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Uranium hexafluoride: laboratory scale synthesis, coordination behaviour towards nitriles and Raman spectra

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Abstract

The synthesis of uranium hexafluoride, UF_6, using uranium metal and chlorine trifluoride is described. The method is suitable for laboratory scale (10–20 g) preparation of pure UF_6. Raman spectra of pure UF_6 have been observed for the solid state and for the first time in cyanogen chloride solution The coordination behaviour of UF_6 towards Lewis bases like cyanogen chloride (ClCN), cyanogen ($(CN)_2$), hydrogen cyanide (HCN) and malononitrile ($CH_2(CN)_2$) was investigated.

Key words: Uranium complexes; Fluoride complexes, Nitrile complexes

Introduction

Exploring the applicability of the extended hard–soft acid–base principle [1] in inorganic chemistry we have extensively studied the coordination behaviour of nitriles (e.g. HCN, ClCN, NC–CN, $CH_2(CN)_2$) towards the Lewis acids AsF_5 and SbF_5 [2–4]. Uranium hexafluoride is known to be a very useful and strong oxidizer and there has been a definite resurgence in both main group and transition metal chemistry using UF_6 as a one-electron acceptor [5, 6]. Although some complexes of UF_6 with coordination numbers higher than six have been reported in the literature (e.g. UF_7^-, UF_8^{2-}) [7] in general the coordination chemistry of uranium compounds in the oxidation state VI is dominated by the dioxo or 'uranyl' (UO_2^{2+}) ion [8]. No example of a nitrile complex of the type $[UF_6(RCN)_n]$ ($n=1$, 2) has been reported. We therefore studied the reaction of UF_6 towards the oxidation stable Lewis acids RCN (R = H, Cl, CN, NC–CH_2).

However, one drawback of UF_6 chemistry is that often the material is either commercially not readily available or only huge amounts are supplied. Moreover, tightening up of safety regulations makes it more and more difficult to ship even small amounts of hazardous chemicals unless harsh (and expensive) precautions are taken. Whereas industrially UF_6 is prepared according to eqn. (1) [9] most of the laboratory scale methods use either expensive flow type reactors (flow tube or tubular reactors; eqns. (2)–(4)) [10, 11] or original publications are not easily accessible (see ref. 12). An account of our work concerning the coordination chemistry and preparation of UF_6 is given below.

$$UO_2 \xrightarrow{HF} UF_4 \xrightarrow{F_2\ (\text{or } ClF_3)} UF_6 \tag{1}$$

$$UO_2 + 3F_2 \xrightarrow{T > 500\ °C} UF_6 + O_2 \tag{2}$$

$$UF_4 + F_2 \xrightarrow{450\ °C} UF_6 \tag{3}$$

$$UF_4 + 2CoF_3 \xrightarrow{275\ °C} UF_6 + 2CoF_2 \tag{4}$$

Experimental

Caution: UF_6 and ClF_3 are strong oxidizers and are toxic. Extensive care must be taken to avoid contact between fluorides and oxidizable materials. Protective clothing and face shields must be worn all times. Using a static reactor the preparation should not be carried out on a substantially larger scale as described below.

Preparation of UF_6

A monel high pressure bomb (Parr, series 4740, $V=71$ ml) equipped with a monel gage block assembly and rupture disc and closed by monel needle valves (Whitey) was rinsed several times with $CFCl_3$, dried and deactivated with F_2 (Solvay; 2 bar, 24 h, 100 °C).

In a typical experiment uranium turnings (Cerac, >99.7%; 8.80 g, 40 mmol) were transferred into the prepassivated reactor. ClF_3 (Air Products; 12.0 g, 130 mmol) was condensed at −196 °C on the nickel vacuum

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line, and the mixture was warmed to room temperature. From outside the reactor was cooled with compressed air by a system of three nozzles. **Caution**: The generated heat warms the outside surface of the bomb substantially. After 1 h all material volatile at −78 °C (generated ClF: m.p. −155.6 °C; b.p. −100.1 °C) [8] was pumped off. The bomb was then warmed to −50 °C and traces of unreacted ClF_3 (ClF_3: m.p. −76.3 °C; b.p. 11.8 °C) [8] were pumped off. The reactor was taken into the dry box, opened and the white, volatile UF_6 (UF_6: m.p. 64.05 °C/1139.6 Torr; subl., 56.54 °C) [7] was immediately transferred into a flamed-out Pyrex vacuum sublimation system. After sublimation, white crystalline UF_6 was recovered (12.0 g, 34 mmol; corresponding to an 85% yield) and identified by Raman spectroscopy.

Raman spectra were recorded at room temperature on a Jobin Yvon Ramanor U 1000 spectrometer by use of the 647.09 nm exciting line of a Kr ion laser.

UF_6 (neat, solid; 30 mW, 1s/point; cm^{-1}): 211 (4)/223 (3) ν_5-UF_6, 519 (4) ν_2-UF_6, 664 (10) ν_1-UF_6.

UF_6 (solution in ClCN, 1 5 mol l^{-1}; 40 mW, 1s/point; cm^{-1}): 205 (1) ν_5-UF_6, 395 (1) δ-ClCN, 527 (1) ν_2-UF_6, 665 (10) ν_1-UF_6, 726 (3) ν-Cl–CN

Reactivity of UF_6 towards nitriles

The apparatus, techniques and chemicals were as previously described [13]. The reactions were carried out in glass NMR or Raman tubes fitted with coaxial PTFE valves (Young). All manipulations were carried out in an inert-gas atmosphere. Gaseous compounds were added volumetrically using a calibrated vacuum line. Raman spectra were recorded as described above. ^1H NMR spectra were recorded at room temperature using a Varian EM 360 (60 MHz). The molar UF_6/nitrile ratio in all experiments was exactly 1:1, the sample/solvent ratio was approximately 1:20.

Results and discussion

The batch reactor ClF_3 fluorination on elemental uranium provides a high yield straightforward synthesis of pure uranium hexafluoride on a laboratory scale (eqn. (5)).

$$U + 3ClF_3 \longrightarrow UF_6 + 3ClF \qquad (5)$$

After purification by sublimation no soluble or insoluble impurities could be detected by Raman spectroscopy. The Raman spectra of neat and dissolved (ClCN) UF_6 are shown in Fig. 1. The observed frequencies and their assignments are summarized in Table 1 and agree well with those previously reported for the solid state and gas phase (Table 1) [14, 15] For the first time we report on the (ClCN) solution characterization of uranium hexafluoride. In view of the high purity of the dissolved sample in ClCN (after pumping off the ClCN pure UF_6 was recovered in quantitative yield!) cyanogen chloride turned out to be a convenient, inexpensive and easy-to-make solvent for UF_6 [10].

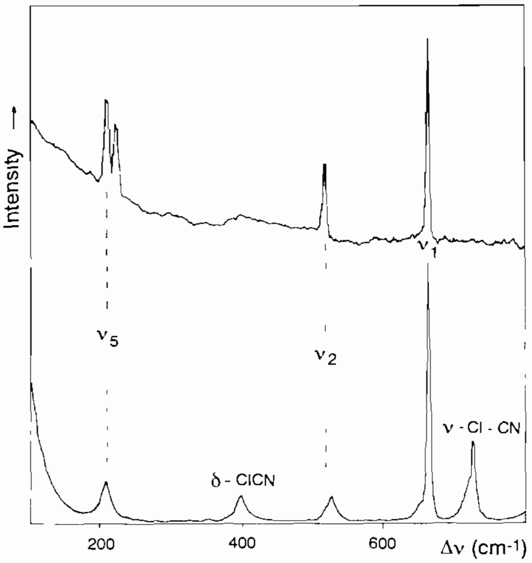

Fig. 1. Raman spectra of neat UF_6 and UF_6 in ClCN solution (see 'Experimental').

TABLE 1 Raman spectra of neat UF_6 and UF_6 in ClCN solution (see 'Experimental'); vapor data were taken from ref 15

	Solid, 20 °C	ClCN solution, 20 °C	Vapor, 85 °C
ν_1	664(10)	665(10)	667(10)
ν_2	519(4)	527(1)	533(2)
ν_5	211(4)/223(3)	205(1)	202(2)

Reactions of 1:1 mixtures of UF_6 and RCN (R = H, Cl, CN, CH_2CN) either in $CFCl_3$ or in $CDCl_3$ solution did not lead to the formation of coordination compounds between UF_6 and the corresponding nitrile species (eqns. (6) and (7)). In all cases the free and uncoordinated nitrile was identified by solution spectroscopy (^1H NMR: HCN, NC–CH_2–CN; Raman: Cl–CN, NC–CN).

$$UF_6 + R\text{–}CN \xrightarrow{\text{R-11, r t}} [UF_6(RCN)] \qquad (6)$$

R = H, Cl, CN

$$UF_6 + NC\text{–}CH_2\text{–}CN \xrightarrow{CDCl_3,\ \text{r t}} [UF_6(NCCH_2CN)] \qquad (7)$$

In order to understand the different coordination behaviour of AsF_5 and UF_6 more fully (i.e. to find out whether the reluctance of UF_6 to coordinate nitriles is a kinetic or a thermodynamic effect) we calculated the number of electrons transferred (ΔN) and the gain in energy (ΔE) for eqns. (8) and (9). The results are summarized in Tables 2 and 3.

TABLE 2 HSAB parameters[a]

	I_p (eV)	E_A (eV)	χ (eV)	η (eV)	Ref
UF_6	14.14	5.0	9.6	4.6	12
AsF_5	15.57	5.3	10.4	5.1	13
HCN	13.6	−2.3	5.7	8.0	13
ClCN	12.34	2.3	7.3	5.0	13
NCCN	13.57	−0.6	6.5	7.1	13

[a] I_p, ionization energy; E_A, electron affinity, χ, absolute electronegativity; η, absolute hernness, $\chi = 0.5\ (I_p + E_A)$, $\eta = 0.5\ (I_p - E_A)$.

TABLE 3 ΔN and ΔE values for the reactions according to eqns. (8) and (9)

Formation of (see eqns (8) and (9))	ΔN	ΔE (eV (kJ mol^{-1}))
$[UF_6(ClCN)]$	0.12	0.138 (29)
$[UF_6(NCCN)]$	0.13	0.205 (20)
$[UF_6(HCN)]$	0.15	0.302 (29)
$[AsF_5(ClCN)]$	0.15	0.243 (23)
$[AsF_5(NCCN)]$	0.16	0.318 (31)
$[AsF_5(HCN)]$	0.18	0.428 (41)

$\Delta N = \Delta\chi/2\Sigma\eta$, $\Delta E = \Delta\chi^2/4\Sigma\eta$.

$$UF_6 + R\text{–}CN \longrightarrow [UF_6(R\text{–}CN)] \qquad (8)$$

$$AsF_5 + R\text{–}CN \longrightarrow [AsF_5(R\text{–}CN)] \qquad (9)$$

Since the HSAB parameters of UF_6 and AsF_5 are very similar these results clearly indicate that the different coordination behaviour of both species and the lack of nitrile heptacoordinated uranium(VI) compounds is due mainly to steric (kinetic) reasons. The experimentally established stability of a ClCN solution towards UF_6 (i.e. neither coordination nor oxidation yielding cyanogen could be observed) can easily be understood in terms of high kinetic stability and eventually ClCN turned out to be one of the most convenient solvents to handle uranium hexafluoride on a laboratory scale.

Conclusions

This study allows the following conclusions to be drawn: (i) the batch reactor ClF_3 fluorination on elemental uranium provides a very convenient high yield laboratory-scale synthesis of pure uranium hexafluoride, (ii) a combined experimental and HSAB study indicates that the lack of neutral heptacoordinated nitrile uranium(VI) complexes is due mainly to kinetic reasons; (iii) the high stability of liquid cyanogen chloride towards dissolved UF_6 makes ClCN a very suitable solvent for UF_6 solution chemistry; (iv) for the first time a ClCN solution Raman spectrum of UF_6 has been reported.

Acknowledgements

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References

1 R.G Pearson, *Inorg Chim Acta, 198–200* (1992) 781, and refs therein

2 M Broschag, T.M. Klapotke and I.C Tornieporth-Oetting, *Inorg Chim Acta, 205* (1993) 167

3 I C. Tornieporth-Oetting, T M. Klapotke, T.S. Cameron, J Valkonen, P Rademacher and K Kowski, *J Chem Soc, Dalton Trans*, (1992) 537

4 I C Tornieporth-Oetting, T.M. Klapötke, U Behrens and P S White, *J Chem Soc., Dalton Trans*, (1992) 2055.

5 G M Anderson and J.M. Winfield, *J Chem Soc, Dalton Trans*, (1986) 337.

6 A. Schulz and T.M. Klapotke, *J Organomet Chem*, in press

7 A.F Holleman and N. Wiberg, *Lehrbuch der Anorganischen Chemie,* Walter de Gruyter, Berlin, 1985, p 1292

8 N N Greenwood and A Earnshaw, *Chemistry of the Elements,* Pergamon, Oxford, 1984, p 1478.

9 K.W Bognall, *The Actinide Elements,* Elsevier, Amsterdam, 1972; see also ref. 12

10 G. Brauer, *Handbuch der Praparativen und Anorganischen Chemie,* Vol 2, F Enke, Stuttgart, 3rd edn , 1978

11 L. Stein and R C. Vogel, *Ind Eng. Chem, 48* (1956) 418.

12 W Bacher and E. Jacob, *Gmelin Handbuch der Anorganischen Chemie. Uran,* Suppl. C8, No 55, Springer, Berlin, 1980.

13 I C. Tornieporth-Oetting and T.M Klapotke, *Chem Ber, 125* (1992) 407

14 R T Paine, R.S. McDowell, L B Asprey and L H Jones, *J. Chem Phys., 64* (1976) 3081.

15 H H Claassen, G.L Goodman, J H. Holloway and H Selig, *J Chem Phys., 53* (1970) 341.