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Note

Synthesis and characterization of uranium triiodide tetrakis(acetonitrile)

J. Drożdżyński
Institute of Chemistry, University of Wrocław, 50-383 Wrocław (Poland)

J.G.H. du Preez
Uranium Chemistry Research Unit, University of Port Elizabeth, PO Box 1600, Port Elizabeth 6000 (South Africa)

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Abstract

The preparation and properties of a new uranium(III) iodo complex compound, $UI_3(CH_3CN)_4$, are reported. The compound belongs to the monoclinic system with $a = 9.6168$, $b = 8.7423$, $c = 7.1858$ Å, $\gamma = 92.99°$ and $V = 603.31$ Å^3. Magnetic susceptibility measurements were carried out by the Faraday method in the 6.5–300 K range. In the 100–300 K region the compound exhibits Curie–Weiss paramagnetism with the paramagnetic constants $\mu_{eff} = 3.44$ BM, $C = 1\,467$ emu K mol^{-1} and $\theta = -80$ K. Solid state electronic absorption and reflectance spectra of the iodo complex have been recorded in the 4000–24 000 cm^{-1} region and are discussed.

Key words: Uranium complexes; Iodide complexes; Acetonitrile complexes

Introduction

So far only a few uranium(III) compounds with iodine have been reported. These are UI_3, UOI, a number of mixed halides of the general formulas UX_2I and UXI_2 (where X = Cl or Br) [1], some exceedingly air and moisture sensitive Lewis base adducts of uranium triiodide of the formulas* $UI_3(THF)_4$, $UI_3(py)_4$ and $UI_3(dme)_2$ [2] as well as recently prepared potassium and rubidium pentaiodo uranates(III) [3].

This paper reports the preparation of the new uranium(III) compound $UI_3(CH_3CN)_4$ together with some of its structural, magnetic and spectroscopic properties. The compound is very easy to prepare and may serve as an excellent starting material for the synthesis of new tervalent uranium iodo complex compounds.

Experimental

Synthesis

The use of uranium turnings for synthesis of uranium(3+) compounds was first applied by Clark *et al.* [2]. For the preparation reported in this paper 5–10 g of uranium turnings were washed with conc. HNO_3, distilled water and finally with dried methyl cyanide. The uranium turnings were placed in an apparatus similar to that described in ref. 4 and dried in a stream of nitrogen. Next, 6.4 g of iodine, 140 cm^3 of methyl cyanide, 10 cm^3 of ethyl acetate and a magnetic stirrer were added. The system was freed from oxygen by connecting it to a vacuum pump and evaporating the solution for 5 to 10 min. The stirring of the solution for 2 to 3 days results in the separation of a microcrystalline, dark brown compound of the formula $UI_3(CH_3CN)_4$. The precipitate was filtered in vacuum and washed with small portions of degassed acetonitrile under an inert atmosphere. All solvents were dried over activated molecular sieves and distilled with nitrogen. Other reagents were of analytical grade.

Analytical data

Calc. for $UI_3(CH_3CN)_4$: U, 30.40; I, 48.62; C, 12.27; N, 7.15. Found: U, 29.82; I, 49.31; C, 12.47; N, 5.35%.

Physical measurements

The X-ray powder diffraction analysis was carried out on a Stoe automated X-ray powder diffractometer using Cu Kα_1 radiation.

Magnetic susceptibilities of a polycrystalline sample, sealed in a quartz tube, were measured by the conventional Faraday method in the 4.2–300 K range in a field of 6 kOe. The values of the magnetic susceptibilities were corrected for diamagnetic increment, $\chi_{dia} = -209.17$ emu K mol^{-1}.

The reflectance spectrum was recorded on a Shimadzu UV 3100 spectrophotometer. In addition a solid state absorption spectrum of a thin film of the compound was recorded on a Cary-Varian 2300 spectrophotometer in the 4000–24 000 cm^{-1} range. In order to obtain the spectrum, a well ground mixture of the compound with some chlorinated naphthalene oil (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.

Solid state IR spectra in the 200–4000 cm^{-1} absorption range were obtained on a Bruker IFS 113v FT-IR

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*THF = tetrahydrofuran, py = pyridine, dme = dimethoxyethane.

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spectrometer using KBr pellets as well as Nujol mulls and polyethylene plates.

Results and discussion

Characterization of the compound

Uranium triiodide tetrakis(acetonitrile) is a crystalline dark brown solid readily soluble in almost all polar organic and inorganic solvents. Contrary to $UI_3(THF)_4$, $UI_3(py)_4$ and $UI_3(dme)_4$ the compound is not soluble in benzene and toluene. In conc. HCl it is soluble with the formation of the characteristic, unstable purple UCl_n^{3-n} complex anions (where $3<n<6$). The compound is not resistant to oxidation by air.

The ^1H NMR spectrum of $UI_3(CH_3CN)_4$ in CD_3OD indicates the presence of free CH_3CN molecules only. Since also all other polar organic solvents will replace CH_3CN from the coordination sphere the ^1H NMR method is not suitable for investigations of the compound.

X-ray powder diffraction analysis

The X-ray powder diffraction patterns could be indexed on the basis of a monoclinic cell with $a=9.6168$, $b=8.7423$, $c=7.1858$ Å, $\gamma=92.99°$, $V=603.31$ Å^3, $D_c=4.08$ g cm^{-1} and the number of formula units $Z=2$. The unit cell parameters were obtained by a least-squares refinement of all 33 observed reflections. The washing of the precipitate with acetonitrile resulted in the obtainment of a very fine crystalline powder not suitable for X-ray analysis. Small amounts of coarse-crystalline samples used in the measurements, were obtained in a preparation without stirring of the solution to be reduced.

Magnetic susceptibility measurements

The inverse magnetic susceptibility versus temperature plot exhibits in the 100–300 K range a linear relationship with the paramagnetic constants $C=\chi_M'(T-\theta)=1.467$ emu K mol^{-1} and $\theta=-80$ K. At lower temperatures it curves first somewhat above and next below the Curie–Weiss line approaching to zero. Such a temperature dependence of the magnetic susceptibility is characteristic for uranium(III) compounds in which the magnetic moments of the crystal field levels $\mu_2 \gg \mu_1$. The derived effective magnetic moment $\mu_{\text{eff}}=2.84\sqrt{C}=3.44$ BM is somewhat lower than the 'free ion' moment but typical for numerous uranium(III) compounds [1].

Electronic spectra

The reflectance (Fig. 1) and solid state electronic absorption spectra are similar to those of other uranium(III) compounds [1].

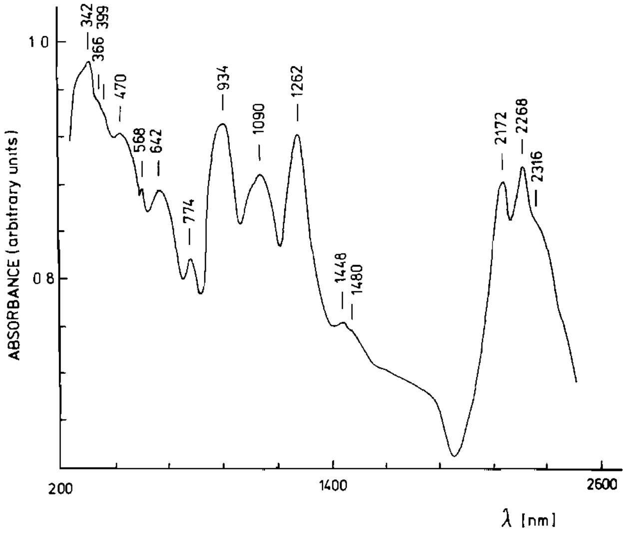

Fig. 1. Reflectance spectrum of $UI_3 \cdot (CH_3CN)_4$.

In the 4000–16 000 cm^{-1} absorption range one observes the characteristic $5f^3 \rightarrow 5f^3$ transitions of the U^{3+} ion. However, as compared with most of the reported uranium(III) absorption spectra the bands are not well resolved [1, 5]. This may be indicative of a very small crystal-field splitting of the L'S'J' bands. Since the bands in the reflectance spectrum are somewhat better resolved, only this spectrum has been included in the paper.

Above this region the $5f^3 \rightarrow 5f^3$ bands are obscured by strong and broad $5f^3 \rightarrow 5f^2 6d^1$ transitions. A comparison of the $UI_3(CH_3CN)_4$ and UI_3 solid state absorption spectra reveals that the first peaks of these bands occur at much higher wave numbers for the former one, i.e. at *c.* 20 000 cm^{-1} for $UI_3(CH_3CN)_4$ and *c.* 14 000 cm^{-1} for UI_3 [6].

A red shift of the first f–d bands has been attributed [1, 5] to the formation of some of the uranium–ligand bonds with a markedly more covalent character as compared with those in the U^{3+} aquo ion e.g. in $UCl_3 \cdot 7H_2O$ [7] or $CsUCl_4 \cdot 3H_2O$ [8]. Hence one may expect that in the investigated compound the uranium–ligand bonds have a distinctly more ionic character than in uranium triiodide.

Infrared spectra

IR spectral investigations show that the complex possesses the characteristic vibrations of the free ligand [9, 10] or those of other uranium(III) complexes with methyl cyanide [11–13]. A comparison of the spectra gives evidence of coordination through the nitrogen atom which is indicated by an increase ($\Delta\nu$) of the $\nu(C{\equiv}N)$ stretching frequency (Table 1) as well as the appearance of some characteristic bands in the 200–250 cm^{-1} absorption range which we have tentatively assigned to the $\nu[U{-}NC(CH_3)]$ stretching vibrations based

TABLE 1. Infrared absorption bands

Description	CH_3CN liquid (cm^{-1}) [9, 10]	$UCl_3 \cdot CH_3CN$ (cm^{-1}) [11]	$UI_3(CH_3CN)_4$ (cm^{-1})
ν_2, symmetric C≡N stretching	2250	2270m (2280sh)	2272 m
$\Delta\nu$		+20	+22
ν_3, symmetric CH_3 deformation	1375.5		1378m
ν_4, symmetric C–C stretching	917	932w	934w
$\nu_3+\nu_4$, combination band	2293	2307w	2300m
ν_7, degenerate rocking	1047.3		1037m

on literature data [14]. The assignment of the other bands (Table 1) follows those reported for CH_3CN [9, 10] as well as for cerium(III) and uranium(III) complexes with methyl cyanide [11–13].

Supplementary material

The observed and calculated *d* spacings together with the observed relative intensities are available on request from the authors.

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