938	8.2	2	3	2	2.5529	2.5541	80.3
−1	2	1	4.8199	4.8029	7.1	2	1	3	2.4121	2.4372	7.6
1	2	1	4.6676	4.6712	7.5	3	0	0	2.3807	2.3966	8.1
−1	1	2	4.1703	4.1955	100.0	2	4	2	2.3511	2.3356	8.7
1	1	2	4.0267	4.0413	10.1	3	2	0	2.3029	2.2910	12.1
1	2	2	3.6776	3.6874	9.7	−1	3	4	2.2724	2.2730	16.8
2	0	0	3.6068	3.5966	27.4	2	3	3	2.2431	2.2294	8.3
2	0	1	3.3523	3.3579	12.3	0	7	1	2.1838	2.1824	39.9
2	2	0	3.2567	3.2651	11.4	−2	4	3	2.1798	2.1564	31.2
−1	1	3	3.1594	3.1631	20.5	−3	2	2	2.1492	2.1399	11.3
1	1	3	3.0463	3.0629	9.8	1	4	4	2.0860	2.0826	13.5
−2	1	2	2.9828	2.9904	11.7	−3	0	3	2.0451	2.0312	10.2
1	2	3	2.9119	2.9000	10.5	−1	5	4	1.9752	1.9680	14.1
2	3	1	2.8171	2.8213	13.1	−2	4	4	1.9204	1.9092	9.8
−1	3	3	2.7349	2.7442	16.0	−3	5	1	1.8759	1.8861	12.4
1	3	3	2.6702	2.6780	9.7	2	4	4	1.8542	1.8437	11.5

Table 3
Magnetic susceptibility data

Compound	Colour	$\chi_{\mathrm{dia}} \times 10^6$ (emu·K·mol^{-1})	Curie–Weiss range (K)	Θ (K)	C (emu·K·mol^{-1})	μ_{eff} (B.M.)
$SrUCl_5$	Deep olive-green	−191	90–300	−127	1.653	3.65
Ba_2UCl_7	Deep black-brown	−276	105–300	−95	1.310	3.25

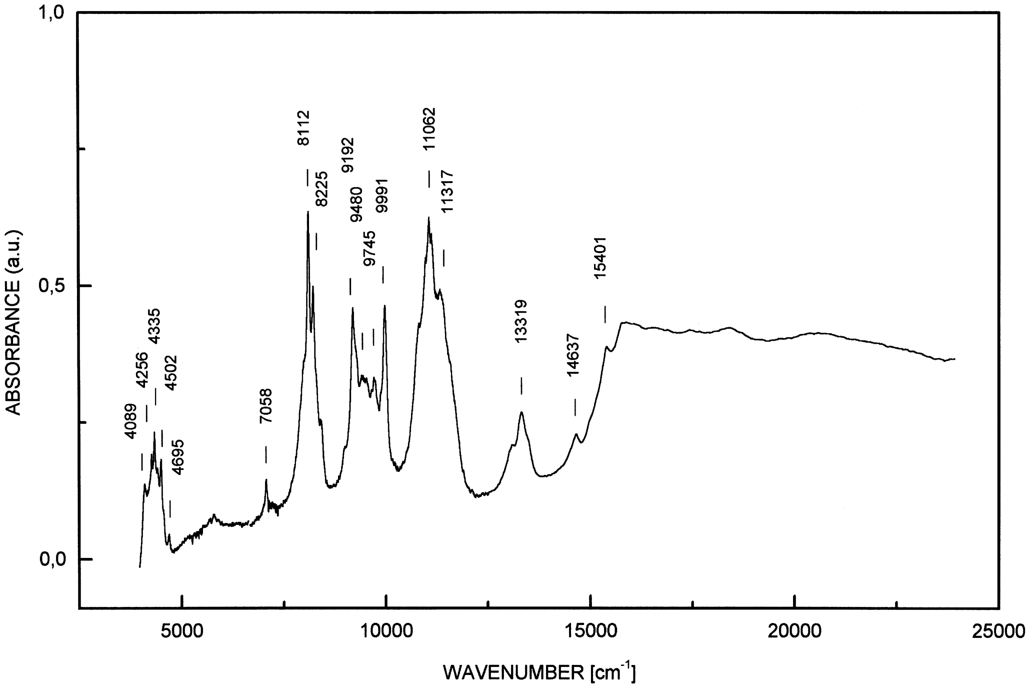

Fig. 1. Solid state electronic absorption spectrum of $SrUCl_5$.

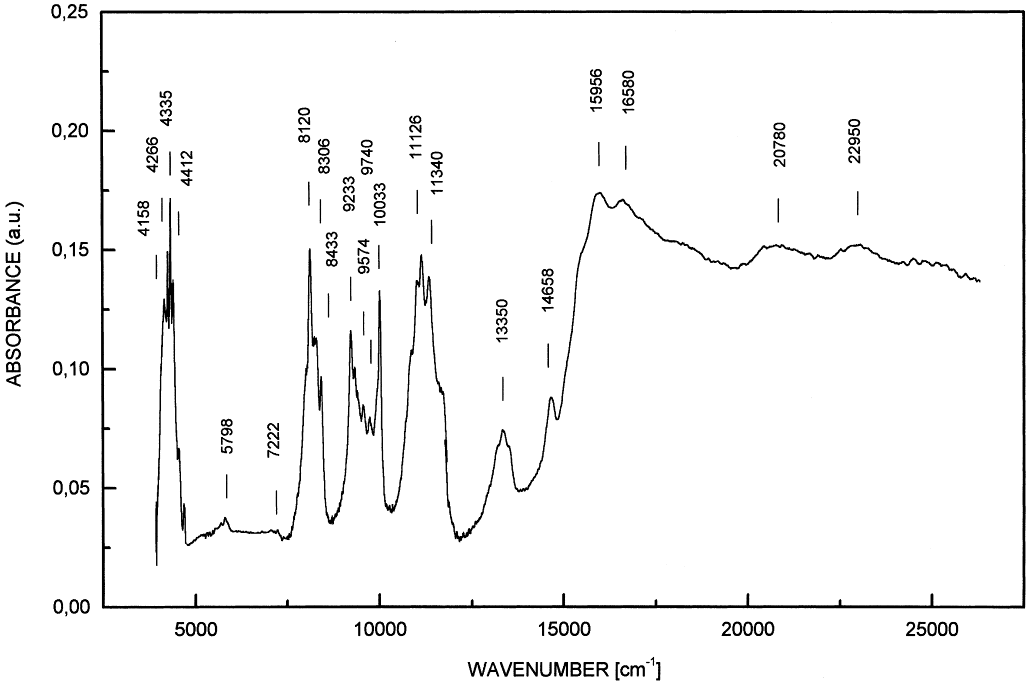

Fig. 2. Solid state electronic absorption spectrum of Ba_2UCl_7.

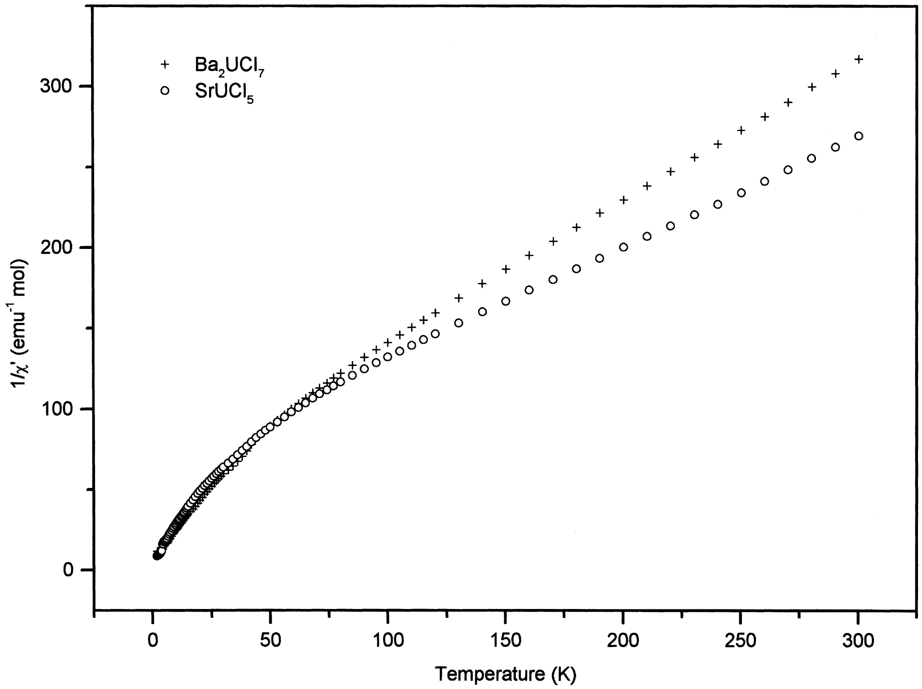

Fig. 3. Inverse magnetic susceptibilities of $SrUCl_5$ and Ba_2UCl_7 vs temperature.

3.4. Electronic spectra

In the 4000–15 000 cm^{-1} range, the solid state electronic absorption spectra of $SrUCl_5$ and Ba_2UCl_7 are typical for uranium(III) complex chlorides and consist of the characteristic $5f^3 \rightarrow 5f^3$ transitions [6] which belong to the $^4I_{11/2}$, $^4F_{3/2}$, $^4I_{13/2}$, $^2H_{9/2}$, $^4F_{5/2}$, $^4S_{3/2}$, $^4G_{5/2}$, $^4I_{15/2}$, $^4F_{5/2}$, $^4G_{7/2}$ and $^4F_{9/2}$ multiplets. Absorption bands of uranium(III) complex compounds which possess some of the uranium-ligand bonds of a somewhat more covalent character than those of the U^{3+} aquo-ion, e.g. in $UCl_3 \cdot 7H_2O$ [8] or $CsUCl_4 \cdot 3H_2O$ [9], are in the 15 000–20 000 cm^{-1} range obscured by very strong and broad $5f^3 \rightarrow 5f^2 6d^1$ bands. A red shift of the first $5f^3 \rightarrow 5f^2 6d^1$ bands from wavenumbers higher than 20 000 cm^{-1} into the visible region of the spectra has been attributed to the formation of inner sphere complexes [6]. In the investigated spectra (Figs. 2 and 3) one does observe the appearance of similar bands however of unusually low intensity which may be indicative of somewhat larger uranium-ligand bond lengths than in other anhydrous uranium(III) complex chlorides.

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