Inorganica Chimica Acta, 115 (1986) 219–222

# Preparation and Properties of Hydrated Uranium(III) Complex Chlorides. Part II. Uranium Trichloride Monomethylcyanide Pentahydrate

E. ZYCH and J. DROŻDŻYŃSKI

*Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland*

Received October 31, 1985

---

## Abstract

The preparation and characterization of a new uranium(III) compound, $UCl_3 \cdot CH_3CN \cdot 5H_2O$, is reported. The complex chloride belongs to the monoclinic system with $a = 1226.(2)$, $b = 1298.(3)$, $c = 662.(1)$ pm, $\gamma = 101.7(2)°$ and $Z = 4$. Magnetic susceptibility measurements were carried out by the Faraday method in the 6.5–300 K range. An antiferromagnetic transition is observed at $T_N = 12$ K. In the 65–300 K region the compound exhibits Curie–Weiss paramagnetism with the paramagnetic constants $C = 1.430$ emu K mol$^{-1}$ and $\theta = -65.7$ K. The electronic spectra of thin layers of the compound have been recorded in the 4000–24 000 cm$^{-1}$ region and discussed.

## Introduction

In the first paper of the series [1], the synthesis and characterization of uranium trichloride heptahydrate has been presented. In this paper the preparation of a new uranium(III) compound, $UCl_3 \cdot CH_3CN \cdot 5H_2O$, together with some structural, magnetic and spectral results, is reported. To the best of our knowledge the compound seems not to have any analogue among the hydrated trivalent lanthanide and actinide halides.

## Experimental

### *Synthesis*

In a typical preparation 4–4.2 g of uranium tetrachloride was shaken for 2–3 min with 100 cm$^3$ of methyl cyanide. Next, a solution of 1.7 cm$^3$ propionic acid and 1.1 cm$^3$ water was added and all thoroughly mixed together. After filtering, the solution was reduced in an inert atmosphere by shaking with a 2.4% liquid zinc amalgam. The inert atmosphere was achieved by evaporation of the solution for about 2 min in an apparatus described in the previous paper [2]. The reduction changed the colour of the solution from olive-green to reddish-brown and resulted in the formation of a wine-red, fine crystalline precipitate of $UCl_3 \cdot 5H_2O \cdot CH_3CN$. If the reduction is carried out very slowly, after 2–3 days a crystalline precipitate in the form of dark-red needles is produced. The precipitate was washed under an inert atmosphere with anhydrous and deoxygenated methyl cyanide and freshly distilled ether, dried *in vacuo* for about 15 min and stored in sealed tubes at temperatures below 18 °C. All reagents used were of analytical grade. For details of the preparation technique see ref. 2.

It is worthwhile to note here that the uranium trichloride heptahydrate reported in ref. 1 may be easily converted into $UCl_3 \cdot 5H_2O \cdot CH_3CN$ by shaking the compound for a couple of minutes with anhydrous methyl cyanide.

### *Decomposition*

Samples of $UCl_3 \cdot 5H_2O \cdot CH_3CN$ weighing 200–300 mg were decomposed on a MOM type 3427 derivatograph at the rate 2.5 deg min$^{-1}$. The specimen was heated to 500 °C in a pure argon atmosphere flowing at approximately 1000 cm$^3$ min$^{-1}$. The loss of 2 mol of $H_2O$ at 60 °C as well as 1 mol of $CH_3CN$ and $H_2O$ at 110 °C is distinctly indicated in the DTG curve. In contrast to $UCl_3 \cdot 7H_2O$, this compound does not lose the last two water molecules at higher temperatures either, but undergoes decomposition with the formation of oxychlorides.

### *Analytical Data*

*Anal.* Calc. for $UCl_3 \cdot 5H_2O \cdot CH_3CN$: U, 50.06; Cl, 22.37; H, 2.76; C, 5.05; N, 2.35. Found: U, 49.40; Cl, 21.70; H, 2.87; C, 5.10; N, 2.29%.

### *Physical Measurements*

Magnetic susceptibilities of a polycrystalline sample, sealed in a quartz tube, were measured by the conventional Faraday method in the 4–200 K range in a field of 6 kOe. The values of the magnetic susceptibilities were corrected for diamagnetic increment, $\chi_{dia} = -141.59 \times 10^{-6}$ emu mol$^{-1}$.

The electronic spectrum was recorded on a Cary 14 spectrophotometer in the 4000–24 000 cm$^{-1}$ absorption range, using thin films of a mixture of the

0020-1693/86/$3.50

compound with some Halowax* oil. In order to obtain these films, the compound was thoroughly mixed with the oil in a dry box, placed between two quartz windows of about 1 cm in diameter and pressed to get a clear and uniform layer.

Solid state IR spectra in the 200–4000 $cm^{-1}$ absorption range were obtained on Perkin–Elmer 180 and 783 spectrophotometers using KBr pellets as well as nujol mulls and polyethylene plates.

## Results and Discussion

### *Characterization of the Compound*

Depending on the size of the crystals, uranium trichloride monomethylcyanide pentahydrate is a dark-red to black, hygroscopic and oxygen-sensitive crystalline solid. When obtained in the form of larger crystals, it is somehow less hygroscopic and less sensitive to oxidation by exposure to air. The compound is very soluble in the more polar organic solvents and with oxidation to U(IV) in water and inorganic acids.

In contrast to $UCl_3 \cdot 7H_2O$ [1], the complex chloride is relatively stable to prolonged pumping at temperatures below 20 °C, which indicates a stronger bonding of at least some of the water molecules. Carefully controlled vacuum thermal decomposition may also lead to the anhydrous trichloride by applying a very effective non-static high vacuum system at low temperatures. The final traces of water can be removed by increasing the temperature gradually to *ca.* 300 °C.

### *X-ray Powder Diffraction Studies*

X-ray photographs proved the high degree of instability of the compound. The encapsulation of the crystals in Lindeman glass capillary tubes did not prevent the decomposition, which seemed to be caused by numerous factors, e.g., humidity, oxygen and evaporation of the coordinated solvent. It was not possible, therefore, to take the Weissenberg photographs to determine the space group. In order to slow down the decomposition, the crystals were coated with Canada balsam and those used for oscillation photographs were put into the capillary tubes. The Laue symmetry $2/m$ and the repeat distance along the morphologically developed edges were determined from oscillation photographs. The indexing of the powder pattern (both Guinier photographs and diffractometric results were employed) was done using the Powder routine established by D. G. Taupin. Only one monoclinic unit cell consistent with the oscillation determined from photographs was found on the basis of 57 lines indexed. The parameters were refined using standard least-squares procedures [3]. Unfortunately, the number of relations among the diffraction lines was too small to reveal the space group extinctions unambiguously.

The crystals are monoclinic with $a = 1296.(2)$, $b = 1298.(3)$, $c = 662.(1)$ pm, $\gamma = 101.7(2)°$, $V = 1007.2 \times 10^3$ $pm^3$, $d_o = 3.1$ Mg $m^{-3}$, $d_c = 3.14$ Mg $m^{-3}$ and $Z = 4$.

### *Magnetic Susceptibility Measurements*

The inverse magnetic susceptibility *versus* temperature plot exhibits in the 65–300 K range a linear relationship with the paramagnetic constants* $C = 1.430$ emu K $mol^{-1}$, $\theta = -65.7 \pm 0.5$ K and magnetic moment $\mu = 3.39 \pm 0.003$ BM. At temperatures lower than 65 K, the plot curves below the Curie–Weiss line with an antiferromagnetic transition at $T_N = 12$ K** (Fig. 1). Until now, antiferromagnetic transitions of uranium(III) compounds have been reported only for $U(HCOO)_3$ [4] and the anhydrous halides [5, 6] and complex halides [7].

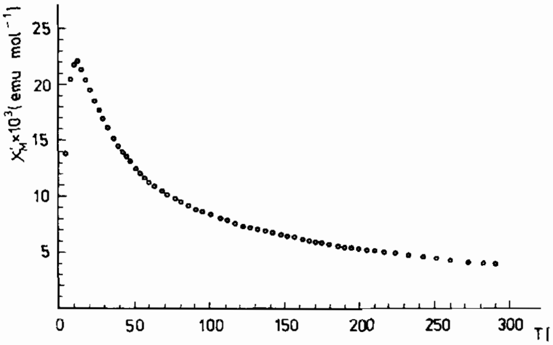

Fig. 1. Molar magnetic susceptibility of $UCl_3 \cdot CH_3CN \cdot 5H_2O$.

The effective magnetic moment obtained is markedly larger than those reported [1] for the heptahydrate (2.95 BM) but smaller compared to the 'free ion' moment (3.7–3.79 BM) [4]. A more detailed analysis of these and other results is in progress.

### *Infrared Spectra*

Preliminary IR spectral studies shows that the compound possesses the characteristic vibrations of the free ligand [8, 9] as well as of $UCl_3 \cdot CH_3CN$ [10] or $CeCl_3 \cdot CH_3CN$ [10]. A comparison of the spectra (Table I) confirmed a coordination through the nitrogen atom which is indicated by the appearance of the $\nu[U-NC(CH)_3]$ frequencies in the 200–240 $cm^{-1}$ absorption range, *i.e.*, at 204w, 210m, 215s, 220m, 235w, 237m and 249m, as well as an

---

*Chlorinated naphthalene, index of refraction = 1.635.

*Magnetic susceptibility constants from the Curie–Weiss law, $\chi = C/(T - \theta)$.

**Néel temperature.

TABLE I. Infrared Absorption Bands[a]

| Description | $CH_3CN$ liquid [7, 9] ($cm^{-1}$) | $CeCl_3 \cdot CH_3CN$ [8] ($cm^{-1}$) | $UCl_3 \cdot CH_3CN$ [8] ($cm^{-1}$) | $UCl_3 \cdot CH_3CN \cdot 5H_2O$ ($cm^{-1}$) |
|---|---|---|---|---|
| $\nu_2$, symmetric C≡N stretching | 2256 | 2272s | 2270m<br>(2280sh) | 2260m<br>(2270sh) |
| $\Delta\nu_2$ | | +22 | +20 | +10 |
| $\nu_3$, symmetric $CH_3$ deformation | 1375.5 | | | 1367 |
| $\nu_4$, symmetric C–C stretching | 917 | 933m | 932w | 926m |
| $\nu_3 + \nu_4$, combination band | 2293 | 2306m | 2307w | 2298m |
| $\nu_7$, degenerate $CH_3$ rocking | 1047.3 | | | 1035 |

[a] s: strong, m: medium, w: weak, sh: shoulder.

increase ($\Delta\nu$) of the $\nu$(C≡N) stretching frequency (Table I). The peaks at about 2300 $cm^{-1}$ have been assigned [8] to a combination band $\nu_3 + \nu_4$ of the symmetric $CH_3$ deformation vibration and the symmetric C–C stretching vibration.

In the spectrum one may also observe the hydrogen-bonded water frequency in the 3100–3500 $cm^{-1}$ absorption range, as well as that typical for the coordinated water multiplet at 400–700 $cm^{-1}$ with components at 425, 460, 500, 550 and 665 $cm^{-1}$, i.e., the rocking and wagging modes. The well resolved bands at 319w, 307w, 286w, 273w, 265w and 258m may be assigned to the uranium–chlorine stretching vibrations.

### *Electronic Spectra*

The solid state absorption spectrum of $UCl_3 \cdot 5H_2O \cdot CH_3CN$ (Fig. 2) exhibits essential differences as compared to the spectra of the aquo-ion [11] or $UCl_3 \cdot 7H_2O$ [1]. In the spectral range 4000–14 000 $cm^{-1}$ one may note somewhat lower band intensities of the f–f transitions, especially of those at 8143 and 9310 $cm^{-1}$, assigned [12, 13] to the $^4I_{13/2}$ and $^2H_{9/2}$ energy levels, respectively. Above this region, at 16 000 $cm^{-1}$, 18 350 $cm^{-1}$ and at higher wave numbers, broad and strong absorption bands are observed. The appearance of such bands in the visible region has been attributed [14] to the formation of inner-sphere uranium(III) complexes, which induce the Laporte allowed $5f^3 \rightarrow 5f^2 6d^1$ transitions. As in the case of the lanthanide solution and solid state spectra [15, 16], it has been shown [17] that the positions of the first strong f–d transitions are shifted towards lower energies with: (i) the increase of the reducing character of the ligands, (ii) a decrease in coordination number, (iii) a decrease in the metal-ligand bond length, and (iv) an increase in covalency. However, no relationship has been found [18] between the wave numbers of these bands and the nepheloauxetic parameter $\delta_{cov}$.

It has also been noted [17] that in the solid state spectra of the more ionic uranium(III) complexes with coordination numbers (*cn*) equal to or higher than 9, the first f–d bands appear in the

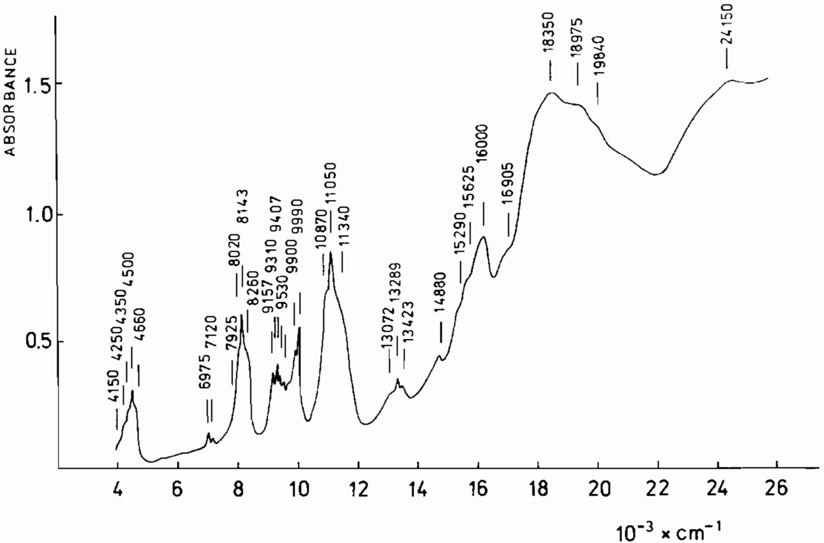

Fig. 2. Absorption spectrum.

absorption range above 21 000 cm$^{-1}$, whereas uranium(III) complexes with lower coordination numbers, e.g., $Cs_2NaUCl_6$ ($cn = 6$) [19], $Rb_2UCl_5$ or $K_2UCl_5$ ($cn = 7$) [7, 20, 21] and $UJ_3$ ($cn = 8$) [22], exhibit strong f–d bands in the visible region.

Hence, the appearance of intense bands in the 16 000–19 000 cm$^{-1}$ region of the investigated absorption spectrum may be evidence of a more covalent character of some of the uranium–ligand bonds as well as of a coordination number lower than 9.

## Acknowledgements

The financial support of the Polish Academy of Sciences and the Institute of Nuclear Research in Warsaw is gratefully acknowledged. The authors would also like to thank Dr. J. Matuszewski of the Department of Inorganic Chemistry, School of Economics, Wrocław, for determination of the X-ray powder diffraction values, as well as Dr. J. Hanuza of the Institute of Low Temperature and Structure Research of the Polish Academy of Science in Wrocław for helpful comments concerning the IR spectra.

## References

1 J. Droździński, *Inorg. Chim. Acta, 109,* 79 (1985).
2 J. Droździński, *Inorg. Chim. Acta, 32,* L83 (1979).
3 J. M. Stewart (ed.), 'The X-Ray System', Technical Report Tr-446 of the Computer Science Center, University of Maryland, College Park, Md., 1976.
4 J. Droździński, K. Schwochau and H.-J. Schenk, *J. Inorg. Nucl. Chem., 43,* 1845 (1980).
5 E. R. Jones Jr., M. E. Hendricks, J. A. Stone and D. G. Karraker, *J. Chem. Phys., 60,* 2083 (1974).
6 Y. Hinatsu, C. Miyake and S. Imoto, *J. Nucl. Sci. Technol., 17,* 929 (1980).
7 J. Droździński and D. Miernik, *Inorg. Chim. Acta, 30,* 185 (1978).
8 P. Venkateswarlu, *J. Chem. Phys., 19,* 293 (1951).
9 R. A. Walton, *Q. Rev., 19,* 126 (1965).
10 J. Mac-Cordick and C. Brun, *C.R. Acad. Sci., Sér. C, t. 270,* 620 (1970).
11 J. Droździński, *J. Inorg. Nucl. Chem., 40,* 319 (1978).
12 J. Droździński and J. G. Conway, *J. Chem. Phys., 56,* 883 (1972).
13 H. M. Crosswhite, H. Crosswhite, W. T. Carnall and A. P. Paszek, *J. Chem. Phys., 72,* 5103 (1980).
14 M. Shiloh and Y. Marcus, *Isr. J. Chem., 3,* 123 (1965).
15 D. E. Henrie, R. L. Fellows and G. R. Choppin, *Coord. Chem. Rev., 18,* 199 (1976).
16 G. Blasse, *Struct. Bonding (Berlin), 26,* 43 (1976).
17 J. Droździński, 'Rare Earth Spectroscopy, Proc. of the Rare Earth Spectroscopy Symposium RES-84, Wrocław, September 10–15, 1985', World Scientific Publishing, Singapore, 1985, pp. 57–80.
18 J. Droździński, *J. Mol. Struct., 114,* 449 (1984).
19 J. Droździński, to be published.
20 J. Droździński, in J. Mulak, W. Suski and R. Troć (eds.), 'Proc. 2nd Int. Conf. Electronic Structure Actinides', Ossolineum, Wrocław, 1976, p. 205.
21 G. Meyer, H. Ch. Gaebell and R.Hoppe, *J. Less-Common Met., 93,* 347 (1983).
22 R. Barnard, J. I. Bullock, B. J. Gellatly and L. F. Larkworthy, *J. Chem. Soc., Dalton Trans.,* 607 (1973).