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Synthesis and characterization of caesium tetrachlorouranate(III) and dicaesium lithium hexachlorouranate(III)

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Abstract

Uranium(III) chloro complexes of formulae $CsUCl_4$ and Cs_2LiUCl_6 were synthesized and characterized by electronic absorption, X-ray powder diffraction and magnetic susceptibility investigation. Cs_2LiUCl_6 crystallizes in the regular system *Fm3m*, with $a=10.671$ Å, $V=1218.03$ Å^3 and $Z=4$. The powder diffraction data for $CsUCl_4$ could not be indexed unambiguously. The following paramagnetic constants were obtained: $C=1.215$ emu K mol^{-1}, $\Theta=-32.7$ K, $\mu_{\mathrm{eff}}=3.13$ B.M. (for $CsUCl_4$) and $C=1.571$ emu K mol^{-1}, $\Theta=-103$ K, $\mu_{\mathrm{eff}}=3.56$ B.M. (for Cs_2LiUCl_6). Solid state electronic spectra of the compounds were recorded in the range 4000–30 000 cm^{-1} and are discussed. An analysis of the $5f^3 \rightarrow 5f^2 6d^1$ transitions in the absorption spectrum of Cs_2LiUCl_6 is presented.

Keywords: Electronic absorption spectra; Elpasolites; f→d transitions; Magnetic susceptibilities; Synthesis; Uranium(3+) chloro complexes; X-ray powder diffraction data

1. Introduction

This paper presents the preparation and X-ray powder diffraction, magnetic and spectroscopic characterization of uranium(3+) chloro complexes of formulae $CsUCl_4$ and Cs_2LiUCl_6. $CsUCl_4$ was first identified during investigations of the binary fused salt system CsCl–UCl_3 together with an X-ray powder diffraction analysis according to which the compound crystallizes in the cubic system with $a=9.16$ Å [1,2]. An analysis of the emission and vibronic transitions in uranium(3+) doped Cs_2LiYCl_6 single crystals has also been reported [3]. No further information on the properties of the compounds is available. The purpose of our investigation was to prepare uranium(III) compounds with a high site symmetry for the central metal ion which offers good opportunities for studying the very complex magnetic and spectroscopic properties of the ion.

2. Experimental procedure

2.1. Synthesis

$CsUCl_4$ was prepared by: (a) vacuum thermal dehydration of $CsUCl_4\cdot 4H_2O$ [4]; (b) heating together in a quartz tube for 2 days stoichiometric quantities of UCl_3 and CsCl at 450°C under a vacuum of about 10^{-6} hPa; (c) heating together under anaerobic conditions stoichiometric amounts of UCl_3 and CsCl for 24 h at 700 and 850°C and then at 500°C for 5 days. With all methods a deep ink-blue fine crystalline, hygroscopic product was obtained.

For the preparation of Cs_2LiUCl_6 a well-ground stoichiometric mixture of CsCl, $NH_4UCl_4\cdot H_2O$ [5] and LiCl was first heated in a quartz tube under a non-static vacuum of ca. 10^{-6} hPa. In order to convert $NH_4UCl_4\cdot 4H_2O$ into UCl_3 [6], the temperature of the furnace was increased slowly from 20 to 350°C. The tube was then sealed and the mixture heated for 24 h at 350°C. Subsequently, the temperature was increased slowly and the mixture heated at 450°C for 60 h yielding a deep ink-blue fine crystalline powder. The compound was stored under nitrogen in sealed tubes.

2.2. Physical measurements

The X-ray powder diffraction analysis of Cs_2LiUCl_6 was carried out at the Institute of Low Temperature and Structure Research, Wrocław, on a Stoe fast powder diffractometer using Cu Kα radiation. The unit cell parameters were obtained by least-squares refinement of 13 of the 14 observed reflections.

Absorption spectra of thin films of the compounds were

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recorded on a Cary 5 NIR–Vis–UV spectrophotometer at 300 K. A well-ground mixture of the compound with some chlorinated naphthalene (index of refraction 1.635) was placed between two quartz windows, approximately 1 cm in diameter, pressed to obtain a transparent layer, and placed in the cell compartment of the spectrophotometer.

The magnetic susceptibilities of polycrystalline samples of the compounds were measured by the Faraday method in the range 4.2–300 K. Corrections for the diamagnetism of the constituent atoms were made using Pascal's constants.

3. Results and discussion

3.1. Characterization of the compounds

The compounds consisted of fine crystalline dark ink-blue solids, readily soluble in numerous polar organic solvents such as methanol, ethanol, formic acid and dimethylformamide. In water and aqueous solution they dissolve with decomposition and oxidation to U(IV). They are soluble in conc. HCl with the formation of the characteristic unstable UCl_n^{3-n} complex anions (where $3<n<6$). The compounds are hygroscopic and sensitive to oxidation on exposure to air.

3.2. X-ray powder diffraction analysis

The powder pattern of Cs_2LiUCl_6 was indexed on the basis of a regular cell with $a=10.6713$ Å and $V=1218.03$ Å^3. There are four molecules per unit cell. The calculated and pyknometrically measured densities are $d_{calc}=3.944$ g cm^{-3} and $d_{exp}=3.91$ g cm^{-3}, respectively. The diffraction data demonstrate that the compound is isostructural with Cs_2LiYCl_6 [7]. Hence, one can assume that, similar to other cubic face-centered elpasolites, the U^{3+} ion has an octahedral environment of six chloride ligands. The observed and calculated d spacing and the relative intensities for Cs_2LiUCl_6 are listed in Table 1.

Table 1
Observed and calculated d spacings and observed relative intensities for Cs_2LiUCl_6

hkl	d_{obs}	d_{calc}	I/I_0
111	6.1582	6.1611	56
	4.4254		11
220	3.7676	3.7729	100.0
311	3.2130	3.2175	37
222	3.0790	3.0805	17
321	2.8674	2.8520	6
400	2.6641	2.6678	45
331	2.4422	2.4482	17
422	2.1780	2.2783	33
511	2.0504	2.0506	9
440	1.8885	1.8864	22
620	1.6890	1.6873	10
444	1.5404	1.5403	8
642	1.4249	1.4260	9

The X-ray powder diffraction data for $CsUCl_4$ did not confirm the previously reported result that the compound posseses cubic symmetry [1]. Irrespective of the method of preparation we always obtained exactly the same powder diffraction pattern (Table 2), indicating a much lower symmetry. This is confirmed by the appearance of relatively strong $5f^3 \rightarrow 5f^3$ transitions in the solid state absorption spectrum, which are indicative of a non-regular environment of the U^{3+} ion (Fig. 1). Since information on corresponding lanthanide compounds with a known crystal structure is not available the diffraction pattern could not be indexed unambiguously.

3.3. Magnetic susceptibility

The inverse magnetic susceptibility vs. temperature plots for $CsUCl_4$ and Cs_2LiUCl_6 follow the Curie–Weiss law above 60 and 85 K, respectively. The obtained paramagnetic constants 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. Such zero-converging character of the plots is typical for lanthanide and actinide ions exhibiting a Kramers doublet in the ground state. The derived magnetic moments are somewhat smaller than the values predicted on the basis of the available intermediate coupling wave functions of the $^4I_{9/2}$ ground state [2,8], but are similar to those reported for other anhydrous uranium(3+) complex chlorides [2]. The absence of magnetic transitions up to 4.2 K indicates that, due to magnetic dilution in the compounds, the interactions between the uranium ions are so weak that magnetic ordering does not occur. Magnetic susceptibility measurements at lower temperatures together with model calculations of the temperature dependence of the magnetic susceptibility are in progress.

3.4. Electronic spectra

The solid state electronic absorption spectrum of $CsUCl_4$ is typical for those uranium(3+) complex compounds which possess uranium–ligand bonds of a somewhat more covalent character [2] as compared with those

Table 2
Observed d spacings and relative intensities for $CsUCl_4$

d_{obs}	I/I_0	d_{obs}	I/I_0
8.409	12	3.042	17
7.353	27	2.953	5
5.576	10	2.848	17
4.828	12	2.751	20
4.264	35	2.624	25
4.041	100	2.526	12
3.870	31	2.428	51
3.714	14	2.295	18
3.654	11	2.135	7
3.401	7	1.995	9
3.181	15		

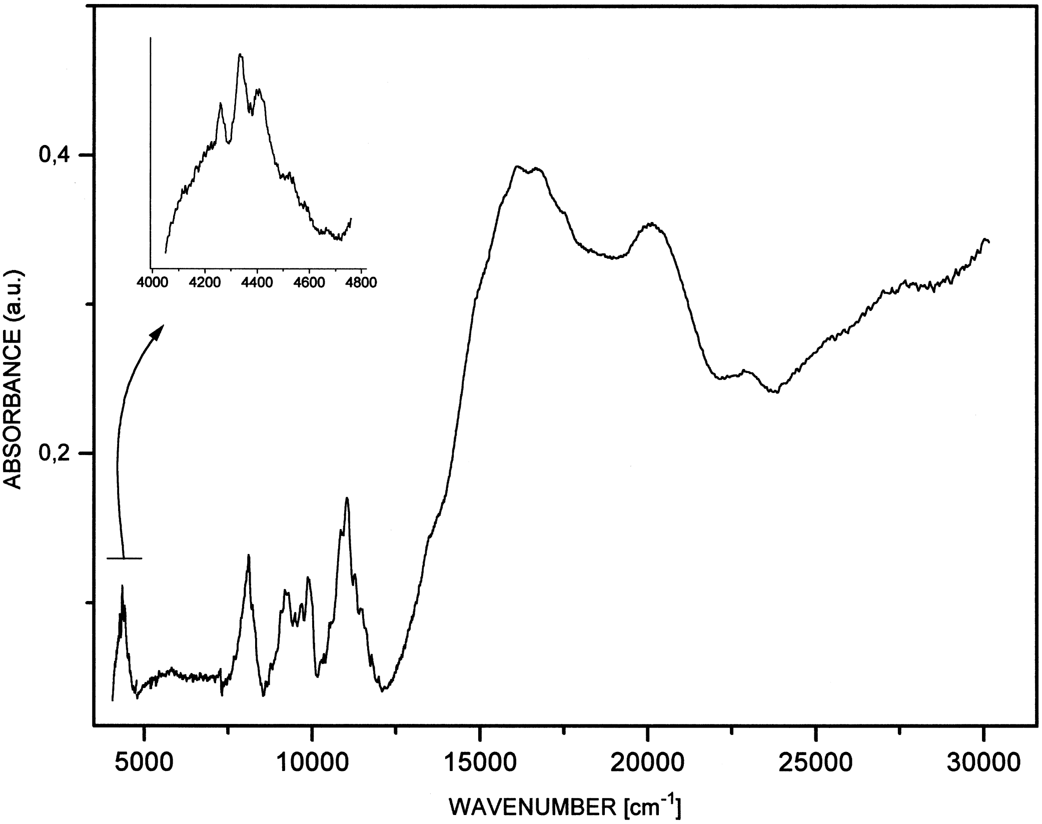

Fig. 1. Solid state absorption spectrum of $CsUCl_4$.

of the U^{3+} aquo-ion, e.g. $UCl_3 \cdot 7H_2O$ [9] and $CsUCl_4 \cdot 4H_2O$ [4]. In the 4000–15 000 cm^{-1} absorption range the investigated spectrum consists of $5f^3 \rightarrow 5f^3$ transitions characteristic of U^{3+}. Above this region, these transitions are obscured by strong and broad $5f^3 \rightarrow 5f^2 6d^1$ bands. The red shift of the first $5f^3 \rightarrow 5f^2 6d^1$ bands from wave numbers higher than 20 000 cm^{-1} into the visible region of the spectra has been attributed to the formation of inner sphere complexes [2].

In the absorption spectrum of Cs_2LiUCl_6 (Fig. 2) one does not observe the characteristic $5f^3 \rightarrow 5f^3$ transitions because the U^{3+} ions are located in the center of symmetry. Hence, pure electric dipole transitions are additionally forbidden and may to some extent appear only due to mixing with odd parity states. They are, however, too weak to be observed in the solid state absorption spectrum of thin layers of the compound. Hence, the spectrum consists only of a number of broad and very intense Laporte allowed $5f^3 \rightarrow 5f^2 6d^1$ transitions (Fig. 2). The wave numbers and relative intensities of these bands are very similar to those observed in the spectra of octahedral $Cs_2NaYCl_6{:}U^{3+}$ [10] and tetragonal $[(CH_3)_4N]_3UCl_6$ [11] complexes. One may distinguish five groups of bands with centers of gravity at 15 830, 19 090, 31 660, 35 000 and 39 220 cm^{-1} (Fig. 2). The interpretation of these transitions was based on the semi-empirical method developed by Johnson and Sandoe [12]. According to this theory the observed f–d bands correspond to $4f^N \rightarrow J_i\gamma_N$ transitions, where $J_i\gamma_N$ is the state of the d-electron in the octahedral crystal field, Δ is the separation between γ_3 and γ_5 in O_h, i.e. the crystal-field splitting of the d-electron level, and J_i is the total angular momentum of the Russel Saunders term derived for the $4f^{N-1}$ core. The $4f^2 5d^1$ configuration is assumed to behave according to the $J_i\gamma_N$ coupling scheme. The observed centers of gravity (I–V) agree very well with the type of energy scheme [11] according to which the separation between the III and I and IV and II bands should be alike. These values are indicated by the parameters Δ and Δ' and were found to be 15 830 and 15 910 cm^{-1}, respectively. On this basis, the excitation energy, $E_{fd} =$

Table 3
Magnetic susceptibility data

Compound	Colour	χ_{dia} ($\times 10^{-6}$) (emu K mol^{-1})	Curie–Weiss range (K)	Θ (K)	C (emu K mol^{-1})	μ_{eff} (B.M.)
$CsUCl_4$	Dark ink-blue	−161	60–300	−36	1.2146	3.16
Cs_2LiUCl_6	Dark ink-blue	−264	85–300	−103	1.571	3.56

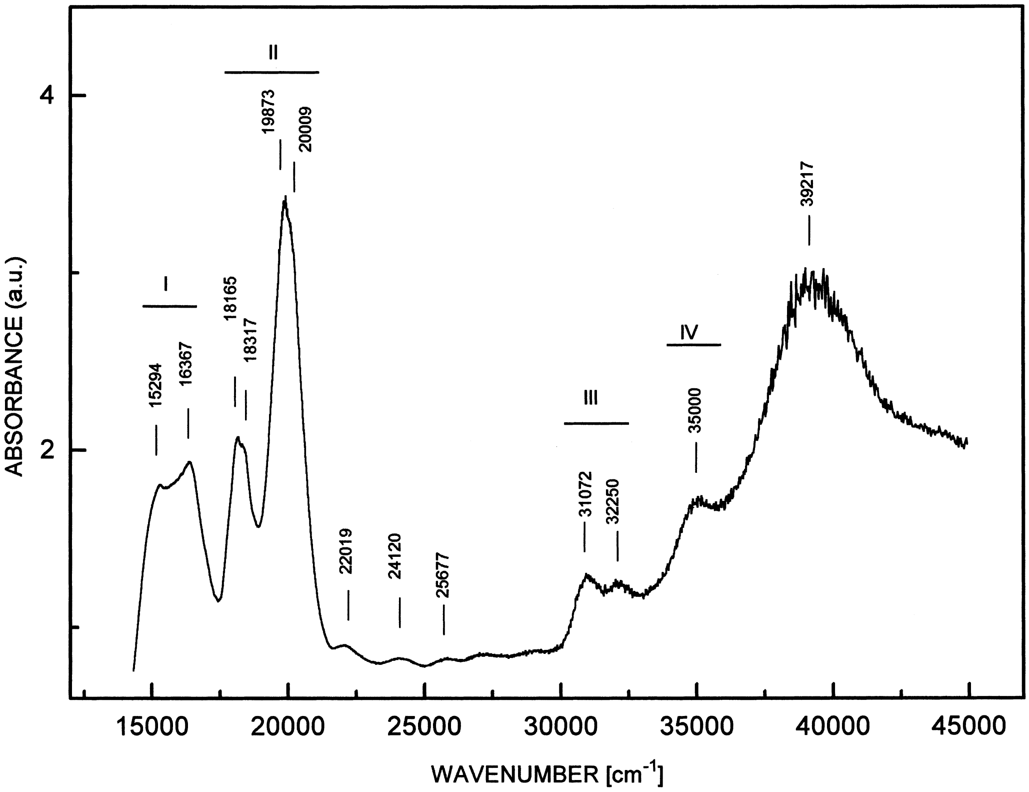

Fig. 2. Solid state absorption spectrum of Cs_2LiUCl_6.

22 160 cm^{-1}, uncorrected for the nephelauxetic effect, was determined together with the separation, $E_{ff} = 3290\ cm^{-1}$, of the first two terms of the $5f^26d^1$ configuration. The positions of the original levels were calculated using the barycenter rule. The excellent agreement obtained between this and previous investigations [10,11] confirms the possibility of analysing the $5f^3 \rightarrow 5f^26d^1$ transitions by means of the $J_i\gamma_N$ scheme of interactions.

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