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CHEMISTRY OF TERVALENT URANIUM. PREPARATION AND PROPERTIES OF $NH_4UBr_4.1.5CH_3CN.6H_2O$

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Summary

The paper presents the preparation, X-ray powder diffraction data as well as some magnetic and spectroscopic properties of a new uranium(III) complex bromide of the formula $NH_4UBr_4.1.5CH_3CN.6H_2O$. The compound crystallizes in the monoclinic system with $a = 11.877$ Å, $b = 6.385$ Å, $c = 6.815$ Å, $\beta = 101.29°$ and $Z = 2$. In the 60–240 K range it follows the Curie–Weiss law with $\theta = -37.24$ K and $\mu_{eff} = 3.20$ B.M. The IR and UV-VIS absorption spectra were recorded in the 80–4000 cm^{-1} and 4000–26000 cm^{-1} spectral ranges respectively. Thermal decomposition at a non-static high vacuum enabled the conversion of the compound into pure and anhydrous UBr_3.

1. Introduction

In previous papers [1–4] we have reported on the synthesis and characterization of a number of anhydrous and hydrated uranium(III) complex compounds. This paper reports the preparation along with some structural magnetic and spectroscopic characterization of a new uranium(III) complex bromide of the formula $NH_4UBr_4.1.5CH_3CN.6H_2O$. Apart from $UBr_3.6H_2O$ [5], no other hydrated uranium(III) complex bromides have been isolated so far [6].

2. Experimental details

2.1. Synthesis

Between 4 and 4.4 g of UBr_4 was added, on shaking, to a mixture of 100 cm^3 of methyl cyanide with an excess of ammonium bromide and left to stand for 10–15 h. Subsequently, 0.5 cm^3 propionic acid, 0.4 cm^3 water and, after 0.5 h, 15 cm^3 of freshly distilled ether were added. After filtering, the solution was reduced in an inert atmosphere by shaking with liquid zinc amalgam. The reduction was accomplished in a relatively simple all-glass apparatus with provisions for precipitation, filtration and drying in an inert atmosphere [1]. The inert atmosphere was

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received by vacuum evaporation of the solution for 1–2 min. The reduction resulted in a change in the colour of the solution from green to dark brown, followed by the immediate formation of a fine crystalline greyish-green precipitate of the formula $NH_4UBr_4.1.5CH_3CN.6H_2O$.

The precipitate was filtered off, washed under an inert atmosphere with a deoxygenated 7:1:0.05 solution of acetonitrile, ether and propionic acid, and then washed with ethyl ether. Finally, the compound was vacuum dried by connecting the filter flask to a vacuum pump for about 5 min. The compound was stored under nitrogen in sealed tubes at temperatures below 15 °C.

UBr_4 was prepared according to the procedure given in ref. 7. Other reagents were of analytical grade.

2.2. *Analytical data*

Calculated for $NH_4UBr_4.1.5CH_3CN.6H_2O$: U, 31.93; Br, 42.88; N, 4.70; H, 2.77; C, 4.83; found: U, 31.77; Br, 42.64; N, 4.73; H, 2.52; C, 4.87.

2.3. *Physical measurements*

The X-ray powder diffraction analysis was carried out at the Institute of Low Temperature and Structure Research in Wrocław on a computerized STADI P diffractometer combined with a Mera 79100 monitor, using Cu $K\alpha_1$ radiation. Unit cell parameters were obtained by a least-squares refinement of all 37 observed reflections.

The magnetic susceptibility was measured by the conventional Faraday method in the 4–300 K range and a magnetic field of 6 KOe, on a polycrystalline

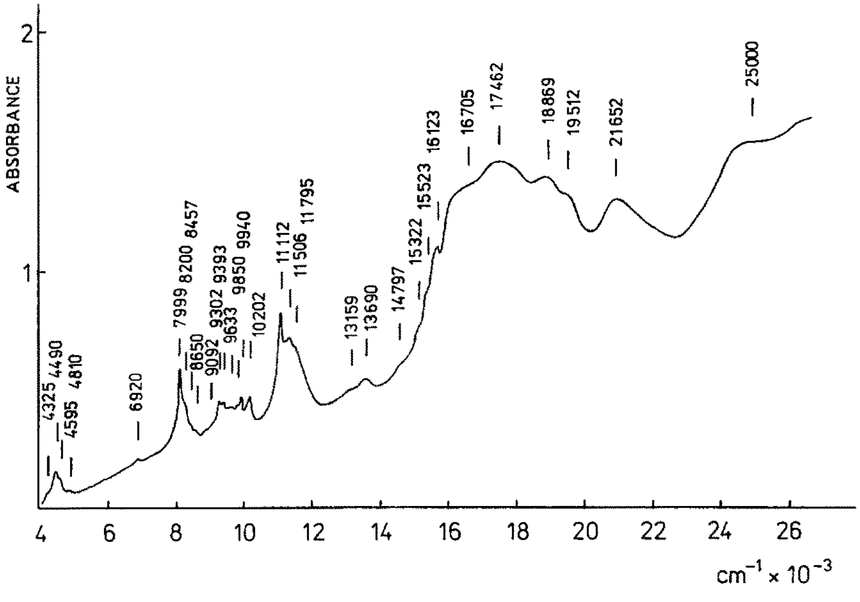

Fig. 1. Absorption spectrum of $NH_4UBr_4.1.5CH_3CN.6H_2O$.

sample sealed in a quartz tube. The values were corrected for diamagnetic increments.

In order to obtain the electronic spectrum, a well-ground mixture of the compound with some Halowax oil (chlorinated naphthalene, index of refraction 1.635) was placed between two quartz windows approximately 1 cm in diameter, pressed to get a transparent and uniform layer, and put into the cell compartment of the spectrophotometer. The solid state absorption spectrum of the thin film was recorded on a Cary-Varian 2300 spectrophotometer in the 4000–20000 cm^{-1} range.

The IR spectrum was recorded on Perkin–Elmer 180 and 789 spectrophotometers using hexachlorobutadiene and nujol mulls, as well as KBr, CaF_2 and polyethylene plates.

3. Results and discussion

3.1. Characterization of the compound

The compound is a pale-green, fine crystalline solid which must be handled under anhydrous and oxygen-free conditions. Somewhat larger crystals are dark green.

The complex is easily soluble in a number of organic solvents, *e.g.* methanol, ethanol, formic acid, tributhylphosphate and dimethylformamide. In water and aqueous solutions it is soluble with oxidation to uranium(IV). Repeatable analytical data show that the compound fits best with a formula containing 1.5 CH_3CN and $6H_2O$ molecules.

The complex bromide may be converted into pure and anhydrous UBr_3 in a thermal high vacuum decomposition at about 10^{-5} to 10^{-6} hPa and temperatures ranging from 20 to 300 °C. The decomposition was performed in a quartz tube connected with an effective, non-static high vacuum system. The temperature was not raised at pressures higher than 10^{-5} hPa. The pyknometrically determined density of UBr_3 was found to be 6.20 g cm^{-3}, which is somewhat better than the value reported in the literature [8]. From X-ray data [8] a value of 6.54 g cm^{-3} was obtained. Analysis calculated for UBr_3: U, 49.82; Br, 50.18; found: U, 50.09; Br, 50.36%.

3.2. X-ray powder diffraction analysis

Table 1 lists the observed and calculated *d* spacings as well as the observed relative intensities for $NH_4UBr_4.1.5CH_3CN.6H_2O$.

The compound crystallizes in the monoclinic system with a primitive unit cell and the following lattice parameters: $a=11.877$ Å, $b=6.385$ Å, $c=6.815$ Å, $\beta=101.29°$ and $V=506.81$ Å^3. There are two molecules per unit cell. The calculated and pyknometrically measured densities are 2.94 g cm^{-3} and 2.82 g cm^{-3} respectively.

3.3. IR spectra

IR investigations show that the compound possesses all of the characteristic frequencies of coordinated CH_3CN and H_2O. The description of the observed

TABLE 1

Observed and calculated *d* spacings and observed relative intensities for $NH_4UBr_4 \cdot 1.5CH_3CN \cdot 6H_2O$

h k l	d_0 (Å)	d_c (Å)	I/I_0
$\bar{1}$ 0 1	6.3526	6.3588	100.0
1 1 0	5.6031	5.5988	27.0
0 1 1	4.6198	4.6166	8.5
$\bar{1}$ 1 1	4.4999	4.5055	34.4
2 1 0	4.3010	4.3027	9.1
1 1 1	4.1130	4.1059	44.3
2 0 1	4.0257	4.0183	46.7
$\bar{3}$ 0 1	3.7031	3.6849	7.5
$\bar{1}$ 0 2	3.3905	3.3928	8.7
0 0 2	3.3471	3.3416	19.5
3 1 0	3.3192	3.3173	54.5
$\bar{2}$ 0 2	3.1795	3.1794	13.5
3 0 1	3.1007	3.1036	6.6
1 0 2	3.0524	3.0573	7.4
$\bar{4}$ 0 1	2.8870	2.8842	12.8
$\bar{2}$ 1 2	2.8466	2.8460	17.5
2 0 2	2.6804	2.6807	19.2
4 1 0	2.6553	2.6494	9.1
$\bar{3}$ 1 2	2.5824	2.5798	12.7
2 2 1	2.4976	2.4996	36.8
$\bar{4}$ 0 2	2.4460	2.4451	3.7
0 2 2	2.3062	2.3083	12.1
$\bar{2}$ 2 2	2.2530	2.2528	9.7
3 2 1	2.2250	2.2253	3.4
1 2 2	2.2147	2.2081	5.4
$\bar{5}$ 1 1	2.1993	2.2030	4.8
4 2 0	2.1508	2.1514	3.9
$\bar{1}$ 1 3	2.1369	2.1402	3.2
2 2 2	2.0522	2.0529	4.6
$\bar{5}$ 1 2	2.0082	2.0077	3.8
$\bar{4}$ 0 3	1.9650	1.9646	4.3
6 0 0	1.9420	1.9412	7.7
$\bar{7}$ 0 1	1.6958	1.6942	4.2
$\bar{4}$ 2 3	1.6745	1.6731	6.4
7 0 0	1.6630	1.6639	6.6
$\bar{6}$ 2 2	1.5941	1.5958	5.2
$\bar{6}$ 1 3	1.5790	1.5794	4.3

bands follows those reported earlier for $UCl_3 \cdot CH_3CN$ [9] and $UCl_3 \cdot CH_3CN \cdot 5H_2O$ [3]. Coordination through the nitrogen atom is indicated by the appearance of the ν[U–NC(CH_3)] frequencies at 236(m) and 212(s) cm^{-1}, as well as by the increase in the $\Delta\nu$ value (Table 2). One observes the typical for coordinated water-strong and broad bands in the 3000–3500 cm^{-1} absorption range, as well as the characteristic contour with components at 470, 570, 590, 605, 625, 650 and 670 cm^{-1}. The well-resolved bands at 113, 120, 132, 146, 160 and 172 cm^{-1} may be assigned to U–Br vibrations and lattice modes.

TABLE 2

IR absorption bands

Description	*CH_3CN liquid [11, 12]* (cm^{-1})	*$NH_4UBr_4.1.5CH_3CN.6H_2O$* ($cm^{-1}$)
ν_2, symmetric C ≡ N stretching	2250	2268 s (2280) s
$\Delta\nu_2$	–	+18
ν_3, symmetric CH_3 deformation	1375.5	1368 m
ν_4, symmetric C—C stretching	917	938 w
$\nu_3 + \nu_4$, combination band	2293	2300 sh
ν_7, degenerate rocking	1047	1030 w

3.4. Magnetic susceptibilities and electronic spectrum

The magnetic susceptibility of the compound has been measured in the 4–300 K range. A linear relationship of $1/\chi'_M$ *vs.* T was observed between 60 and 240 K with the paramagnetic constants $\mu_{eff} = 3.2$ B.M. and $\theta = -37.24$ B.M. The magnetic moment is very similar to the values reported for $UCl_3 \cdot CH_3CN \cdot 5H_2O$ [3] but is markedly lower than those predicted for the "free ion" ($\mu_{eff} = 3.7$–3.79 B.M.) [6, 10]. The reduction in these values has been interpreted as a result of the extent of the ground level crystal-field splitting. At somewhat lower and higher temperatures the plot curves slightly below and above the Curie–Weiss line respectively.

The solid state absorption spectrum of the complex bromide exhibits no essential differences as compared with the earlier reported spectra of hydrated and anhydrous uranium(III) complex chlorides [2–4, 6]. Typically, for the spectra in the 4000–14000 cm^{-1} absorption range a number of relatively weak and narrow $5f^3$–$5f^3$ bands are observed, exclusively. Above this region the bands are obscured by parity-allowed $5f^3$–$5f^26d^1$ transitions. One may note also an expected, more or less significant red shift of the band maxima. A detailed discussion of magnetic and spectroscopic properties of uranium(III) compounds is given elsewhere [6].

Acknowledgments

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