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Review

Tervalent uranium compounds

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Abstract

This review presents the preparation procedures and characterisations of almost all hitherto identified tervalent uranium compounds. Emphasis is placed on crystallographic and optical properties of the compounds. Spectroscopic properties of uranium(3+) doped single crystals are also discussed. Extensive physical data of the compounds, such as crystallographic, thermodynamic, infrared and magnetic data as well as atomic and crystal-field parameters are summarized in a table.

Keywords: Uranium(3+) compounds; Syntheses; Physical data; Crystal structures; Spectroscopic and crystal-field data

1. Introduction

Until the end of the 1960s binary uranium(3+) trihalides were almost exclusively investigated, due to the fact that, at that time all known uranium(III) compounds were to a large degree sensitive to oxidation and had very poor solubility in aprotic organic solvents. The development of new preparative methods made possible the synthesis of about 200 uranium(III) compounds [1,2]. However, the uranium trihalides and complex halides still remain the only relatively well-investigated group of uranium(3+) compounds. U^{3+} doped CaF_2 and $LiYF_4$ single crystals proved to be good laser materials and uranium trichloride has found application in large scale isotope separation of ^{235}U. The chemistry as well as the spectroscopic properties of this ion were the subject of extensive investigations in our laboratory. Some results were presented by Drożdżyński [1,3–5] and Grenthe et al. [6] in a number of review articles. The coordination compounds of the actinides were reviewed recently by Burns et al. [2]. Other review articles will also be cited as the source of chemical and physical properties of the compounds in order to keep the reference number at a reasonable limit. This paper presents the current status of uranium(3+) compound investigations.

2. General characteristics

Almost all uranium(3+) compounds are more or less easily oxidized in air, especially in a humid atmosphere. In aqueous solutions they are rapidly oxidized but in pure, thoroughly deoxygenated solvents U^{3+} ions are fairly stable. In concentrated hydrochloric acid the compounds generate intense deep-red solutions characteristic of $[UCl_n]^{3-n}$ complex anions. Uranium(III) compounds exhibit a variety of colors (see Table 1) and most of them are also readily soluble in some more polar organic solvents.

Trivalent uranium possesses the [Rn] $5f^3$ electronic configuration with a $^4I_{9/2}$ ground state. The configuration consists of 17 electrostatic energy states, which are split by spin-orbit interaction into 41 “free ion” SLJ levels. The effect of the environment results in the subsequent removal of the degeneracy of the states up to 182 crystal-field levels, which occur within the energy range 0–50 000 cm^{-1}. Due to less effective shielding of the filled s and p shells, the spin orbit parameters $\zeta_{5f} \approx 2\zeta_{4f}$ and the F^k electrostatic interaction parameters are about one-third smaller than the corresponding parameters for neodymium(3+) ions. In consequence the electrostatic terms are closer together and the lager spin-orbit interaction results in some overlapping of almost all of the SLJ multiplets.

3. Absorption and luminescence spectra

High resolution, low temperature absorption spectra are available for numerous uranium(3+) compounds and U^{3+} doped single crystals [1,3,6] (see Table 1). Relatively sharp and well-separated absorption bands arising from $5f^3 \rightarrow 5f^3$ transitions were observed from 4000 up to 15 000–21 000 cm^{-1}. One may notice significant differences in the visible range [7], connected with the appearance of strong and broad $5f^3 \rightarrow 5f^2 6d^1$ bands, allowed by the Laporte rule. A close relationship between the red shift of the first intense f–d bands and an increase of covalence/decrease of the uranium-halogen distances, was provided by Drożdżyński [1,3], Karbowiak et al. [8] and Zych et al. [9]. No simple dependence between the energy of these transitions and the site symmetry of the U^{3+} ion could be derived. An analysis of the $5f^N \rightarrow 5f^{N-1}6d^1$ transitions in low temperature absorption spectra of U^{3+} doped Cs_2NaYCl_6, Cs_2LiYCl_6, Cs_2NaYBr_6, $CsCdBr_3$ and $Cs_3Lu_2Cl_9$ single crystals was reported by Karbowiak and Drożdżyński [10]. The f–d transitions were observed in the 14 000–21 000 cm^{-1} range as fine structured broad bands and were assigned to transitions from the $^4I_{9/2}$ ground multiplet of the $5f^3$ configuration to crystal-field levels arising from the configurations $5f^2(^3H_4)6d(t_{2g})^1(\Gamma_{8g})$ (baricenter at ∼16 000 cm^{-1}) and $5f^2(^3H_4)6d(t_{2g})^1(\Gamma_{7g})$ (baricenter at ∼19 000 cm^{-1}).The most prominent feature of the spectra is the vibronic a_{1g} progression built on each of the zero-phonon lines. Superimposed on these progression are further vibronic electric dipole transitions corresponding to even parity vibrations of $M(U)Cl_6^{3-}$ or to host lattice modes. In addition, some low intensity bands observed at ∼18 600 cm^1 and above 21 000 cm^{-1} were assigned as transitions to energy levels of the $5f^2(^3F_2)$–$6d(t_{2g})^1(\Gamma_{8g})$ and $5f^2(^3F_2)$–$6d(t_{2g})^1(\Gamma_{7g})$ configurations, respectively. The positions of the first f–d transition in the U^{3+} doped elpasolites lie at 33 400 cm^{-1}, at lower energy than those of the isoelectronic Nd^{3+} ion in the

Table 1
Properties of selected uranium(III) compounds[a]

Formula	Selected properties and physical data[b], lattice constants[c], references[d]
UF_3	*General properties*: grey to black powder or purplish black crystals. Separate crystals show a deep-violet colour under the microscope; density: 8.9 g/cm^3; m.p. > 1140 °C with decomposition. Stable in air at room temperature. At 900 °C it is quantitatively converted to U_3O_8. Disproportionates at about 1000 °C in an inert atmosphere to UF_4 and U. Is insoluble in water and cold aqueous acids but slowly undergoes oxidation. This proceeds with the formation of uranium(IV) and uranyl compounds at 100 °C. UF_3 dissolves rapidly in nitric acid–boric acid mixtures. Chlorine, bromine and iodine react to give UF_3X (X = Cl, Br or I) [87]. *X-ray single-crystal and neutron diffraction data*: hexagonal; $P6_3cm$, C_{6v}^3, No. 185; $Z = 6$; or trigonal: $P\bar{3}c1$, D_{3d}^4, No. 165; $Z = 6$, CN = 11, $a = 7.73$, $c = 7.341$; d(calc.) = 8.95–8.99; d(exp.) = 9.18. Structure type of LaF_3; the symmetry is reported to be either trigonal (space group $P\bar{3}c1$-D_{3d}^4, No. 185) or hexagonal (space group $P6_3cm$-C_{6v}^3, No. 165). Two coordination numbers 9 and 11 are also taken into consideration. Both structures may be considered as distorted ideal polyhedra with a bimolecular hexagonal cell (space group $P6_3/mmc$). The polyhedra are fully capped trigonal prisms in which fluorine atoms (CN = 11) are located on all corners and outside the two triangular and the three square boundary planes. The main difference between the two different structures is a slight displacement of the atoms forming the prism and the atoms outside the triangular surfaces normal to c. The bond lengths to the corresponding prism atoms in $P\bar{3}c1$ are 3.01 (2×), 2.48 (2×) and 2.63 (2×) Å and in $P6_3cm$ these are 2.53 (2×), 2.81 (2×), 2.45 and 3.09 Å, respectively. The cap atoms in both structures fit firmly (bond lengths 2.42–2.48 Å). The U—F bond distance is 2.32 Å [161–163]. *Thermodynamic data*: UF_3(cr): $\Delta_f G_m^o = -1432.5$ (4.7)[e], $\Delta_f H_m^o = -1501.4$(4.7)[e], $S_m^o = 123.4$(0.4)[e]; $C_{p,m}^o = 95.1$(0.4)[e]. UF_3(g): $\Delta_f G_m^o = -1062.9$(20.2)[e], $\Delta_f H_m^o = -1065.0$(20.0)[e], $S_m^o = 347.5$(10.0)[e]; $C_{p,m}^o = 76.2$(5.0)[e]. $\Delta S_{f,298}^o = -54.7$(0.7)[f]; [87,164–166]. *Magnetic susceptibility data*. $\mu_{eff.} = 3.67$ B.M. (125–300 K)[g]; $\theta = -110$ K. $\mu_{eff.} = 3.66$ B.M. (293–723 K)[d]; $\theta = -98$ K, log(p/mmHg) = 4187/T + 3.945 [67,167,168]. *Atomic and crystal-field parameters*: $E_{avg} = 20006$(30), $F^2 = 38068$(108), $F^4 = 32256$(177), $F^6 = 16372$(198), $\zeta_{5f} = 1613$(11); $\alpha = 26.1$(6), $\beta = -793$(40), $\gamma = 2085$(104); $T^2 = [298.0]$, $T^3 = [48.0]$, $T^4 = [255.0]$, $T^6 = [-285.0]$, $T^7 = [332.0]$, $T^8[305.0]$; $M^0 = [0.67]$, $M^2 = [0.37]$, $M^4 = [0.26]$; $P^2 = [1276]$, $P^4 = [608]$, $P^6 = [122]$; $B_0^2 = 216$(60), $B_2^2 = -319$(49), $B_0^4 = 1479$(78). $B_2^4 = 679$(62), $B_4^4 = 1615$(62), $B_0^6 = 2373$(79), $B_2^6 = -2201$(62), $B_4^6 = -1631$(630), $B_6^6 = -1106$(63); $n = 75$; $\sigma = 33.6$ [100]. *Other available information*: absorption spectra [169]; photoelectron spectra [170]; EPR and NMR data [67]; fused-salt systems [171].
$NaUF_4$	*General properties*: peritectic decomposition point of α-$NaUF_4$: 775 °C; α–β transformation temperature 595 °C. *X-ray powder diffraction data*. hexagonal, C_{3h}^1, $P\bar{6}$, No. 174; $a = 6.167$, $c = 3.770$; d(calc.) = 5.92; tricapped trigonal prism sharing ends to form chain [87,172].
Na_2UF_5	*X-ray single-crystal and neutron diffraction data*: cubic, space centred, $Z = 4$; $a = 7.541$(6); d(calc.) = 5.87 [87,173].
K_2UF_5	*General properties*: peritectic point 848 °C, air sensitive. *X-ray powder diffraction data*. cubic; structure type of CaF_2; $a = 6.62$(1); $Z = 1.6$; d(calc.) = 3.74 [174].
K_3UF_6	*General properties*: purple-brown, extremely moisture sensitive. *X-ray powder diffraction data*. cubic, face centred; $a = 9.20$ [175,176].
$K_3U_2F_9$	*General properties*: peritectic point: 750 °C, air sensitive. *X-ray powder diffraction data*. cubic; structure type of CaF_2; $a = 6.00$(1); $Z = 0.8$; d(calc.) = 4.67 [174].
$K_5Li_2UF_{10}$	*General properties*: reddish-brown; hygroscopic, air-sensitive; insoluble in methanol [32]. *X-ray powder diffraction data*: orthorhombic; space group $Pnma$, D_{2h}^{16}; No. 62; $a = 20.723$, $b = 7.809$, $c = 6.932$ Å, $V = 1121.89$ Å^3, $Z = 4$; is isostructural with $K_5Li_2NdF_{10}$ and $K_5Li_2LaF_{10}$; d(calc.) = 3.77 and d(exp.) = 3.69 g cm^{-3} [32]. *Atomic and crystal-field parameters*[i]: $E_{ave} = 19752$(25); $F^2 = 38407$(75); $F^4 = 34185$(102); $F^6 = 20031$(95); $\alpha = 27.4$(6.6); $\beta = -1005$(47); $\gamma = [1317]$; $\zeta = 1627$(15); $P^2 = 1618$(76); $B_0^2 = 922$(79)/705; $B_2^2 = 783$(60)/139; $B_0^4 = -750$(106)/−482; $B_1^4 = 26$(122)/185; $B_2^4 = 41$(135)/30; $B_3^4 = 1424$(149)/1699; $B_4^4 = 2463$(116)/2550; $B_0^6 = 241$(138)/172; $B_1^6 = 321$(97)/964; $B_2^6 = -49$(148)/−330; $B_3^6 = 1293$(125)/843; $B_4^6 = 631$(165)/157; $B_5^6 = -114$(148)/−642; $B_6^6 = -938$(78)/387; $\sigma^d = 37$; $n = 70$; r.m.s. = 37 cm^{-1} for 70 assigned levels; total splitting of $^4I_{9/2} = 714$ cm^{-1} [32]. *Magnetic data*: $\mu_{eff.} = 2.60$ B.M. [32].
$RbUF_4$	*X-ray powder diffraction data*: hexagonal; structure type of KYF_4; $a = 8.54$(1), $c = 10.72$(2); $Z = 6$, d(calc.) = 5.84 [177].
Rb_3UF_6	*General properties*: purple-brown, extremely moisture sensitive. *X-ray powder diffraction data*: cubic, face centered; $a = 9.5074$ [175,176,178].
Cs_3UF_6	*General properties*: purple-brown, extremely moisture sensitive. *X-ray powder diffraction data*: cubic, face centered; $a = 10.6$ [175,176,178].
$UZrF_7$	*General properties*: reddish-brown, slowly oxidizes on air at room temperature. *X-ray powder diffraction data*: monoclinic, isotypic with $SmZrF_7$, $Z = 2$; $a = 6.1000$(6), b=5.833(8), $c = 8.436$(10) $\beta = 102°69' \pm 0.07°$ $V = 292.81$ Å^3; d(calc.) = 5.25; d(exp.) = 5.40 [179]. *Magnetic susceptibility data*: $\mu_{eff.} = 3.80$ B.M. (100–300 K)[d]; $\theta = -85$ K [179].
UZr_2F_{11}	*General properties*: slowly oxidizes in air at room temperature. $\mu_{eff.} = 3.90$ B.M. (100–300 K)[d]; $\theta = -101$ K. *X-ray powder diffraction data*: monoclinic; $Z = 2$, $a = 5.308$(6), $b = 6.319$(8), $c = 8.250$(8), $\beta = 105°41' \pm 0.05°$, $V = 266.81$ Å^3; d(calc.) = 5.22, d(exp.) = 5.20 [179].
UCl_3	*General properties*: Hygroscopic olive-green powder or dark-red crystals; not soluble in anhydrous organic solvents; dissolves somewhat in glacial acetic acid. Oxidized more or less rapidly in aqueous solutions. Is a strong reducing agent both in solution and the solid state. m.p. 837 °C; disproportionates to U and UCl_4 at 840 °C. b.p. = 1657 °C; density: 5.51 g/cm^3; oxidizes in air at room temperatures [86]. *X-ray single-crystal and neutron diffraction data*: hexagonal; $P6_3/m$, C_{6h}^2, No. 176; the coordination polyhedron is a symmetrically tricapped trigonal prism arranged in columns in the c-direction; Each column is surrounded trigonally by three others at 1/2c in such a manner that the prism atoms of one chain become the cap atoms of the neighboring one. $a = 7.452$(6), $c = 4.328$(4), d(U—Cl) = 2.928(3), (6×); d(U—Cl) = 2.934(5), (3×); d(U—Cl) = 4.816(4) (to neighbour chain); d(Cl—Cl) = 3.342(5); d(Cl—Cl) = 3.410(3); (face atom-cap atom); d(calc.) = 5.51; d(exp.) = 5.43 [180,181]. *Thermodynamic data*: UCl_3(cr): $\Delta_f G_m^o = -796.1$(2.0)[e], $\Delta_f H_m^o = -863.7$(2.0)[e], S_m^o=158.1(05)[e]; $C_{p,m}^o$=95.1(0.5)[e]. UCl_3(g): $\Delta_f G_m^o = -521.7$(20.2)[e], $\Delta_f H_m^o = -523.0$(20.0)[e], S_m^o=380.3(10.0)[e]; $C_{p,m}^o = 82.4$(5.0)[e]. log(p/mmHg) = −11149/T + 8.90(590–790 K); log(p/mmHg) = −11552/T + 8.97(>790) [86,164,165]. *Magnetic susceptibility data*: $\mu_{eff.} = 3.76$ B.M. (70–300 K)[g]; $\theta = -75$ K; $T_N = 20$ K; $\mu_{eff.} = 3.03$ B.M. (350–509)[d]; $\theta = -29$ K [182]. *Atomic and crystal-field parameters*: $E_{avg} = 19331$(42), $F^2 = 37719$(154), $F^4 = 30370$(202), $F^6 = 19477$(218), $\zeta = 1606$(13); $\alpha = 31$(5), $\beta = -939$(40), $\gamma = 2087$(115); $T^2 = 460$(81); $T^3 = 59$(25), $T^4 = 159$(39), $T^6 = -144$(46), $T^7 = 356$(42), $T^8 = [300]$; $M^o = [0.663]$; $P^2 = 1639$(65); $B_0^2 = 370$(42), $B_0^4 = -359$(76), $B_0^6 = -1704$(74); $B_6^6 = 935$(60); $n = 58$; $\sigma = 35.8$ [18,21,30,183]. *Other available information*: synthesis [1,84,86]; fused salt system; EPR and NMR data [67,86]; low temperature absorption spectrum [21,30].

Table 1 (*Continued*)

Formula	Selected properties and physical data[b], lattice constants[c], references[d]
$UCl_3{\cdot}7H_2O$	*General properties*: grayish-ink-blue needles, readily soluble in numerous organic solvents; relatively resistant against oxidation by air at temperatures lower than 15 °C; loses some of its crystallization water at higher temperatures or at high vacuum; may be completely dehydrated at 260 °C [69]. *X-ray single-crystal data*: triclinic; $P\bar{1}$, C_i^1, No.2; $a = 7.902(1)$; $b = 8.210(2)$; $c = 9.188(2)$; $\alpha = 70.53(3)^\circ$; $\beta = 73.14(3)^\circ$; $\gamma = 81.66(3)^\circ$; $V = 537.0(2)$ (Å^3); $Z = 2$; d(calc.) = 2.910 (g/cm^3). The crystals are built up from separate $[U_2Cl_2(H_2O)_{14}]^{4+}$ and Cl^- ions. The characteristic features of this structure are dimers formed by two uranium ions connected through the Cl1 bridging chlorine atoms. d(U─Cl) = 2.915(1) and 2.894(1); d(U─O) = from 2.515(3) to 2.573(3) [70]. *Atomic and crystal-field parameters*: $E_{avg} = 19827(17)$, $F^2 = 40488(58)$, $F^4 = 32544(81)$, $F^6 = 22866(75)$, $\zeta = 1622(10)$; $\alpha = 28(5)$, $\beta = -622(35)$ $\gamma = 1148$; $T^2 = 306$, $T^3 = 42$, $T^4 = 188$, $T^6 = -242$, $T^7 = 447$, $T^8 = 300$; $M^0 = 0.672$, $M^2 = 0.372$, $M^4 = 0.258$; $P^2 = 1216$, $P^4 = 608$, $P^6 = 122$; $B_0^2 = -126(76)$, $B_1^2 = [-109]$, Im$B_1^2 = -423(47)$, $B_2^2 = -209(53)$, Im$B_2^2 = -350(55)$,$B_0^4 = 188(106)$, $B_1^4 = [-99]$, Im$B_1^4[-81]$, $B_2^4 = [-66]$, Im$B_2^4 = [-238]$, $B_3^4 = [136]$, Im$B_3^4 = -529(83)$, $B_4^4 = [374]$, Im$B_4^4 = [-491]$, $B_0^6 = [-130]$, $B_1^6 = 428(90)$, Im$B_1^6 = [-77]$, $B_2^6 = [171]$, Im$B_2^6 = 133$ [100], $B_3^6 = [-251]$, Im$B_3^6 = [-14]$, $B_4^6 = -489(110)$, Im$B_4^6 = -1832(81)$, $B_5^6 = [160]$, Im$B_5^6 = 1197(96)$, $B_6^6 = -498(98)$, Im$B_6^6 = -241(91)$; $\sigma = 36$; $n = 94$ [31]. *Magnetic susceptibility data*: $\mu_{eff.} = 2.95$ B.M. (10–300 K)[g]; $\theta = -32.7$ K; $C = 1.0839$ emu K mol^{-1} [69]. *Other available information* NIR and visible absorption spectrum, decomposition [31,69], low temperature absorption spectrum, AOM parameters (AOM = angular overlap model) [31].
$UCl_3{\cdot}6H_2O$	*General properties*: purple plates; *X-ray single crystal data*: monoclinic, P12/nl, $a = 9.732(2)$; $b = 6.593(1)$; $c = 8.066(2)$; $\beta = 93.56(3)^\circ$; $V = 516.51$ (Å^3); $Z = 2$; d(calc.) = 2.909; The basic units of the crystal structure are Cl^- anions and $[UCl_2(H_2O)_6]^+$ cations. The U as well as O(1), O(2) and O(3) atoms are each eight-coordinated, whereas the Cl(2) and Cl(1) chloride atoms are seven and six coordinated, respectively. One characteristic feature of this structure is the existence of hydrogen bonds which link the uranium eight-coordinated polyhedra, forming a three-dimensional network [70].
$UCl_3{\cdot}CH_3CN{\cdot}5H_2O$	*General properties*: deep-red; soluble in polar organic solvents. *X-ray powder diffraction data*: monoclinic; $Z = 4$, $a = 12.96(2)$, $b = 12.98(3)$, $c = 6.62(1)$, $\beta = 101.7(2)^\circ$, $V = 1007.2$ Å^3; d(calc.) = 3.14, d(exp.) = 3.10 [72]. *Infrared data*: 2260m, 2270sh cm^{-1} (ν_2, sym. C≡N stretching); 1367 cm^{-1} (ν_3, sym. CH_3 deform.); 926m cm^{-1} (ν_4, sym. C─C stretching); 2298 ($\nu_3 + \nu_4$, combination band); 1035 cm^{-1} (ν_7, degenerate CH_3 rocking) [72]. *Magnetic susceptibility data*: $\mu_{eff.} = 3.39$ B.M.(65–300 K)[g], $C = 1.430$ emu K mole^{-1}, $\theta = -65.7$ K, $T_N = 12$ K [72]. *Other available information*: NIR and visible absorption spectrum; decomposition [72].
$UCl_3{\cdot}2H_2O{\cdot}2CH_3CN$	*General properties*: deep dark reddish needles. *X-ray single-crystal data*: triclinic: $P\bar{1}$, C_i^1, No.2; $a = 7.153(1)$; $b = 8.639(2)$; $c = 10.541(2)$; $\alpha = 108.85(3)^\circ$; $\beta = 105.05(3)^\circ$; $\gamma = 93.57(3)^\circ$; $V = 587.6(3)$ (Å^3); $Z = 2$; d(calc.) = 2.61 (g/cm^3); d(U─Cl) = 2.775; d(U─Cl) to the bridging anions = 2.860–2.901; d(U─O) = 2.468–2.485; d(U─U) = 4.605. The U^{3+} ion is eight-fold coordinated by five chlorine anions and two water molecules and one methyl cyanide, which are forming a distorted bicapped trigonal prism. The characteristic feature of this structure is the link of the uranium atoms through two common edges of the Cl1 and Cl3 chlorine atoms into an infinitive zigzag chain in the [0 1 0] direction [70].
$CsUCl_4$	*General properties*: deep ink-blue; soluble in polar organic solvents [90]. *X-ray powder diffraction data*: could not be unambigously indexed. *Magnetic susceptibility data*: $\mu_{eff.} = 3.16$ B.M. (60–300)[g]; $\theta = -36$ K; $C = 1.2146$ [emu K mol^{-1}] [90]. *Other information available*: X-ray powder diffraction data; NIR, Vis, and UV absorption spectra [90].
K_2UCl_5	*General properties*: purple; soluble in polar organic solvents, m.p. = 608 °C – congruently; *X-ray single crystal data*: orthorhombic; *Pnma*, D_{2h}^{16}, No. 62; $Z = 4$. Monocapped trigonal prisms $[UCl_7]$ are connected via two opposite common edges to chains, $[UCl1_{1/1}Cl2_{1/1}Cl3_{1/1}Cl4_{4/2}]^{-2}$, that run in the [0 1 0] direction of the unit cell. $a = 12.7224(7)$, $b = 8.8064(6)$, $c = 7.9951(5)$, $V = 1348.8(1)$: d(calc.) = 3.68, d(exp.) = 3.67 [60]. *Atomic and crystal-field parameters for U^{3+}:K_2LaCl_5 single crystals*: $F^2 = 38952(160)$, $F^4 = 32707(180)$, $F^6 = 22336(274)$, $\zeta = 1621(2)$; $M^0 = [0.67]$, $M^2/M^0 = [0.552]$, $M^4/M^0 = [0.388]$, $P^2 = [1216]$, $P^4/P^2 = [0.5]$, $P^6/P^2 = [0.1]$; $T^2 = [306]$, $T^3 = [42]$, $T^4 = [188]$, $T^6 = [-242]$, $T^7 = [447]$, $T^8 = [300]$; $B_0^2 = 733$ (56), $B_0^4 = 1553(140)$, $B_0^6 = 402(39)$, $B_2^2 = -362(78)$, $B_2^4 = 727(153)$, $B_4^4 = 379(156)$, $B_4^6 = 614(99)$, $B_1^2/B_0^2 = 0.847$, $B_1^4/B_0^4 = -0.155$, $B_3^4/B_0^4 = 0.417$, $B_1^6/B_0^6 = -1.983$, $B_2^6/B_0^6 = -0.428$, $B_3^6/B_0^6 = -1.045$, $B_5^6/B_0^6 = -1.090$, $B_6^6/B_0^6 = 1.353$, $n = 37$. $\sigma = 26$, $N_v = 3069$ [13]. *Infrared data*: ν(U─Cl, stretching) = 140–220 [73]. *Magnetic susceptibility data*: antiferromagnetic; one dim. ordering temp. = 15.1; $T_N = 3.6(2)$ or 3.7(2); heat cap. 3.8(1); $\mu_{eff.} = 3.56$ B.M. (120–300 K)[g]; $\theta = -21.5$ K [59,73]. *Other information available*: IR, NIR, and Vis absorption spectra; magnetic susceptibilities [73]; luminescence and low temperature spectra of U^{3+}:K_2LaCl_5 [185]; magnetic phase transitions [57]; fused salt systems [185]; crystal-field analysis of U^{3+}:K_2LaCl_5 single crystals [13].
Rb_2UCl_5	*General properties*: violet-red; soluble in polar organic sovents; m.p. = 575 °C – incongruently. *X-ray powder diffraction data*: orthorhombic; *Pnma*, D_{2h}^{16}, No. 62; $Z = 4$; monocapped trigonal prisms $[UCl_7]$ are connected via two opposite common edges to chains; $a = 13.1175(8)$, $b = 8.9782(6)$, $c = 8.1871(7)$, $V = 1451.19(2)$ Å^3; d(calc.) = 4.04, d(exp.) = 4.07; d(U─Cl) = 2.774 to 2.846; d(U─U) = 4.651 (interchain); d(U─U) = 7.88 (intrachain) [60]. *Magnetic susceptibility data*: antiferromagnetic; one dim. ordering temp. = 11.1; $\mu_{eff.} = 3.49(2)$ B.M. (40–300 K)[g]; θ = −13.2 K; $C = 1.52(2)$ [60,73]. *Infrared data*: IR: ν(U─Cl, stretching) = 100–260 [73]. *Other information available*: NIR and visible absorption spectrum; magnetic susceptibilities [60,73]; fused salt systems [185].
Cs_2UCl_5	*General properties*: m.p. = 370 °C – decomposition in the solid state. *X-ray powder diffraction data*: orthorhombic; $Z = 4$, $a = 12.03$, $b = 9.76$, $c = 9.37$; d(calc.) = 4.08, d(exp.) = 4.02 [185]. *Other information available*: fused salt systems [185].
$(NH_4)_2UCl_5$	*General properties*: violet. *Magnetic susceptibility data*: $\mu_{eff.} = 3.54$ B.M. (17–220 K)[g]; $\theta = -26.0$ K; $\mu_{eff.} = 3.47$ B.M. (220–300 K)[c]; $\theta = -37.5$ K; $T_N = 7.8$ K [73]. *Infrared data*: ν(U─Cl, stretching) = 140–260 [73]. *Other information available*: NIR and Vis absorption spectra [73].
$SrUCl_5$	*General properties*: deep olive-green. *X-ray powder diffraction data*: could not be indexed. *Magnetic susceptibility data*: $\mu_{eff.} = 3.65$ B.M., (90–300 K)[g]; $C = 1.653$ emu K mole^{-1}, $\theta = -127$ K. *Other information available*: X-ray powder diffraction data; NIR and Vis absorption spectra [78].

Table 1 (*Continued*)

Formula	Selected properties and physical data[b], lattice constants[c], references[d]
$[(CH_3)_3N]_3UCl_6$	*General properties*: dark violet-blue fine crystalline powder. *X-ray powder diffraction data*: tetragonal; $a = 13.020$, $c = 7.825$; $Z = 2$; $V = 1326.48$ Å^3; d(calc.) = 1.68, d(exp.) = 1.6. *Infrared data* (in cm^{-1}): 110m [$\delta(UCl_6)$ A_u]; 123m,b [$\delta(UCl_6)$ E_u] 203s [lattice or cation vib.]; 236s [$\nu_s(UCl_6)$ A_u]; 259s [$\nu_{as}(UCl_6)$ E_u]. Raman (in cm^{-1}): 79sh [lattice]; 89w [$\delta(UCl_6)$ E_g]; 104w [$\delta(UCl_6)$ B_g]; 131m [lattice or cation vib.]; 226vs [$\nu_{as}(UCl_6)$ A_g]; 237sh [$\nu'(UCl_6)$ A_g]; 268w [$\nu_s(UCl_6)$ B_g]. *Magnetic susceptibility data*: $\mu_{eff.}$ = 3.36 B.M. (200–300K)[g] $\theta = 17$; $T_N = 4.8$ K; $C = 1.5058$ emu K mol^{-1}. *Other information available*: solid state NIR, Vis and UV absorption spectra [77].
RbU_2Cl_7	*General properties*: pale-brown; soluble in polar organic solvents. *X-ray powder diffraction data*: orthorhombic; $Z = 4$, $a = 12.86(5)$, $b = 6.89(1)$,$c = 12.55(2)$, d(calc.) = 4.80(3), d(exp.) = 4.74(3). Structure type of $RbDy_2Cl_7$ [88,185]. *IR transmission and Raman spectra*: IR (in cm^{-1}): 281s, 271s, 210s, 202vs, 195sh, 190vs, 181vs, 169vs, 150sh [ν(U—Cl)]; 130m,125m,114m, 90m [δ(Cl—U—Cl)]; 83sh, 70m, 55w [T'(Rb/U)]; RS (in cm^{-1}): 262w, 227,s,b, 189s,165s [ν(U—Cl)]; 142m,120m,95w [δ(Cl—U—Cl)]; 85m,62m T'(Rb/U) [54]. *Atomic and crystal-field parameters for U^{3+}:RbY_2Cl_7 single crystals*: for side (1): E_{ave} = 19244(12), F^2 = 39245(124), F^4 = 31462(199), F^6 = 23195(205), ζ = 1614(2); α = 26.8(0.9), $\beta = -819(38)$, γ = [1093] M^0 = [0.67], M^2 = [0.37], M^4 = [0.26], P^2 = [1216], P^4 = [608], P^6 = [121.6]; T^2 = [306], T^3 = [42], T^4 = [188], $T^6 = [-242]$, T^7 = [447], T^8 = [300]; $B_0^2 = -1057(78)$, B_0^4 = 224(147), B_0^6 = 113(168), $B_2^2 = -680(55)$, $B_2^4 = -856(99)$, $B_4^4 = -821(96)$, B_2^6 = 795(78), B_4^6 = 191(119), B_6^6 = 1163(93); n = 65. σ = 25, N_v = 3613. For site (2): E_{ave} = 19230(16), F^2 = 39127(156), F^4 = 31321(284), F^6 = 23492(255), ζ = 1611(2); α = 26.5(1.1), $\beta = -811(51)$, γ = [1093] M^0 = [0.67], M^2 = [0.37], M^4 = [0.26], P^2 = [1216], P^4 = [608], P^6 = [121.6]; T^2 = [306], T^3 = [42], T^4 = [188], $T^6 = [-242]$, T^7 = [447], T^8 = [300]; $B_0^2 = -1113(105)$, B_0^4 = 1109(105), B_0^6 = 902(180), $B_2^2 = -630(76)$, $B_2^4 = -1132(137)$, $B_4^4 = -1195(114)$, $B_2^6 = -505(128)$, B_4^6 = 70(125), $B_6^6 = -1301(97)$; n = 66. σ = 31, N_v = 4354 [22]. *Magnetic susceptibility data*: $\mu_{eff.}$ = 3.76 B.M., C = 1.750 emu K mol^{-1}, $\theta = -80$ K. *Other information available*: NIR and Vis low temperature absorption spectrum; magnetic susceptibility data; luminescence and excitation spectra [34]; low temperature absorption spectrum and crystal-field analysis of U^{3+}:RbY_2Cl_7 [22].
Ba_2UCl_7	*General properties*: deep black-brown; soluble in polar organic solvents. *X-ray powder diffraction data*: monoclinic; $P2_1/c$,C_{2h}^5, No. 14; a = 7.20, b = 15.61, c = 10.66, β = 91.1°, V = 1197 Å^3; d(calc.) = 4.22, d(exp.) = 4.14 [78,88,185]. *Atomic and crystal-field parameters for U^{3+}:Ba_2YCl_7*: E_{ave} = 19457(18), F^2 = 39913(59), F^4 = 33021(93), F^6 = 23081(97), ζ_{5f} = 1617(7); α = 35.29(4.5), $\beta = -1095(31)$, γ = 1202(51); T^2 = 293, T^3 = 50, T^4 = 183, $T^6 = -183$, T^7 = 407, T^8 = 300; $M^2 = 0.55\ M^0$, $M^4 = 0.38\ M^0$; $P^4 = 0.5\ P^2$, $P^6 = 0.1P^2$; B_0^2 = 838(52), $B_1^2 = -250(51)$, Im$B_1^2 = -168(64)$, $B_2^2 = -357(50)$, Im$B_2^2 = -363(53)$, B_0^4 = 875(86), B_1^4 = 952(59), ImB_1^4 = [11], B_2^4 = 1046, ImB_2^4 = 758(69), B_3^4 = [27], Im$B_3^4 = -376(76)$, B_4^4 = 261(73), ImB_4^4 = [27], $B_0^6 = -1084(94)$, B_1^6 = 496(77), ImB_1^6 = [85], B_2^6 = [7], ImB_2^6 = [33], B_3^6 = 411(83), ImB_3^6 = [37], $B_4^6 = -753(65)$, ImB_4^6 = 171(89), $B_5^6 = -20(54)$, Im$B_5^6 = -100(72)$, $B_6^6 = -214(78)$, Im$B_6^6 = -307(81)$; n = 65, σ = 25; N_v = 3154. *Magnetic susceptibility data*: $\mu_{eff.}$ = 3.25 B.M., (105–300 K)[g], C = 1.310 emu K mole^{-1}, $\theta = -95$ K. *Other information available*: IR, NIR and Vis absorption spectra [78]; crystal-field and AOM (angular overlap model) parameters [24].
Cs_2LiUCl_6	*General properties*: deep ink-blue crystals. *X-ray powder diffraction data*: cubic; $Fm3m$, O_h^5, No.225; $Z = 4$, a = 10.671, V = 1218.03 Å^3; d(calc.) = 3.9444, d(exp.) = 3.91 [90]. *Atomic and crystal-field parameters for U^{3+}:Cs_2LiUCl_6 single crystals*: E_{ave} = 19267(71), F^2 = 38820(194), F^4 = 29960(188), F^6 = 21414(247), ζ = 1622(20); α = [27], $\beta = [-830]$, γ = [1093] M^0 = [0.67], M^2 = [0.37], M^4 = [0.26], P^2 = [1216], P^4 = [608], P^6 = [122]; T^2 = [306], T^3 = [42], T^4 = [188], $T^6 = [-242]$, T^7 = [447], T^8 = [300]; B_0^4 = 4647(99), B_0^6 = 278(73); n = 27. σ = 57, N_v = 5496 [23]. *Magnetic susceptibility data*: $\mu_{eff.}$ = 3.56 B.M. (85–300)[g]; C = 1.571 emu K mole^{-1}, $\theta = -103$ K [90]. *Other information available*: X-ray powder diffraction data, NIR, Vis and UV absorption spectra, magnetic susceptibilities [90]; absorption, vibronic and emission spectra; crystal-field parameters [90,23].
K_2NaUCI_6	*X-ray powder diffraction data*: hexagonal; C_{3v}^1, $P3m1$, No.156. isostructural with α-K_2LiAlF_6; a = 7.28(1), c = 17.79(2), $Z = 3$; V = 816.53; d(calc.) = 3.35(1), d(exp.) = 3.41(5) [88,89]. *Other information available*: thermodynamic data [186].
Rb_2NaUCI_6	*X-ray powder diffraction data*: trigonal; $Z = 6$, a = 7.27(2), c = 35.51(10); d(calc.) = 3.93(3), d(exp.) = 3.98(2); structure type of Rb_2LiAlF_6 and Cs_2NaCrF_6 [88,89]. *Thermodynamic data*: ΔH° of formation from bin. = -25.1 ± 0.9 kJ/mol, ΔH° of formation from components = 14.6 ± 1.9 kJ/mol [186].
Cs_2NaUCl_6	*General properties*: ink-blue; soluble in polar organic solvents. *X-ray single-crystal data*: cubic; $Fm\bar{3}m$, O_h^5, No.225; $Z = 4$, a = 10.937(1), V = 1308.3(5) Å^3; Each of the uranium or sodium ions is octahedrally surrounded by six chloride ions at a distance of 2.723(9) and 2.746(9) Å, respectively. The cesium ions (site symmetry T_d) are surrounded by twelve equidistant chloride ions with d(Cs—Cl) = 3.867(8) Å. d(U—Cl) = 2.723(9), d(U—U) = 7.734; d(calc.) = 3.754, d(exp.) = 3.71 [187]. *Atomic and crystal-field parameters for U^{3+}:Cs_2NaUCl_6 single crystals*: E_{ave} = 19241(76), F^2 = 38708(207), F^4 = 29955(200), F^6 = 21228(265), ζ = 1614(22); α = [27]), $\beta = [-830]$, γ = [1093] M^0 = [0.67], M^2 = [0.37], M^4 = [0.26], P^2 = [1216], P^4 = [608], P^6=[122]; T^2 = [306], T^3 = [42], T^4 = [188], $T^6 = [-242]$, T^7 = [447], T^8 = [300]; B_0^4 = 4914(109), B_0^6 = 363(77); n = 25. σ = 61, N_v = 5816 [23]. *Magnetic properties*: $\mu_{eff.}$ = 2.49 B.M. (4-20)[g]; $\theta = 0.53$ K. $\mu_{eff.}$ = 2.92 B.M. (25-50)[d]; $\theta = 9.6$ K [188]. *Other information available*: thermodynamic properties [186]; NIR, Vis and UV low temperature absorption and luminescence spectra; crystal-field parameters [23]; IR spectra [55].
NaU_2Cl_6 or $(Na^+)(U^{3+})_2(e^-)(Cl^-)_6$	*X-ray single-crystal data*: hexagonal; $P6_3/m$,C_{6h}^2, No 176; $Z = 1$; a = 7.5609(3), c = 4.3143(3), d(U—Cl) = 2.945 (6×) and 2.977 Å (3×), d(Na—Cl) = 2.878 (6×)]. The compound is isostructural with $NaPr_2Cl_6$ and may be described as a stuffed derivative of UCl_3 [110].
$KUCl_4{\cdot}4H_2O$	*General properties*: violet-red; soluble in polar organic solvents [71]. *X-ray powder diffraction data*: orthorhombic; $Z = 2$, a = 6.971, b = 6.638, c = 11.317, V = 523.6 Å^3; d(calc.) = 3.11, d(exp.) = 3.08 [8]. *Infrared data*: 650, 610 cm^{-1} (U—OH_2 rocking); 470s cm^{-1} (U—OH_2 wagging); 300w cm^{-1} ν(U—OH_2 stretching); 222sh, 214s, 198s cm^{-1} ν(U—Cl, stretching); 166s cm^{-1} ν(U—Cl—U, stretching or lattice); 130s cm^{-1} δ(Cl—U—Cl, stretching or lattice); 107s, 88sh cm^{-1} (lattice modes) [71]. *Magnetic susceptibility data*: $\mu_{eff.}$ = 3.72 B.M. (100–300 K)[g]; C = 1.716 emu K mol^{-1}; $\theta = -69.3$ K.

Table 1 (*Continued*)

Formula	Selected properties and physical data[b], lattice constants[c], references[d]
$RbUCl_4{\cdot}4H_2O$	*General properties*: violet-red; soluble in polar organic solvents. *X-ray powder diffraction data*: orthorhombic; $Z=2$, $a=6.999$, b=6.673, $c=11.375$; $V=531.3$ Å^3; d(calc.) = 3.36, d(exp.) = 3.34 [8]. *Other information available*: magnetic susceptibility data; IR, NIR and Vis absorption spectra [71].
$NH_4UCl_4{\cdot}4H_2O$	*General properties*: dark red-violet; soluble in polar organic solvents [8,71]. *X-ray single-crystal data*: orthorhombic, $P2_12_12$, D_2^3, No. 18; $Z=2$; $a=7.002(2)$, $b=11.354(3)$, $c=6.603(2)$; $V=524.94(14)$ Å^3. The U^{3+} cation is coordinated by four Cl^-, ions and four H_2O molecules. The crystal is built up from 8 coordinated U^{3+} polyhedra, which are connected via O—H·Cl hydrogen bonds. d(U—Cl) (2×) = 2.845(4); d(U—Cl)) (2×) = 2.847(4); d(U—O) (2×) = 2.510(11); d(U—O) (2×) = 2.568(10); d(calc.) = 2.973, d(exp.) = 2.97 [8]. *Atomic and crystal-field parameters*: $F^2=39911$ (85), $F^4=33087(149)$, $F^6=22048(160)$, $\zeta=1627.3(8.8)$; $\alpha=33.0(3.7)$, $\beta=-973.1(29.3)$, $\gamma=1316.9(85.4)$; $T^2=306$, $T^3=42$, $T^4=188$, $T^6=-242$, $T^7=447$, $T^8=300$; $M^0=0.672$, $M^2=0.372$, $M^4=0.258$; $P^2=1216$, $P^4=608$, $P^6=122$; $B_0^2=721(47)/[698]$, $B_2^2=428(39)/[403]$, $\mathrm{Im}B_2^2=-460(39)/[-515]$, $B_0^4=[-814]$, $B_2^4=[-858]$, $\mathrm{Im}B_2^4=[118]$, $B_4^4=[-670]$, $\mathrm{Im}B_4^4=[-22]$, $B_0^6=[-403]$, $B_2^6=[-612]$, $\mathrm{Im}B_2^6=[838]$, $B_4^6=[-549]$, $\mathrm{Im}B_4^6=[-197]$, $B_6^6=[-1063]$, $\mathrm{Im}B_6^6=[-96]$, $\sigma=30$, $n=83$ [7]. *Infrared data* (in cm^{-1}): 650, 610 (U—OH_2, rocking); 494s (U—OH_2, wagging); 299ms [ν(U—OH_2) stretching]; 222s, 202s ν(U—Cl, stretching); 175ms [ν(U—Cl—U), stretching or lattice]; 130s [δ(Cl—U—Cl), bending]; 114ms, 84sh (lattice modes) [71]. *Magnetic susceptibility data*: $\mu_{\mathrm{eff.}}=3.53$ B.M. (100–240 K)[g]; $C=1.560$ emu K mol^{-1}, $\theta=-72.5$ K) [71]. *Other information available*: magnetic susceptibility data; NIR and Vis absorption spectra low temperature absorption spectra and crystal-field analysis [7,71].
$KUCl_4{\cdot}3H_2O$	*General properties*: green; hygroscopic and air sensitive [76]. *X-ray powder diffraction data*: monoclinic; $a=6.9373$; $b=7.2658$; $c=9.5209$; $\beta=96.71^\circ$, $V=476.62$ Å^3; $Z=2$; d(calc.) = 3.30 [76]. *Infrared data*: IR: ν(U—OH_2, rocking) = 635s, 575s; ν(U—OH_2, wagging) = 480; ν(U—OH), stretching = 425, 280sh; ν(U—Cl), stretching = 260s, 238, 202; ν(U—Cl—U), stretching or lattice = 169, 125; δ(Cl—U—Cl), bending = 144, 125; ν(stretching and bending modes of coordinated water) = 1600; (3170, 3215, 3360, 3420) [76]. *Magnetic susceptibility data*: $\mu_{\mathrm{eff.}}=3.70$ B.M. (150–300 K)[g]; $C=1.7033$ emu K mol^{-1}, $\theta=-80$ K [76]. *Other information available*: X-ray powder diffraction data; IR, NIR and Vis absorption spectra [76].
$RbUCl_4{\cdot}3H_2O$	*General properties*: greenish-brown to brown; hygroscopic and air sensitive [76]. *X-ray powder diffraction data*: monoclinic; $a=8.8986$; $b=6.9738$; $c=8{,}0517$; $\beta=100^\circ$, $V=490.75$ Å^3; $Z=2$; d(calc.) = 3.51 [76]. *Infrared data*: ν(U—OH_2, rocking) = 650, 615, 600; ν(U—OH_2, wagging) = 485; ν(U—OH), stretching = 380, 285sh; ν(U—Cl), stretching = 255s, 220, 190; ν(U—Cl—U), stretching or lattice = 151, 157; δ(Cl—U—Cl), bending = 132, 127, 121, 118; ν(stretching and bending modes of coordinated water) = 1565, 1580, 1605, 3470; (3180, 3210, 3350, 3420, 3470). *Magnetic susceptibility data*: $\mu_{\mathrm{eff.}}=3.57$ B.M. (100–300 K)[g], $C=1.5766$ emu K mol^{-1}, $\theta=-64$ K) [76]. *Other information available*: NIR and Vis absorption spectra [76].
$CsUCl_4{\cdot}3H_2O$	*General properties*: brown-green; soluble in polar organic solvents [74,75]. *X-ray single-crystal data*: monoclinic, $P2_1/m$, C_{2h}^2, No. 11; $Z=4$; $a=7.116(1)$, $b=8.672(2)$, $c=8.071(2)$, $\beta=99.28(3)^\circ$, $V=956.96$ Å^3; d(U—Cl) = 2.957 (3×), d(U—O) = 2.552 (3×) (mean values) [75]; tricapped trigonal prism consisting of six Cl and three O atoms (of the water molecules). Cesium is surrounded by eight chlorine atoms in the shape of a distorted cube which is capped by two non-bonded water ligands at a mean distance of 360.2 pm. The $[U(Cl1)_4(Cl2)_2(H_2O)_3]$ polyhedra are connected via two common edges of chloride (Cl1) ligands of two triangular faces of the trigonal prism of chloride ions to an infinite zigzag chain in the [0 1 0] direction. *Atomic and crystal-field parameters*: $F^2=39876(58)$, $F^4=33279(77)$, $F^6=23598(68)$, $\zeta_{5f}=1648.3(10.3)$; $\alpha=26.2(4.3)$, $\beta=-889(38)$, $\gamma=1131(94)$; $T^2=306$, $T^3=42$, $T^4=188$, $T^6=-242$, $T^7=447$, $T^8=300$; $M^0=0.672$, $M^2=0.372$, $M^4=0.258$; $P^2=1216$, $P^4=608$, $P^6=122$; $B_0^2=-411(46)/[-390]$, $B_2^2=614(45)/[573]$, $\mathrm{Im}B_2^2=610(46)/[614]$, $B_0^4=[-699]$, $B_2^4=[-398]$, $\mathrm{Im}B_2^4=[-525]$, $B_4^4=[-1039]$, $\mathrm{Im}B_4^4=[-49]$, $B_0^6=[-1046]$, $B_2^6=[-58]$, $\mathrm{Im}B_2^6=[794]$, $B_4^6=[-119]$, $\mathrm{Im}B_4^6=[-173]$, $B_6^6=[-27]$, $\mathrm{Im}B_6^6=[-691]$, $\sigma=34$; $n=77$ [7]. *Magnetic susceptibility data*: $\mu_{\mathrm{eff.}}=3.39$ B.M., $C=1.430$ emu K mol^{-1}, $\theta=-67.7$ K) [76].*Other information available*: NIR and Vis low temperature absorption spectra; crystal-field analysis [7,76].
$NH_4UCl_4{\cdot}3H_2O$	*General properties*: greenish-brown to brown; hygroscopic and air sensitive [76]. *X-ray powder diffraction data*: monoclinic; $a=13.7693$; $b=8.8990$; $c=7.8643$; $\beta=95.65^\circ$, $V=956.95$ Å^3; $Z=4$; d(calc.) = 3.12 [76]. *Infrared data*: (in cm^{-1}): ν(U—OH_2, rocking) = 615sh, 590s; ν (U—OH_2, wagging) = 470s; ν(U—OH), stretching = 385, 290sh; ν(U—Cl), stretching = 266s, 232; ν(U—Cl—U), stretching or lattice = 172; δ(Cl—U—Cl), bending = 147, 128; ν(stretching and bending modes of coordinated water) = 1585, 1600; $\nu_4(NH_4)=1404$ vs; $\nu_2(NH_4)=1670$, $\nu_4+\nu_6(NH_4)=1770$, $2\nu_4-\nu_5(NH_4)=2710$, $\nu_1(NH_4)=3040$, $\nu_3(NH_4)=3160$vs. Magnetic susceptibility data: $\mu_{\mathrm{eff.}}=3.71$ B.M. (75–300 K)[d]; $C=1.7073$ emu K mole^{-1}, $\theta=-54$ K [76]. *Other information available*: NIR and Vis absorption spectra; magnetic susceptibility data [76].
UOCl	*General properties*: red; insoluble. *X-ray single-crystal data*: tetragonal; D_{4h}^7, $P4/nmm$, No. 129; (PbFCl type of structure); $Z=2$, CN = 9, $a=4.043$, $c=6.882$; d(U—Cl) = 2.373 (2×), d(U—Cl) = 3.074 (1×), d(U—Cl) = 3.150 (4×) [116,189]. *Infrared data*: (in cm^{-1}): 500m (E_u), 340s (A_{2u}) [115]. *Magnetic susceptibility data*: $\mu_{\mathrm{eff.}}=3.40$ B.M., $\theta=-145$ K (240–300 K[g]) [115]. *Thermodynamic data*: $\Delta_fG_m^o=-785.7(4.89)$[e], $\Delta_fH_m^o=-833.9(4.2)$[e], S_m^o=102.5(8.4)[e]; $C_{p,m}^o$=71.0(5.0)[e]. $\mu_{\mathrm{eff.}}=3.40$ B.M. (240–300K)[d]; $\theta=-145$ K [164,165]. *Other information available*: photo-electron spectra [190].
U(NH)Cl	*Crystallographic data*: tetragonal; D_{4h}^7; $P4/nmm$, No.129; $a=3.972(5)$, $b=3.972(5)$, $c=6.81(1)$; $Z=2$; $V=107.44$; d(calc.) = 8.91 [191].
$Cs_2U[Cl_9\ O_3(TaCl)_6]$	*Crystallographic data*: trigonal/rhombohedral; $P\bar{3}1c$, D_{3d}^2, No.163; $a=9.1824(5)$, $b=9.1824(5)$, $c=17.146(2)$; $Z=2$, $V=1252.01$; d(calc.) = 5.75 [192].

Table 1 (*Continued*)

Formula	Selected properties and physical data[b], lattice constants[c], references[d]
UBr_3	*General properties*: reddish-brown; is much more hygroscopic and sensitive to oxidation in air than UCl_3; soluble in acetic acid, dimethylacetamide; somewhat more stable solutions are formed in formamide, methyl acetate, dimethylacetamide and acetic acid. Is reduced by calcium to metallic uranium at high temperatures; density: 6.53 g/cm^3; m.p. = 835 °C, b.p. = 1537 °C. X-ray single-crystal data: hexagonal (UCl_3 type of structure), $P6_3m$, C^2_{6h}, No.176; Z = 2, CN = 9, a = 7.942(2), c = 4.441(2), (a = 7.9519 Å, c = 4.448; d(calc.) = 6.54, d(exp.) = 5.98; d(U—Br) = 3.145 Å (3.150 Å) to the three capping Br atoms, d(U–Br) = 3.062 Å (3.069 Å) to the six Br atoms at the prism vertices, d(Br—Br) = 3.652 Å (3.663 Å) at the trigonal prism face edge and d(U—U) = 4.441 Å (4.448 Å) along the c-direction. The face Br—U—Br angle is 73.21Circ (73.3Circ). [1,193,198]. Thermodynamic properties: UBr_3(cr): $\Delta_f G^o_m = -673.2(4.2)$[e], $\Delta_f H^o_m = -698.7(4.2)$[e], $S^o_m = 192.98(0.5)$[e]; $C^o_{p,m} = 105.83(0.5)$[e]. UBr_3(g): $\Delta_f G^o_m = -408.1(20.5)$[e], $\Delta_f H^o_m = -371.0(20.0)$[e], $S^o_m = 403.0(15.0)$[e]; $C^o_{p,m} = 85.20(5.0)$[e]. K; log(p/mmHg) = $-16420/T + 22.95 - 3.02 \log T$ (298–1000 K). log(p/mmHg) = $-15\,000/T + 27.54 - 5.03 \log T$ (1000–1810 K) [164,165,199]. Atomic and crystal-field parameters: E_{avg} = 19213(74), F^2 = 37796(265), F^4 = 30940(313), F^6 = 20985(315), ζ = 1604(19); α = 27(8), β = −823(54), γ = 1647(168); T^2 = 374(125), T^3 = 29(34), T^4 = 262(58), T^6 = −258(77), T^7 = 264(60), T^8 = [300]; M^o = [0.6630]; P^2 = 1707(89); B^2_0 = 410(50), B^4_0 = −452(86), B^6_0 = −1637(77), B^6_6 = 722(63); n = 47; σ = 36.5 [30]. Magnetic susceptibility data: $\mu_{eff.}$ = 3.29 B.M. (350–483 K)[g]; θ = 25 K, T_N = 15 K [182]. Other available information: NIR, Vis and UV absorption spectra [30]; fused salt systems [86], crystal-field analysis of U^{3+}:$LaBr_3$ [28]; photoelectron spectra [190].
$UBr_3 \cdot 6H_2O$	*X-ray powder diffraction data*: monoclinic, $P2/n$; a = 10.061, b = 6.833, c = 8.288, β = 92.99°, V = 285.00 Å^3 [111].
K_2UBr_5	*General properties*: dark violet; soluble in polar organic sovents; m.p. 625 °C – congruently. *X-ray powder diffraction data*: orthorhombic, *Pnma*, D^{16}_{2h}, No. 62; Z = 4, CN = 6, a = 13.328(1), b = 9.2140(7), c = 8.4337(5), V = 1559.5(2); d(calc.) = 4.53; d(exp.) = 4.51 [60,194]. *Thermodynamic data*: $\Delta H^o_{f,298}$ = −384.3(1.0)[f] [113,199]. *Atomic and crystal-field parameters for U^{3+}*: *K_2LaBr_5 single crystals*: F^2 = 38962(131), F^4 = 32779(168), F^6 = 22488(224), ζ = 1626(2); M^0 = [0.67], M^2/M^0 = [0.552], M^4/M^0 = [0.388], P^2 = [1216], P^4/P^2 = [0.5], P^6/P^2 = [0.1]; T^2 = [306], T^3 = [42], T^4 = [188], T^6 = [−242], T^7 = [447], T^8 = [300]; B^2_0 = 603(47), B^4_0 = 1142(143), B^6_0 = 305(39), B^2_2 = −315(76), B^4_2 = 582(177), B^4_4 = 242(171), B^6_4 = 501(97), B^2_1/B^2_0 = 0.954, B^4_1/B^4_0 = −0.123, B^4_3/B^4_0 = 0.415, B^6_1/B^6_0 = −2.246, B^6_2/B^6_0 = −0.223, B^6_3/B^6_0 = −1.200, B^6_5/B^6_0 = −0.993, B^6_6/B^6_0 = 0.757, n = 38. σ = 26, N_v = 2402 [13]. *Magnetic susceptibility data*: antiferromagnetic; one dim. ordering temperature = 9.8(5); T_N = 2.6(3) or 3.8(3); heat cap. 2.7(1) $\mu_{eff.}$ = 3.52(1) B.M. (40–300 K)[g]; θ = −21.2 K; C = 1.55(1). *Infrared data*: d(U—Br) stretching vibrations: 110m, 124m, and 145s,br. *Other available information*: NIR, Vis an UV absorption spectra [60,194] magnetic phase transitions [57]. IR and thermodynamic data [113,163,199]; melting point diagrams [112].
Rb_2UBr_5	*General properties*: violet; polar organic solvents; m.p. 600 °C – congruently. *X-ray powder diffraction data*: orthorhombic, *Pnma*, D^{16}_{2h}, No. 62; Z = 4, CN = 6, a = 13.670(1), b = 9.3900(8), c = 8.6046(4), V = 1663.1(2) [60]. *Thermodynamic data*: $\Delta H^o_{f,298}$ = −384.3(1.0)[f] [113,198]. *Magnetic susceptibility data*: antiferromagnetic; one dimensional ordering temp. = 7.(1); $\mu_{eff.}$ = 3.46(1) B.M. (30–300 K)[g]; θ = −4.6(8) K; C = 1.50(1) [60]. *Infrared data*: d(U—Br) stretching vibrations: 111m, 124m, and 144s,br. [113,199]. *Other available information*: magnetic data; NIR, Vis an UV absorption spectra [60]; melting point diagrams [112].
Cs_2UBr_5	*General properties*: violet; m.p. 420 °C, congruently. *X-ray powder diffraction data*: orthorhombic; isostructural with Cs_2DyCl_5; Z = 4, CN = 6, a = 15.79(4), b = 9.85(5), c = 7.90(1); d(calc.) = 4.85(4)7, d(exp.) = 4.86 [88]. *Thermodynamic data*: $\Delta H^o_{f,298}$ = −395.0(1.2)[f] [113,198]. *Infrared data*: d(U—Br) stretching vibrations: 110m, 124m, and 149s,br. [113]. *Other available information*: melting point diagrams [112].
Rb_3UBr_6	*General properties*: dark-violet; m.p. 695 °C, congruently. *X-ray powder diffraction data*: cubic; face-centered; a = 11.03(2), d(calc.) = 4.79 [112].
Cs_3UBr_6	*General properties*: dark-violet; m.p. 758 °C, congruently. *X-ray powder diffraction data*: cubic; face-centered; a = 11.51(2); d(calc.) = 4.83 [185]. *Thermodynamic properties*: $\Delta H^o_{f,298}$ = −496(3)[f,h] [186,199].
K_2NaUBr_6	*X-ray powder diffraction data*: tetragonal, *P4/nbm*, D^3_{4h}, No. 125; Z = 4, a = 10.81(1), c = 11.30(1); d(calc.) = 4.09, d(exp.) = 4.04 [186]. *Other available information*: thermodynamic properties [186].
Cs_2NaUBr_6	*X-ray powder diffraction data*: cubic, *Pa3*, T^6_h, No. 205; Z = 4, a = 11.439(2), d(calc.) = 4.44, d(exp.) = 4.43 [186]. *Other available information*: thermodynamic properties [186].
UOBr	*X-ray powder diffraction data*: tetragonal (PbFCl type of structure), D^7_{4h}, *P4/nmm*, No.129; CN = 9; a = 4.063(1), c = 7.447(2) [115]. *Magnetic susceptibility data*: $\mu_{eff.}$ = 3.67 B.M. (250–300 K)[g]; θ = −140 K [115]. Infrared data: (in cm^{-1}): 500m (E_u), 320s (A_{2u}) [115]. *Other available information*: photoelectron spectra [170].
$K_2UBr_5 \cdot 2CH_3CN \cdot 6H_2O$	*General properties*: brown-red. *Magnetic susceptibility data*: $\mu_{eff.}$ = 3.33 B.M. (60–150 K)[f]; θ = −39.5(8) K; C = 1.382. *Infrared data*: ν_2(symmetric C≡N, stretching) = 2264m, 2276m; ν_3(symmetric CH_3, deformation) = 1366s; ν_4(symmetric C—C, stretching) = 936w; $\nu_3 + \nu_4$(combination band) = 2300; ν_7(degenerate, CH_3) = 1030. *Other available information*: decomposition; NIR, Vis and UV absorption spectra [80].
$Rb_2UBr_5 \cdot CH_3CN \cdot 6H_2O$	*General properties*: blue-violet. *Magnetic susceptibility data*: $\mu_{eff.}$ = 3.34 B.M. (80–240 K)[g]; θ = −63.2 K; C = 1.407. *Infrared data*: ν_2(symmetric C≡N, stretching) = 2256m, 2264m; ν_3(symmetric CH_3, deformation) = 1369s; ν_4(symmetric C—C, stretching) = 920w; $\nu_3 + \nu_4$(combination band) = 2292; ν_7(degenerate, CH_3) = 1032. *Other available information*: decomposition; NIR, Vis and UV absorption spectra [80].

Table 1 (*Continued*)

Formula	Selected properties and physical data[b], lattice constants[c], references[d]
$(NH_4)[UBr_2(CH_3CN)_2{\cdot}(H_2O)_5]Br_2$	*General properties*: brown. *X-ray single-crystal data*: orthorhombic, *Pnma*, D_{2h}^{16}, No. 62; $Z=4$, $a=8.98(2)$, $b=9.99(2)$, $c=20.24(4)$, $V=1816(7)$ Å^3; d(U—Br1) = 3.074(4); (2×), d(U—O1) = 2.538(12) (2×); d(U—O2) = 2.549(14) (2×), d(U—N1) = 2.517(30) (1×); d(U—N2) = 2.688(26) (1×), d(U—O3) = 2.652(20) (1×); d(calc.) = 2.74, d(exp.) = 2.81 [9]. *Infrared and Raman data* (in cm^{-1}): IR; $\nu(H_2O)$ with hydrogen bond character = 3325s,b; (3114s,b; 2952w); $\nu(CH_3)$ = 2921w; (2851w); combination band = 2307w; ν_s(C≡N) = 2273w; δ(HOH) = 1606m; $\delta_{as}(CH_3)$ = 1399s; (1378s); $\delta_s(CH_3)$ = 1189w, 1144w; δ(U—OH_2) = 1078w; $\rho(CH_3)$ = 1044w; ν(C—C) = 971w, 938w, 922w; ρ(U—OH_2) = 887w, 770w,721w; ω(U—OH_2) = 663vs,b, 670vs,b, 400–590s,vb; ν(U—OH_2) = 387m, 306m; $\nu(UN_2)$ = 202m; $\nu(UBr_2)$ = 157m,b, 115sh; $\delta(UBr_2)$ = 82w; (62w, 59w,47w, 37w). Raman; ν_s(C≡N) = 2280m; δ(HOH) = 1631m; $\delta_{as}(CH_3)$ = 1415w; (1356m); $\delta_s(CH_3)$ = 1261w, 1186w; δ(U—OH_2) = 1123m; $\rho(CH_3)$ = 1063m; ν(C—C) = 952w, 826w; ρ(U—OH_2) = 729w; ω(U—OH_2) = 651w, 611w, 536w; ν(U—OH_2) = 536w, 455m,b, 326w; $\nu(UN_2)$ = 282w; $\nu(UBr_2)$ = 195sh, 149 [9]. *Other available information*: magnetic susceptibility data; IR, Raman, NIR, Vis and UV spectra; factor group analysis [9].
UI_3	*General properties*: black; extremely moisture sensitive, soluble: methanol, ethanol, ethyl acetate, dimethyl-acetamide, acetic acid forming unstable U(III) solutions; m.p. = 766 °C; Is corrosive and attacks glass, which at 800 °C is reduced to silicon. Spontaneous oxidation within 1 min was observed in organic solvents like dioxan, pyridine, acetonitrile, dimethylformamide or acetone [103]. *X-ray single crystal and neutron diffraction data*: orthorhombic, ($TbCl_3$ and $PuBr_3$ type of structure), *Cmcm*, D_{2h}^{17}, No. 63; $a=4.334(6)$, $b=14.024(18)$, $c=10.013(13)$, $Z=4$. The coordination polyhedron is a bicapped trigonal prism, the third capping Br^- anion being withdrawn by bonding with another U atom; d(U—Il) = 3.165(12) (2×) and d(U—I2) = 3.244(8) (4×) (to the prism iodine atoms), d(U—I2) (2×) = 3.456(11) (to the cap iodine atoms), d(I2—I2) = 3.679(18) Å and d(U—U) = 4.328(5) Å. d(calc.) = 6.78, d(exp.) = 6.38 [86,107]. *Thermodynamic data*: UI_3(cr): $\Delta_f G_m^o = -466.122(4.9892)$[e], $\Delta_f H_m^o = -466.900(4.200)$[e], $S_m^o = 221.800(8.400)$[e]; $C_{p,m}^o = 112.100(6.000)$[e]; UI_3(g): $\Delta_f G_m^o = -198.654$ (25.2178)[e], $\Delta_f H_m^o = -137.000(25.000)$[e], $S_m^o = 431.200(10.000)$[e]; $C_{p,m}^o = 86.000(5.000)$ [86,164,165]. *Magnetic susceptibility data*: $\mu_{eff.} = 3.65$ B.M. (25–200 K)[g]; $\theta = -34$ K, $T_N = 3.4$ K; $\mu_{eff.} = 3.31$ B.M. (350–394 K)[d]; $\theta = 5$ K [108,181,182]. *Other available information*: diffuse reflectance spectra [103].
$UI_3{\cdot}4CH_3CN$	*General properties*: dark-brown. *X-ray powder diffraction data*: monoclinic; $Z=2$, $a=9.6168$, $b=8.7423$, $c=7.1858$, $\beta=92.99°$; $V=603.31$ Å^3; d(calc.) = 4.08 [122]. *Other available information*: magnetic susceptibility data; IR, NIR, Vis and UV absorption spectra [122].
$UI_3(THF)_4$	*General properties*: dark-purple. *X-ray single crystal data*: monoclinic, $P2_1/c$; C_{2h}^5, No.14; $Z=4$, $a=8.750(3)$, $b=16.706(16)$, $c=17.697(16)$, $\beta=93.64(3)$, $V=2582$ Å^3; d(calc.) = 2.33. The compound is mononuclear with a pentagonal bipyramidal coordination geometry about the uranium ion. Two iodide atoms with an average U—I lengths of 3.111(2) Å are axially coordinated. The third iodide ion and the four THF ligands lie in the equatorial plane with an U—I distance of 3.167(2) Å and average U—O distances of 2.52(1) Å [96]. *Other available information*: synthesis and reactivity; single crystal X-ray diffraction data; thermal gravimetric analysis; vibrational spectrum; ^{1}H NMR spectrum; electronic absorption spectrum [96].
K_2UI_5	*General properties*: deep-blue. *X-ray powder diffraction data*: orthorhombic; *Pnma*, D_{2h}^{16}, No. 62; $Z=4$, CN = 6, $a=14.293(1)$, $b=9.8430(5)$, $c=9.1067(5)$, $V=1929.1(2)$Å^3; d(U—I) = 3.182 to 3.275; d(U—U) = 5.143 (interchain); d(U—U) = 7.778 (intrachain) [60]. Monocapped trigonal prisms [UCl_7] are connected via two opposite common edges to chains. *Atomic and crystal-field parameters for U^{3+}:K_2LaI_5 single crystals*: $F^2=38433(145)$, $F^4=32700(142)$, $F^6=22352(246)$, $\zeta=1626(2)$; $M^0=[0.67]$, $M^2/M^0=[0.552]$, $M^4/M^0=[0.388]$, $P^2=[1216]$, $P^4/P^2=[0.5]$, $P^6/P^2=[0.1]$; $T^2=[306]$, $T^3=[42]$, $T^4=[188]$, $T^6=[-242]$, $T^7=[447]$, $T^8=[300]$; $B_0^2=463(46)$, $B_0^4=531(142)$, $B_0^6=295(26)$, $B_2^2=-220(63)$, $B_2^4=158(127)$, $B_4^4=41(186)$, $B_4^6=238(145)$, $B_1^2/B_0^2=0.836$, $B_1^4/B_0^4=-0.185$, B_3^4/B_0^4=0.247, $B_1^6/B_0^6=-2.603$, $B_2^6/B_0^6=-0.159$, $B_3^6/B_0^6=-0.708$, $B_5^6/B_0^6=-0.363$, $B_6^6/B_0^6=0.695$, $n=33$. $\sigma=23$, $N_v=1520$ [13]. *Magnetic susceptibility data*: antiferromagnetic; one dim. ordering temperature = 2.4(2); $T_N=1.4(1)$ heat cap. = 1.45(3) $\mu_{eff.} = 3.75(1)$ B.M. (7–300 K)[g]; $\theta=-12.0(5)$ K; $C=1.76(1)$ [60]. *Other available information*: NIR, Vis and UV absorption spectra, magnetic phase transitions [60,57]; low temperature absorption spectrum of U^3:K_2LaI_5: [184]; crystal-field analysis of U^{3+}:K_2LaI_5 single crystals [13]; IR and thermodynamic data [113].
Rb_2UI_5	*General properties*: blue-violet solid. *X-ray powder diffraction data*: orthorhombic, *Pnma*, D_{2h}^{16}, No. 62; $Z=4$; CN = 6, $a=14.546(2)$, $c=10.026(2)$, $b=9.249(1)$, $V=2031.1(5)$ Å [60]. *Other available information*: NIR, Vis and UV absorption spectra [60]. IR and thermodynamic data [113].
UOI	*General properties*: deep blue solid. *X-ray powder diffraction data*: tetragonal; (PbFCl type of structure), *P4/nmm*; D_{4h}^7, No. 129; CN = 9, $a=4.062(1)$, $c=9.208(2)$ [115]. *Magnetic susceptibility data*: $\mu_{eff.} = 3.56$ B.M. (220–300 K)[g]; $\theta=-150$ K [115]. *Infrared data*: (in cm^{-1}): 490m (E_u), 315s (A_{2u}) [115].
$UBrCl_2$	*General properties*:black with a greenish tinge; m.p.=(800 °C). *Thermodynamic data*: $UBrCl_2$(cr): $\Delta_f G_m^o = -760.3(9.8)$[e], $\Delta_f H_m^o = -812.100(8.4)$[e], $S_m^o = 175.700(16.7)$[e]; $\Delta S_{f,298}^o = -49.8$[f] [86].
UBr_2Cl	*General properties*: black with a greenish tinge; m.p.=(775 °C). *Thermodynamic data*: UBr_2Cl(cr): $\Delta_f G_m^o = -714.389(9.8765)$[e], $\Delta_f H_m^o = -750.600(8.400)$[e], $S_m^o = 192.500(16.700)$[e]; $\Delta S_{f,298}^o = -45.7$[f] [86,164,165].
Other mixed halides: (i) UCl_2I; (ii) $UClI_2$; (iii) UBr_2I; (iv) $UBrI_2$.	*General properties*: extremely moisture sensitive; (i) black, ∼750; (ii) black, ∼725; (iii) black, ∼700; (iv) black, ∼690 [86].
$U_2(SO_4)_3{\cdot}8H_2O$	*General properties*: brown; insoluble in organic solvents; relatively stable towards oxidation by air; *X-ray powder diffraction data*: orthorhombic; *Cmca*; D_{2h}^{18}; No. 64; $a=9.93$, $b=9.57$, $c=17.40$; $Z=4$; d(calc.) = 3.7, d(exp.) = 3.4 [117,120].*Other available information*: diffuse reflectance spectra; magnetic susceptibility data, decomposition analysis [117].

Table 1 (*Continued*)

Formula	Selected properties and physical data[b], lattice constants[c], references[d]
$(NH_4)U(SO_4)_2{\cdot}4H_2O$	*General properties*:Olive-green; insoluble in organic solvents; previously reported as $(NH_4)U(SO_4)_2{\cdot}4.5H_2O$ [117,120]. *Single crystal X-ray data*: monoclinic; $P2_1/c$; C_{2h}^5, No. 14; $a = 6.7065(2)$, $b = 19.0328(6)$, $c = 8.8305(3)$, $\beta = 97.337(1)^\circ$; $Z = 4$; CN = 9; d(U—O) = 2.37–2.60 (to sulfate ion); d(U—OH_2) = 2.47–2.56; d(calc.) = 3.07, d(exp.) = 3.0. The coordination sphere about each U atom consists of nine O atoms contributed by four sulfate groups and three water molecules. The fourth water molecule is not coordinated [117,120]. *Other available information*: diffuse reflectance and IR spectra; magnetic susceptibility data, decomposition analysis.
$RbU(SO_4)_2{\cdot}4H_2O$	*General properties*: Olive-green; insoluble in organic solvents. *X-ray powder diffraction data*: monoclinic; $P2_1/c$; C_{2h}^5; No. 14; $a = 6.66$, $b = 19.06$, $c = 8.75$; $\beta = 97^\circ$; d(calc.) = 3.5, d(exp.) = 3.2 [117]. *Other available information*: diffuse reflectance spectra; magnetic susceptibility data, decomposition analysis [117].
$CsU(SO_4)_2{\cdot}5.5H_2O$	*General properties*: olive-green; insoluble in organic solvents. *X-ray powder diffraction data*: orthorhombic, $a = 16.92$, $b = 18.\ 89$, $c = 14.56$; $Z = 8$; d(calc.) = 3.7, d(exp.) = 3.7 [117]. *Other available information*: diffuse reflectance spectra; magnetic susceptibility data, decomposition analysis [117].
$U(HCOO)_3$	*General properties*: olive-green; insoluble in organic solvents; slowly undergoes oxidation in air at room temperatures. *X-ray powder diffraction data*: rhombohedral; $R3m$; C_{3v}^5; No. 160; $a = 10.659$, $c = 4.104$, $V = 403.8$; $Z = 3$; CN = 9; d(calc.) = 4.60, d(exp.) = 4.58 [81]. *Atomic and crystal-field parameters*: $E_{avg} = 19488$ (38), $F^2 = 39746(133)$, $F^4 = 32457(23)$, $F^6 = 23232(242)$, $\zeta_{5f} = 1612(11)$; $\alpha = 30(6)$, $\beta = -951(40)$, $\gamma = 999(129)$; $T^2 = [293.0]$, $T^3 = [50.0]$, $T^4 = [183.0]$, $T^6 = [-183.0]$, $T^7 = [407.0]$, $T^8 = [300.0]$; $M^0 = [0.67]$, $M^2 = [0.37]$, $M^4 = [0.26]$; $P^2 = [1216.00]$, $P^4 = [608]$, $P^6 = [122]$; $B_0^2 = 1360(43)$; $B_0^4 = -1345(70)$, $B_0^6 = 1059(67)$, $B_3^4 = -1443(68)$, $B_3^6 = -553(70)$, $B_6^6 = 932(72)$; $n = 49$; $\sigma = 33$; $N_v = 3658\ cm^{-1}$ [29]. *Magnetic susceptibilities*: $\mu_{eff.} = 3.70$ B.M. (140–300 K)[g]; $\theta = -137$ K, $C = 1.699$ [81]. *Infrared data*: ν_3(HCOO) deform. sym. = 774; ν_6(HCCO) deform. out of plane = 1080; ν_2(OCO) stret. sym. = 1348; ν_5(HCOO) deform. asym. = 1399, 1418; ν_4 (O—C—O) stret. asym.1575; ν_1 (C—H) stret. = 2900; metal-oxygen vibrations = 268, 242,224, 174, 148 and 122 [81]. *Other available information*: IR and NIR absorption spectra; low temperature absorption spectrum; f–f band intensity analysis; magnetic susceptibility data [81].
$[(C_2H_5)_4N]_4U(NCS)_7$	*General properties*: plain-blue, fine crystalline solid; hygroscopic and air sensitive; readily soluble in polar organic and inorganic solvents. *X-ray powder diffraction data*: tetragonal; $I4/mmm$; D_{4h}^{17}; No = 139; $a = 11.564(2)$, $c = 45.801$, $V = 6125.0(9)$; $Z = 4$; d(calc.) = 1.162 [53]. *Infrared data*: IR: 3010w, 2976s, 2945m, 2909sh, 2856m, 2075sh, 2048vs,b, 2035sh, 1483s, 1475s, 1452s, 1438s, 1416w, 1393s, 1362m, 1300w, 1200sh, 1174s, 1150sh, 1127,w, 1096w, 1067m, 1052m, 998s, 970sh, 959m, 904,w, 890sh, 850w, 784s, 738w, 600w,b, 481m, 477m, 415w, 350sh,b, 305w, 261m, 220sh,b, 177s, 102m, 89m, 72m; Raman: 2096m, 2073vs, 1825, 1006, 772m, 480w, 482w, 260m, 208sh [53]. *Other available information*: NIR, Vis and UV solid state absorption spectra; assignments of the IR and Raman frequencies based on theoretical considerations; crystal structure of the isostructural $[(C_2H_5)_4N]_4Nd(NCS)_7$ compound [53].
$U[N(SiMe_3)_2]_3{\cdot}1/3(C_6H_{12})$	*General properties*: deep purple, air sensitive crystals. *X-ray single crystal data*: trigonal; $P\bar{3}1c$, D_{3d}^2, No.163; $a = 16.370(2)$, $c = 8.302(1)$; $Z = 2$, $V = 1926.7(1)$. The uranium coordination possesses a pyramidal geometry. The U atom is disordered above and below the plane defined by three N atom by 0.456(1) Å; d(U—N) = 2.320(4) Å, d(N—Si) = 1.713(4) Å. *Magnetic susceptibility data*. $\mu_{eff.} = 3.354(4)$ (35–280 K)[g] for $U[N(SiMe_3)_2]_3$, $\Theta = -13$ K [128]. *Other available information*: ^{1}H NMR.
$\{N[CH_2CH_2N(Si(Bu^t){\cdot}Me_2)U\}_2(\mu^2\text{-}\eta{:}\eta^2\text{-}N_2)$	*General properties*: dark red, air sensitive. *X-ray single crystal data*: monoclinic, $P2_1/n$; $a = 19.549(2)$, $b = 16.2751(14)$, $c = 21.517(2)$, $\beta = 105.61(3)^\circ$; $Z = 4$; d(calc.) = 1.487. The dinitrogen ligand is bound in a side-on bridging mode between two uranium centers. The (triamidoammine) uranium fragments are of trigonal monopyramidal geometry. The U atoms are out of the planes defined by the three respective amido nitrogen atoms by 0.84 and 0. 84 Å. Apical amino d(N—U) = 2.555(5) and 2.601(5); d(U—N) dinitrogen = from 2.39 to 2,44 Å [130]. *Solution magnetic susceptibility*: $3.22\mu_B$ per U atom between 218 and 293 K.
$\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}{\cdot}THF$	*X-ray single crystal data*: monoclinic, $P2_1/c$; C_{2h}^5, No.14; $a = 21.726(7)$, $b = 15.378(6)$, $c = 25.007(8)$; $\beta = 106.07(4)^\circ$; $V = 8028(10)$ Å^3, Z = 4; d(calc.) = 1.289 g cm^{-3}; The compound is monomeric with five N atoms of the amide ligands coordinated to the U atom in an approx. trigonal-bipyramidal geometry. d(U—N) = vary from 2.26(3) to 2.38(2); d(average) = 2.34 [132]. Infrared spectra: 3272(vw), 1400(s), 1379(s), 1357(m), 1328(s), 1253(s,br), 1215(m), 1169(w), 1150(m), 1138(m), 1111(m), 1054(s), 1041(m), 906(s), 884(s), 838(s), 744(s), 624(w), 538(m) [132].Other available information: ^{1}H NMR and UV–vis–NIR spectrum (200–1600 nm) [132].
U[HB(3,5-Me_2pz)$_3$]$_2$I; pz = 3-*tert*-butyl-5-methyl-pyrazolyl	*General properties*: dark blue, air sensitive crystalline powder. *X-ray single crystal data*: triclinic, $P\bar{1}$, C_i^1, No. 2; $a = 11.866(2)$, $b = 15.062(2)$, =11.423(2), $\alpha = 93.12(1)^\circ$, $\beta = 115.32(1)^\circ$, $\gamma = 82.84(1)^\circ$, $V = 1831.1$ Å^3, $Z = 2$; d(calc.) = 1.740; two of the pyrazolyl nitrogen atoms are at normal U—N distances of 2.559(6) and 2.591(5) Å. In the third one the lone pair of the potential donor atom, N31, is not pointing at the U atom but, instead, it is the N—N bond of the pyrazolyl ring which is brought into side-on bonding interaction. The coordination geometry is a capped octahedron. d(U—N31) = 2.807(5); d(U—N32) = 2.833(5) Å; d(U—I) = 3.220(1) [135]. *Other available information*: ^{1}H NMR spectra [135].
$[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}{\cdot}(THF)_2]{\cdot}THF$; pz = 3-*tert*-butyl-5-methyl-pyrazolyl	*General properties*: black prismatic air sensitive crystals. *X-ray single crystal data*: orthorhombic; $P2_12_12_1$; D_2^3, No. 18; $Z = 2$; $a = 10.386(1)$, $b = 13.115(1)$, $c = 26.556(2)$;$Z = 4$; $V = 3617.3(5)$; d(calc.) = 1.828. The monomeric complex is seven coordinated by two pyrazolyl nitrogen atoms, two iodide atoms and two oxygen atoms of the neutral ligand and by an agostic B—H···U interaction. d(U—I1) = 3.104(2), d(U—I2) = 3.132(2), d(U—N1) = 2.55(2), d(U—N2) = 2.50(2), d(U—O1) = 2.51(2); d(U—O2) = 2.584(12); d(U···B)=3.19; d(U···H1A) = 2.79 [195]. *Infrared spectra*: 2420s, 2280w, 2240w, 2200m, all ν(B—H); 1525s, 1260w, 1240w, 1210w, 1160s, 1120w, 1110w, 1060w, 1010s, ν(asym. C—O—C), 980w,910w, 890m, 880s, 850s, ν(sym. C—O—C), 790s, 735s, 730s, 720m, 650m, 630s, 605s, 520m, 465m, 390w, 320w and 300w [195]. *Other available information*: ^{1}H NMR and UV–vis spectra [195].

Table 1 (*Continued*)

Formula	Selected properties and physical data[b], lattice constants[c], references[d]
$[UI_2\{H(\mu\text{-}H)B(3'Bu,5Me\text{-}pz)_2\}\cdot(OPPh_3)_2]$; pz = 3-*tert*-butyl-5-methylpyrazolyl	*General properties*: dark red air sensitive solid. *X-ray single crystal data*: monoclinic; $P2_1/n$; $a = 17.950(3)$, $b = 19.866(3)$, $c = 18.793(2)$; $\beta = 96.894(12)^\circ$; $Z = 4$; d(calc.) = 1.517. The monomeric complex is seven coordinated by two pyrazolyl nitrogen atoms, two iodide ions and two oxygen atoms of the neutral ligand and by an agostic B—H···U interaction. d(U—I1) = 3.164(2), d(U—I2) = 3.199(2), d(U—N1) = 2.61(2), d(U—N2) = 2.58(2), d(U—O1) = 2.36(2); d(U—O2) = 2.351(14); d(U···B) = 3.11; d(U···H1A) = 2.62; d(P1···O1) = 1.50(2); d(P2···O2) = 1.52(2) [195]. *Infrared spectra*: IR (nujol): 2440s, 2280m, 2250w, 2240w, all ν(B-H); 1585s, 1530s, 1480s, 1370s, 1355m, 1135s, 1305w, 1255s, 1235m, 1200m, 1170m, 1155m, 1145s, 1115s, 1095m, 1080m, 1070s, 1020s, 1010m, 990s, 970w, 920w, 890s, 790w, 780s, 750s, 720s, 690s, 550s and 460w. *Other available information*: ^{1}H NMR spectra and UV–vis-spectra [195].
$[U\{Ph_2B(pz)_2\}_3]$; pz = 3-*tert*-butyl-5-methylpyrazolyl	*General properties*: prismatic air sensitive red crystals. X-ray single crystal data: triclinic $P\bar{1}$, C_i^1, No.2; $a = 13.565(1)$; $b = 15.715(2)$; $c = 15.929(2)$; $\alpha = 118.957(9)^\circ$; $\beta = 92.650(11)^\circ$; $\gamma = 97.36(2)^\circ$; $V = 2923.7(6)$ (Å^3); $Z = 2$; d(calc.) = 1.447 (g/cm^3). In the monomeric complex the U atom is six coordinated by the nitrogen atoms of the chelating $Ph_2B(pz)_2$ ligands which are arranged in a trigonal prismatic geometry around the U atom. d(U—N) = from 2.487 to 2.569(7) Å [195]. Infrared spectra: IR (nujol): 1491m, 1480sh, 1270s, 1250sh, 1180sh, 1170s, 1135m, 1100w, 1050s, 1025sh, 970m, 910w, 890w, 880s, 825m, 800m, 770w, 740s, 720s, 700s, 640s, 620s and 330m. Other available information: ^{1}H NMR, spectra and UV–vis spectra [195].
$[(UL^1)_2]$I L^1 = tris[3-(2-pyridyl) -pyrazol-1-yl] borate	*General properties*: dark green microcrystalline air sensitive solid. *X-ray single crystal data*: monoclinic; C_2/c; C_{2h}^6, No. 15; $a = 21.715(4)$, $b = 12.119(2)$, $c = 18.552(3)$ (2), $\beta = 107.78(2)^\circ$; $V = 6851(2)$ Å^3; $Z = 4$; d(calc.) = 1.793. The uranium ion is 12 coordinated and has an approximately icosahedral (3:6:3′) coordination geometry, with 3 and 3′denoting mutually staggered sets of pyrazolyl donor atoms, and 6 denoting a puckered arrangement of 6 pyridyl donor atoms interleaved around the equator. d(U—N) = from 2.671(7) to 2.981(6) Å [138].
$[U(O\text{-}2,6\text{-}Pr^i_2C_6H_3)_3]_2$	*General properties*: dark purple, very air sensitive crystals; soluble in ether and hydrocarbons. *X-ray single crystal data*: monoclinic, $P2_1/a$; $a = 9.616(2)$, $b = 21.260(7)$, $c = 17.236(5)$, (= 107.31(1)°, $Z = 2$; d(calc.) = 1.520. The compound adopts an unprecedented structure, that of a bis (-arene-bridged centrosymmetric dimer, $[U(O\text{-}2,6\text{-}Pr^i_2C_6H_3]_2$. Each U atom is ligated by three terminal phenoxide oxygen atoms and an arene ring of a phenoxide bound to its symmetry-related uranium partner. Two (^{6}-arene bridges [d(U—C) = 2.92(2) (av)] hold the dinuclear unit together with a d(U—U) separation of 5.34 Å. d(U—O) = 2.214(7) Å (bridging phenoxides) and d(U—O) = 2.132(8) Å (terminal phenoxides) [139]. *Other available information*: ^{1}H NMR spectra [139].
$[U\{H_2B(tim^{Me})_2\}_2(THF)_3[BPh_4]$ $[H_2B(tim^{Me})_2]^-$ = dihydrobis(thioimidazolyl)borate	*General properties*: red-brown, air sensitive powder. *X-ray single crystal data*: triclinic, $P\bar{1}$, C_i^1, No.2; $a = 12.818(4)$, $b = 16.290(3)$, $c = 18.355(10)$, $\alpha = 113.09(3^\circ$, $\beta = 106.39(3)^\circ$, $\gamma = 97.91(2)^\circ$, $V = 3246(2)$ Å^3; $Z = 2$; d(cal.) = 1.355 Mg/m^3. The thioimidazolyl ligands coordinate through two thione sulfur atoms and one of the hydrogen atoms attached to the boron atom, so that each ligand consists of two six-membered and one eight membered chelate rings. The uranium atom is nine coordinated in a distorted tricapped trigonal prismatic geometry [141]. *Infrared spectra*: 2380 br. ν(B—H), 1575 ν(C=C, BPh_4), 1015 ν(asym. C—O—C, thf), 860 ν(sym. C—O—C, thf) [141]. *Other available information*: ^{1}H NMR spectra [141].
$[U\{H(Ph)\ B(tim^{Me})_2\}_2\cdot(THF)_3[BPh_4]$	*General properties*: red-brown, air sensitive powder. *X-ray single crystal data*: monoclinic, $P2_1/c$; C_{2h}^5, No. 14; $a = 15.792(2)$, $b = 18.071(3)$, $c = 22.989(4)$; $\beta = 100.09(1)^\circ$; $V = 6459(2)$ Å^3, $Z = 4$; d(calc.) = 1.444 Mg/m^3; d(U—S) = from 2.912(3) to 2.937(3); d(U—O1) = 2.541(7), d(U—O2) = 2.528(7), d(U—O3) = 2.621(7). The thioimidazolyl ligands coordinate through two thione sulfur atoms and one of the hydrogen atoms attached to the boron atom, so that each ligand consists of two six-membered and one eight membered chelate ring. The uranium atom is nine coordinated in a distorted tricapped trigonal prismatic geometry [141]. *Infrared spectra*: 2320 ν(B-H···U), 1575 ν(C=C, BPh_4), 1550 ν(C=C, Ph-B), 1020 ν(asym. C—O—C, thf), 860ν(sym. C—O—C, thf) [141]. *Other available information*: ^{1}H NMR spectra [141].
$[U(OTf)_2(OPph_3)_4][OTf]$ Tf = triflate	*General properties*: red powder. *X-ray single crystal data*: triclinic, $P\bar{1}$, C_i^1, No.2; $a = 13.694(1)$, $b = 14.734(1)$, $c = 19.420(1)$, $\alpha = 92.143(4)^\circ$, $\beta = 108.393(4)^\circ$, $\gamma = 91.460(4)^\circ$, $Z = 2$, $V = 3713(3)$ Å^3; d(calc.) = 1.609 g/cm^3;), d(U—O) = varied from 2.348(4) to 2. 645(5); d(U—O($OPPh_3$) = average 2.36(2). The uranium atom is surrounded by seven oxygen atoms of monodentate and bidentate triflate ligands, which form a distorted pentagonal bipyramid [142].
U(III)$(BH_4)_2$dicylohexyl-(18-crown-6)]$_2$U(IV)$Cl_5(BH_4)$	*General properties*: brown crystals. *X-ray single crystal data*: tetragonal; $P\bar{4}$; S_4^1; No. 81; $a = 18.227(7)$, $c = 9.757(2)$, $V = 3241$ Å^3; $Z = 2$; d(calc.) = 1.75 Mg m^{-3}. The U(III) atom is inserted in the crown cavity as a monovalent cation $[U(BH_4)_2]^+$ and possesses a pseudo-octahedral environment. The metal ion is coordinated to two BH_4^- lying in an axial position on each side of the crown (B12-U1-B11) = 173(5)° [196].
[U(tpa)I_3(py)] tpa = tris[(2-pyridyl) methyl]amine	*General properties*: brown, air sensitive crystalline solid; soluble in tetrahydrofuran, acetonitrile, pyridine and other coordinating solvents. *X-ray single crystal data*: monoclinic, $P2_1$, C_2^2, No.4; $a = 9.6979(6)$, $b = 15.3561(9)$, $c = 9.9489(6)$ (1), $\beta = 115.894(1)^\circ$; $V = 1332.86(14)$ Å^3; $Z = 2$. d(U—N) = from 2.629(8) to 2.706(8); d(U—I1) = 3.2612(7), d(U—I2) = 3.2944(7), d(U—I3) = 3.1893(7).The uranium ion is eight coordinated by the tetradentate tpa, three iodide ions and one pyridine molecule [145]. *Other available information*: ^{1}H NMR spectra [145].

Table 1 (*Continued*)

Formula	Selected properties and physical data[b], lattice constants[c], references[d]
$U(III)(BH_4)_2$dicylohexyl-(18-crown-6)]$_2U(IV)Cl_5(BH_4)$	*General properties*: brown crystals, *X-ray single crystal data*: tetragonal; $P\bar{4}$; S_4^1; No = 81; a = 18.227(7), c = 9.757(2), V = 3241 Å^3; Z = 2; d(calc.) = 1.75 Mg m^{-3}. The U(III) atom is inserted in the crown cavity as a monovalent cation $[U(BH_4)_2]^+$ and possesses a pseudo-octahedral environment. The metal ion is coordinated to two BH_4^- lying in an axial position on each side of the crown (B12-U1-B11) = 173(5)° [195].
$[U(Mentb)_2]_3$·3pyMentb= tris[(*N*-methylbenzimidazol-2-ylmethyl] amine	*General properties*: green, air sensitive solid. X-ray single crystal data: orthorhombic, *Pbca*; D_{2h}^{15}; No.61; a = 21.598(4), b = 22.296(5), c = 27.992(6); V = 13480(5) Å^3, Z = 8; d(U—N) = 2.527(6) to 2.756(5). The uranium ion is eight coordinated by two tetradentate Mentb with the ligand arms wrapped around the metal in a pseudo-D_3 symmetric arrangement [145]. Other available information: ^{1}H NMR spectra [145].
$[UI_2(tbpa)I_2]$I(pyridine) (tbpa = tris[(2,2′-bypirydin-6-yl)methyl]amine	*General propertie*: brown crystalline solid; air sensitive; soluble in tetrahydrofuran, acetonitrile, pyridine and other coordinating solvents. *X-ray single crystal data*: monoclinic, $P2_1/c$; C_{2h}^5, No. 14; a = 9.736(2), b = 17.951(4), c = 22.436(5); β = 95.52(3)°; V = 3903.0(13) Å^3, Z = 4; d(calc.) = 2.075; d(U—N) = from 2.595(4) to 2.697(4); d(U—I1) = 3.2568(8), d(U—I2) = 3.3286(7). The U atom is nine-coordinate with tbpa and two iodine atoms forming a capped square antiprismatic coordination geometry [146].
$U(BH_4)_3$·3THF (THF = tetrahydrofuran)	*General properties*: brown-green crystals; soluble in organic solvents. *X-ray single crystal data*: triclinic, $P\bar{1}$, C_i^1, No.2; a = 7.770(4), b = 9.610(6), c = 13.176(11), α = 84.42(6)°, β = 84.56(6)°, γ = 88.27(5)°, Z = 2, V = 976(1) Å^3. Each of the uranium atoms is coordinated to three boron atoms and three oxygen in a distorted facial-octahedral arrangement with d(U—B1) = 2.69(1), d(U—B2) = 2.64(2),), d(U—B3) = 2.63(2), d(U—O1) = 2.579(8), d(U—O2) = 2.570(10); d(U—O3) = 2.541(10); d(calc.) = 1.69 [152].
$U(BH_4)_3$·(dmpe)$_2$ [dmpe = $M_2PCH_2CH_2PMe_2$]	*General properties*: olive-green crystals (in reflected light) and red (in transmitted) light. *X-ray single crystal data*: tetragonal; $I42d$; D_{2d}^{12}; No = 122; a = 14.509(4), c = 24.426(10), V = 5141.7 Å^3; Z = 8; d(exp.) = 1.35 g cm^{-1}. The U atom is at the centre of a pentagonal bipyramid, the equatorial plane consisting of four P atoms, the two demp groups and one B atom (B2) of one of the three BH_4^- group. The remaining two B atoms are located on the tops of the bipyramid. d(U—B1) = 2.68(4), d(U—B2) = 2.84(3), d(U—P1) = 3.139(8), d(U—P2) = 3.051(9); d(calc.) = 1.35 [153].
$U(BH_4)_3$·(ph$_2$Ppy)$_2$·1/2C_6H_6 [ph$_2$Ppy = 2-(diphenyl-phosphino)-pyridine]	*General properties*: purple, soluble in organic solvents. *X-ray single crystal data*: monoclinic; $C2/c$, C_{2h}^6, No. 15; a = 19.482(2), b = 12.176(2), c = 18.529(3), β = 109.71(1)°, V = 4137.8 Å^3; Z = 4; d(calc.) = 1.36. The U atom is at the centre of a distorted pentagonal bipyramid of B, P and N atoms. Three U-B bonds through tridentate hydrogen bridges are indicates by IR data. d(U—B1) = 2.61(2), d(U—B2) = 2.656(8), d(U—P) = 3.162(1), d(U—N) = 2.659(4); d(calc.) = 1.36 [154]. *Other available information*: ^{1}H NMR and IR spectra [154].
$U(BH_3CH_3)_3$·(dmpe)$_2$; [dmpe = 1.2-bis(dimethylphosphino -ethane)]	*General properties*: brown–black needles, extremely air-sensitive, soluble in organic solvents. *X-ray powder diffraction data*: tetragonal; $P4_32_12$; D_4^8; No = 96; a = 11.297(4), c = 23.030(20), V = 2939.1 Å^3; Z = 4. d(U—B1) = 2.66(1), d(U—B2) = 2.62(1) (2×), d(U—P1) = 3.174(3), d(U—P2) = 3.085(3) (2×); d(calc.) = 1.412. The U atom is at the center of a distorted pentagonal bipyramid of B and P atoms. The equatorial plan consists of 2P(1), 2P(2), a B(1) and an U atom. The B(2) atoms are 2.58 Å above and below the pentagonal plane. The boron atoms are connected to the U atoms by tridentate hydrogen bridges [155]. *Infrared data*: 2950m, 2310w, 2165m, 1420w, 1290m, 1260w, 1215m (br) 1140w, 1075w, 940m, 930m, 890m, 825w, 730m, 720m, 700m, 690m, 640m [155]. *Other available information*: ^{1}H NMR spectra [155].

[a] Values were selected in part from review articles of Brown [86], Bacher and Jacob [87], Freestone and Holloway [197], Guillaumont et al. [164] and Grenthe et al. [165].

[b] m.p.: melting point (°C); b.p.: boiling point. Standard symbols of thermodynamic data are used: (cr) – crystalline; (g) – gaseous; $\Delta_f G_m^o$ (kJ mol^{-1}), ΔG_f^o (kcal/mol) – standard molar Gibbs energy of formation at 298.15 K; $\Delta_f H_m^o$ (kJ mol^{-1}), $\Delta H_{f,298}^o$ (kcal mol^{-1}) – standard molar enthalpy of formation; S_m^o (J K^{-1} mol^{-1}) – standard molar entropy at 298.15 K; $C_{p,m}^o$ (J K^{-1} mol^{-1}) –standard molar heat capacity at 298.15 K. C_p – molar heat capacity (J mol^{-1} K^{-1}); ΔS (cal mol^{-1} K^{-1}) – entropy of reaction; C, Θ – paramagnetic constants from the Curie Weiss law $C = \chi'_M (T - \Theta)$ (emu K mol^{-1}); $\mu_{eff} = 2.84\sqrt{C}$ – effective magnetic moment [B.M.]; T_N – ordering temperature [K]; log(p/mmHg) = $-A/T + B$ – ClogT: vapour pressure equation for indicated temperature range. Atomic and crystal-field parameters; F^k and ζ_{5f} = electrostatic and spin-orbit interaction; α, β, γ; = two-body correction terms; $T^i t_i$ (i = 2,3,4,6,7,8) = three-particle configuration interaction; M^j (j = 0, 2 and 4) = spin-spin and spin-other-orbit relativistic corrections; P^k (k = 2, 4 and 6) = electrostatically correlated spin-orbit perturbation; B_q^k = crystal-field parameters; values in parenthesis indicate parameter errors; parameters in square brackets were kept constant during the final fitting procedure; standard deviation: $\sigma = \sum_i [(\Delta_i)^2/(n-p)]^{1/2}$ (cm^{-1}), where Δ_i is the difference between the observed and calculated energies, n the number of levels fitted, and p is the number of parameters freely varied; IR = infrared active (cm^{-1}), vs: very strong; s: strong, m: medium; ms: medium strong; w: weak, sh: shoulder; b: broad.

[c] All values are in Å; d-density (g cm^{-1}); CN – coordination number.

[d] In square brackets.

[e] Values recommended by the Nuclear Energy Agency [163].

[f] Values in kcal K^{-1}.

[g] Temperature range with linear relationship of χ_M^{-1} against T.

[h] Estimated values.

[i] Numbers after slash are B_q^k parameter values calculated from AOM parameters: e_σ = 1192, e_π = 403 and e_δ = 28 cm^{-1}.

same crystals. Transitions to the e_g levels of the U^{3+} ion are observed as broad and unstructured bands at wave numbers higher than 38 000 cm^{-1}. On the basis of ab initio calculations, Seijo and Barandiaran [11] obtained excellent overall agreement between theoretical and the experimental 5f and 6d energy levels. An extensive analysis of $5f^3 \rightarrow 5f^26d^1$ transitions in the absorption spectrum of U^{3+} doped $SrCl_2$ and Cs_2NaYCl_6 single crystals were also reported by Karbowiak [12]. In the isostructural series of U^{3+} doped K_2LaX_5 (X = Cl, Br, I) single crystals the substitution of Cl^- by I^- results in a shift of about 1000 cm^{-1} [13]. An analysis of the nephelauxetic effect and crystal field splitting in this series of compounds has shown that that the crystal field parameters smoothly decrease in this series.

The first attempt to analyse the energy levels of U^{3+} ions was performed by Carnall and Wybourne [14] and was completed by Drożdżyński and Conway [15] and Drożdżyński [16,17] on the basis of low temperature absorption spectra. The first crystal-field analyses of U^{3+} doped single crystals was reported by Crosswhite et al. [18] for U^{3+}:$LaCl_3$ single crystals. In recent years low-temperature emission and polarized absorption spectra of U^{3+} ions, diluted in various host crystals, enabled the further crystal field analyses of the ion in different site symmetries (in parenthesis): $LiYF_4$ (S_4) [19], $LaCl_3$ (C_{3h})] [20,21], RbY_2Cl_7 (C_{2v}) [22], (K_2LaX_5 (C_s) (X = Cl, Br or I) [13], Cs_2NaYCl_6 (O_h), Cs_2LiYCl_6 (O_h) [23], Ba_2YCl_7 (C_1) [24], Cs_2NaYBr_6 (O_h) [25], $CsCdBr_3$ (C_{3v}) [26], $Cs_3Lu_2Cl_9$, $Cs_3Y_2I_9$ (C_{3v}) [27] and $LaBr_3$ (C_{3h}) [28]. Such analyses were also performed for polycrystalline samples of $U(HCOO)_3$ (C_{3v}) [29], UCl_3, UBr_3 (C_{3h}) [30], $UCl_3{\cdot}7H_2O$ (C_i) [31], $CsUCl_4{\cdot}3H_2O$ (C_s), $NH_4UCl_4{\cdot}4H_2O$ (C_2) [7], $K_5Li_2UF_{10}$ (C_s) [32] and a $ZnCl_2$ based glass [33].

The energy levels of the U^{3+} ion in the different site symmetries were assigned and fitted to a semi-empirical Hamiltonian representing the combined atomic and crystal-field interactions. Karbowiak et al. have shown [7,13,24,25,31] that in cases where the U^{3+} ion had the lowest site symmetry (C_1 or C_s) ab initio calculations made possible the determination of the starting values by a simplified angular overlap model. This approach can predict the structure of the ground multiplet and the positions of the crystal-field levels in the 17 000–25 000 cm^{-1} range quite well, though they are usually obscured by strong f–d bands. The inclusion of contributions from two-electron correlation crystal-field interactions decreased the r.m.s. standard deviations and enabled in some of the multiplets a correction to a previous erroneous ordering of the irreducible representations [21,24,30]. Optical investigations of U^{3+}:RbY_2Cl_7 revealed that there are two different intrinsic U^{3+} sites in this crystalline host [22], each with an approximate C_{2v} site symmetry. This is a unique system to study the weak coupling between an f-element and its ligands because the two intrinsic sites are almost identical in coordination and symmetry, except for a small difference in the average trivalent metal–chloride distances. A third minor site has also been determined with a weaker crystal-field. Transitions to the two sites were distinguished by time-gated site-selective spectroscopy. An analysis of the luminescence and excitation spectra enabled a definitive assignment of 22 crystal field levels for both site symmetries as well as of the total crystal-field splitting of the ground multiplet [34].

One of the most complete crystal-field energy level and line-strength analyses for any uranium(III) system was presented by Karbowiak et al. [21] for low temperature absorption spectra of U^{3+}:$LaCl_3$ single crystals. The inclusion of contributions from two electron correlation crystal-field interactions could eliminate the major discrepancies between the calculated and observed energy levels. The investigations provide also a detailed analysis of line intensities associated with transitions between individual Stark levels. An up-conversion green emission after excitation either of the $^2H_{9/2}$ level by a red laser light or of the $^2H_{9/2}$ level by an IR laser light were detected by Dereń et al. [35]. The anti-Stokes emission is reported to result from a successive absorption of photons by absorption in the excited state and/or by a cross-relaxation within the U^{3+}–U^{3+} pair of ions.

Low temperature emission and absorption spectra of U^{3+} doped Cs_2NaYCl_6 and Cs_2LiYCl_6 single crystals [23] enabled the assignment of the vibronic transitions and crystal field levels of the U^{3+} ion. The zero phonon transitions were identified from an analysis of the vibronic side bands as well as in least-squares fits by applying a semiempirical Hamiltonian. “Free ion” and crystal-field parameters could be obtained for the first time for the U^{3+} ion in an octahedral crystal-field environment. The two sets of values calculated for the elpasolites are in good agreement with values reported in literature for other U^{III} systems, since the variation of the N_v parameter with the maximum Stark splitting of the ground multiplet in the different matrices is linear. Unique examples of vibronic transitions associated with the $5f^3 \rightarrow 5f^26d^1$ transitions, built on the envelope of a vibrational progression were presented and analysed.

An efficient luminescence, observed in U^{3+} doped Cs_2NaYCl_6, Cs_2LiYCl_6 and Cs_2NaYBr_6 single crystals in the visible and near infrared regions, were attributed to transitions from the lowest components of the $^4I_{11/2}$, $^4G_{7/2}$ and $^4F_{3/2}$ levels to the crystal-field components of the $^4I_{9/2}$ ground state and to the $^4G_{7/2} \rightarrow {}^4F_{3/2}$ transition [23,25,36–39]. The energies of the most prominent vibronic features were assigned to the specific vibrational modes of the UX_6^{3-} moiety or to the lattice modes [23,25,36,37,40]. Unique examples of vibronic transitions associated with the electric dipole allowed $5f^3 \rightarrow 5f^26d^1$ transitions were observed above 14 000 cm^{-1}. The zero-phonon lines are accompanied by a number of vibrational progressions combined with the even $S_1(a_{1g})$ mode. The observed poorer resolution of the vibronic side bands in U^{3+}:Cs_2NaYBr_6, especially those coupled with the f–d transitions was attributed to the splitting of the Γ_8 level, which most probably results from a lowering of the O_h symmetry due to a cubic to tetragonal phase transition at low temperatures.

An anti-Stokes emission was exclusively noticed for the bromide elpasolite under excitation in the near infrared region

[39]. The emission observed in the visible region results from excited state absorption and was efficient at low temperatures only. Non-radiative transitions were associated with a fast energy transfer through the 6d levels to lower lying 5f levels. In Cs_2NaYCl_6 the emissions were strongly affected by non-radiative transitions, such as cross-relaxation. The dependence of the phenomena on the environment of the uranium ion has also been discussed.

Karbowiak et al. [24] have presented a detailed procedure for calculations of crystal-field parameters for very complex f-electronic systems in an analysis of high quality low temperature absorption and luminescence spectra of U^{3+}(0.3%):Ba_2YCl_7 single crystals, where the U^{3+} ions possess C_1 site symmetry. The applied AOM approach can predict the B_q^k crystal-field parameters quite well. The approach is especially important in all cases where low site symmetries or a paucity of experimental data prevents the application of the B_q^k parametrization procedures. The analysis can be seen as a general method that makes the interpretation of the f-electron spectra of low symmetry systems tractable. The value of the crystal-field strength parameter, N_v, corresponds well with those determined for U^{3+} in other chloride single crystals.

For the first time, an analysis of low temperature absorption, luminescence and excitation spectra of mixed valence (U^{4+}, U^{3+}):Ba_2YCl_7 single crystals was reported by Karbowiak et al. [41]. Efficient luminescence was observed at 7 K from the $^4G_{7/2}$ and $^4F_{9/2}$ levels of the U^{3+} ions as well as $^1D_2$ and $^1I_6$ of U^{4+}. Under a similar excitation power the emission from the U^{4+} ions, due to transitions from the $^1D_2$ level with a life-time of 9.2 μs, was stronger by a factor of 30 than that of U^{3+}. For the U^{4+} ions a very strong anti-Stokes emission was observed due to an energy transfer processes. The power dependence with a slope of 1.0 indicates, that upconversion is indeed very efficient and dominates over the linear decay for the depletion of the intermediate excited states. Contrary to U^{4+} for which emission was observed even at room temperature the emission of U^{3+} ions was strongly quenched at higher temperatures. An energy transfer between these ions occurs due to the presence of U^{3+} and U^{4+} ions in the host crystal. The dependence was described by an equation with an activation energy term and the process is explained by a participation of the closely positioned $5f^26d^1$ configuration.

One major and two minor U^{3+} sites were observed in the absorption and emission spectra of U^{3+} in $CsCdBr_3$ single crystals [26]. The different decay time values, obtained for the emitting $^4G_{7/2}$ level from the three sites, support this statement. A symmetric dimer center of the form – U^{3+} – m(Cd vacancy) – U^{3+} – was defined as the principal *A* site. A comparison of the N_v crystal field strength parameter, for U^{3+} ions in different host crystals, shows that the site symmetry is an important factor influencing the crystal field strength. The emission observed from the $^4G_{7/2}$ level is strongly influenced by temperature due to strong phonon coupling of the $5f^3$ levels with the nearby $5f^26d^1$ states. Visible upconversion fluorescence, observed when pumping the $^4I_{9/2}$–($^4F_{7/2}$ + $^4I_{15/2}$) absorption transition of the principal site, was attributed to excited-state absorption (ESA).

A comparison of the low temperature emission and polarized absorption spectra of U^{3+}:$Cs_3Lu_2Cl_9$ and U^{3+}:$Cs_3Y_2I_9$ single crystals (C_{3v} site symmetry) [27] with those of the U^{3+}:Cs_2MYX_6 elpasolites (M = Li or Na; X = Cl or Br) (O_h site symmetry) shows, that the energy level structure is mainly determined by the cubic part of the crystal field potential. Since U^{3+} ions doped in the $Cs_3Lu_2Cl_9$ [42] and $Cs_3Y_2I_9$ host crystals possess the same, C_{3v}, local site symmetry, the crystals were found to be suitable for investigation of effects connected with the change of the U^{3+} environment on values of the energy levels and Hamiltonian parameters. The mixing of allowed f–d character into $5f^3$ wavefunctions via odd-parity crystal field terms is significantly larger for the iodide crystal, for which the first f–d states are positioned at as low energy as 12 000 cm^{-1}.

An analysis of the optical spectra of U^{3+}:K_2LaX_5 (X = Cl, Br or I) series of single crystals, performed by Karbowiak et al. [13], enabled the reassignment of some of the earlier reported crystal-field levels as well as the determination of the "free ion" and crystal-field parameters for a U^{III} system with a very low site symmetry of the metal ion. The values of the B_k^q and N_v parameters smoothly decrease in the K_2LaX_5:U^{3+} (X = Cl, Br or I) series of complexes. The observed red shift of the $^{2S+1}L_J$ levels was expressed by the ratio $b = F^2(\text{crystal})/F^2(\text{free ion})$ or $r_{42} = F_4/F_2$.

Solution and solid state spectra of a number of uranium(3+) complexes with chlorine, nitrogen and oxygen donor ligands were investigated by Drożdżyński [43]. The effects of solvents and complex formation on the spectroscopic intensities of the f–f transition as well as an analysis of the nephelauxetic effect and the phenomenon of hypersensitivity were discussed.

Analyses of $5f^3 \rightarrow 5f^3$ transition intensities for both solution [17,44,45] and solid-state spectra [15] revealed rather poor agreement between the observed and calculated oscillator strengths. Relatively small r.m.s. deviations, of the order 10^{-6} to 10^{-7}, were obtained for the absorption spectra of UCl_3 in hexamethylphosphortriamide [46,47] and an UCl_3 doped $ZnCl_2$ based glass [33,48], only. The absorption and emission bands of the glass were relatively broad due to the presence of many U^{3+} sites in the sample. The decay time of the observed emission in the visible region changes from 7 μs at 14 K to 0.8 μs at room temperature. These are so far the only spectroscopic investigations performed for a chloride glass doped with tervalent uranium compounds. Recently the most complete intensity analysis for any uranium(III) system, based on the Judd–Ofelt theory, was reported for U^{3+}(0.25%):$LaCl_3$ single crystals [49]. Reasonably good agreement with the experimental data was obtained provided some of the L′S′J′ band areas were combined. In order to check the validity of the calculations, the Ω_λ intensity parameters were used for the determination of transition probabilities and these in turn for calculations of radiative life times.

Temperature induced line broadening and line shift measurements were performed for U^{3+} doped K_2LaCl_5, $LaCl_3$ [50,51] and RbY_2Cl_7 [52] single crystals. The investigation was chosen as a method for the determination of the $\bar{\alpha}$ electron–phonon coupling parameters. The value of this parameter was found to be considerably lower in $LaCl_3$ than in K_2LaCl_5 but larger when compared with that of Nd^{3+} in $LaCl_3$. The electron–phonon coupling is also stronger for U^{3+} in the tribromide as compared with the trichloride host; this was attributed to a larger covalency of the first compound. Investigations of (U^{3+},U^{4+}):RbY_2Cl_7 enabled for the first time the determination of the electron–phonon coupling parameters for two slightly different U(1) and U(2) intrinsic sites of the U^{3+} ions in the single crystal as well as for U^{4+} in the same RbY_2Cl_7 host crystal. The parameters were determined by a fit of the experimentally observed line widths to an equation containing the temperature dependent broadening due to the Raman two-phonon process. Comparison of the values of the $\bar{\alpha}$ electron–phonon coupling strength parameter for U^{3+} ions in the two intrinsic sites has shown, that they are larger for the U(2) site by 28–40%, which is in accordance with the stronger crystal field influencing the ions at this site. The differences of the electron–phonon coupling strength are also in accordance with the differences in the decay time recorded for emission observed from the $^4F_{9/2}$ multiplet.

A description of the characteristic IR frequencies has been reported for almost all uranium(3+) compounds (see Table 1). An extensive analysis of the IR and Raman spectra was reported for $[(C_2H_5)_4N]_4U(CNS)_7$ [53], RbU_2Cl_7 [54], Cs_2NaUCl_6 [55] and the A_2UX_5 (A = K, Rb; X = Cl, Br or I) series of compounds [56]. A factor group analysis was used to identify the energy and symmetry of the observed modes in the complex halides. The assignment of the phonons to the representative molecular vibrations was performed on the basis of a normal coordinate analysis. The vibrational characteristics of the halide double bridges such as energy, symmetry, force constants, potential energy distribution, atomic displacements, direction of the transition dipole moments and mean square amplitudes were collected and discussed. These compounds may act as model systems for the investigation of intra- and inter-chain interactions as well as for the examination of the role of such bridging bonds on its physical and chemical phenomena as e.g. of the reported by Keller et al. [57] short range one dimensional magnetic ordering.

4. Magnetic properties

Magnetic susceptibility measurements of numerous uranium(3+) complex compounds have been carried out over wide temperature ranges. The paramagnetic constants from the Curie–Weiss law $\chi'_m = C/(T-\theta)$ and the effective magnetic moments $\mu_{eff.} = 2.84\sqrt{C}\mu_B$ are summarized in Table 1. The magnetic structure and properties of $KUCl_4$ [58] and the M_2UCl_5 (M = K or Rb) [59] type of chloro complexes were established from neutron diffraction studies on polycrystalline samples. An extensive physical analysis of the magnetic interactions and magnetic ordering phenomena in the M_2UX_5 (M = K or Rb; X = Cl, Br or I) series of compounds were reported by Krämer et al. [60]. The application of elastic and inelastic neutron scattering experiments along with specific heat measurements allowed a consistent picture of the magnetic phases.

The trihalides show remarkable cooperative effects, which were studied both experimentally by Murasik et al. [61–63] and theoretically by Łyżwa and Erdös [64] and Plumer and Caillé [65]. UCl_3 and UBr_3 undergo an unusual, for actinide compounds, magnetic phase transition. An one-dimensional, short-range magnetic order along the *z*-axis of the hexagonal lattice develops at about 15 K for UBr_3 and 22 K for UCl_3 which results from strong antiferromagnetic interactions between the nearest neighbors. A three dimensional ordering appears in UBr_3 and UCl_3 when the uranium magnetic moments order in each plane perpendicular to the *z*-axis to a '0 +−' configuration at $T_N = 6.5$ and 5.3 K, respectively. At temperatures below $T_t = 2.7$ K for UBr_3 and $T_t = 2.5$ K for UCl_3 the magnetic moments exhibit smaller values and become oriented parallel to the equivalent *x*- or *y*-axes. The reorientation of the moments is reported to be rare in the actinide ions due to an usually strong anisotropy, which determines the direction of the moment [66]. The results of paramagnetic resonance measurements for U^{3+} ions substituted in CaF_2, SrF_2 and $LaCl_3$ single crystals were summarized by Kanellakopoulos [67] and Drożdżyński [1]. Some magnetic properties are collected in Table 1.

5. Survey of the preparation methods

The synthesis of uranium(III) compounds requires oxygen free conditions. At temperatures higher than 600 °C the syntheses ought to be carried out in tantalum or molybdenum tubes in order to avoid side reactions with silica. The majority of the compounds were prepared either by reduction of suitable uranium(IV) compounds and solutions of tetravalent uranium halides by various reducing agents or by heating stoichiometric amounts of appropriate reagents together in an inert atmosphere.

One of the most simple and convenient small-scale methods for preparing uranium(3+) compounds from solution was reported by Drożdżyński [68]. This is based on the reduction of uranium tetrachloride or – bromide solutions in organic solvents such as methyl cyanide or formic acid, with liquid zinc amalgam. The syntheses were accomplished in a Schlenk type all-glass apparatus with provision for reduction, precipitation, filtration and drying in an inert atmosphere. The method enabled, among others, the synthesis of $UCl_4{\cdot}7H_2O$ [69,70], $UCl_4{\cdot}6H_2O$ [70], $MUCl_4{\cdot}4H_2O$ (M = K, Rb or NH_4) [7,71], $UCl_3{\cdot}nCH_3CN{\cdot}2H_2O$ ($n = 2$ or 5) [70,72], M_2UCl_5 (M = K, Rb or NH_4) [73],

MU_2Cl_7 (M = K, Rb or Ph_4As) [68], $MUCl_4{\cdot}3H_2O$ (M = Cs, K, Rb or NH_4) [74–76], $[(CH_3)_4N]_3UCl_6$ [77], $SrUCl_5$ [78], Ba_2UCl_7 [78], $[C_2H_5)_4N]_4U(SCN)_7$ [53], $(NH_4)[UBr_2(CH_3CN)_2(H_2O)_5]Br_2$ [9,79], $K_2UBr_5{\cdot}2CH_3CN{\cdot}6H_2O$ [80], $Rb_2UBr_5{\cdot}CH_3CN{\cdot}6H_2O$ [80], $U(HCOO)_3$ [81,82] as well as numerous uranium(3+) complexes with cyclic polyethers and aromatic diamines [83]. Some of the compounds are very good starting materials for the synthesis of other uranium(3+) compounds, e.g. by thermal vacuum dehydration of $NH_4UCl_4{\cdot}4H_2O$ and $NH_4UBr_4$1.5 $CH_3CN{\cdot}6H_2O$ high quality UCl_3 was obtained [84] and UBr_3 [85], and $KUCl_4{\cdot}4H_2O$ was used for the preparation of $[(C_2H_5)_4N]_4U(NCS)_7$ [53].

Metallothermic reductions are also satisfactory and practical procedures [1,86], especially for the preparation of UF_3 and UCl_3. Metallic uranium and aluminum were most frequently employed as well as several other metals such as Zn, Be, Mg, Ti or Zr. Reduction with uranium metal was used for the preparation of UOCl, UOBr and UOI and with metallic zinc for the synthesis of UCl_3, UBr_3 and UI_3. For the preparation of the binary halides reduction with hydrogen may be also conveniently employed [1,86].

A large number of tervalent uranium complex halides were prepared by solid state reactions, among others: MUF_4, M_2UF_5 (M = Na or K), M_3UF_6 (M = Rb or Cs) [87], $MUCl_4$, M_2UCl_5 (M = K or Rb), $SrCl_2{\cdot}UCl_3$, $2BaCl_2{\cdot}UCl_3$, $RhCl_4{\cdot}4UCl_3$, $ThF_4{\cdot}UCl_3$, $UF_4{\cdot}2UCl_3$, $7UF_4{\cdot}UCl_3$, $ThCl_4{\cdot}UCl_3$, $4PbCl_3{\cdot}UCl_3$, $U(Al_2Cl_7)_3$, M_2UBr_5, M_3UBr_6 (M = K, Rb or Cs) [1,86] and M_2NaUCl_6 (M = Cs, K or Rb) [88,89], $CsUCl_4$, Cs_2LiUCl_6 [90] and M_2NaUBr_6 (M = K or Rb) [89] and RbU_2Cl_7 [54].

The synthesis of a number of hydrated sulfato and chloro complexes was accomplished by electrochemical reductions [91,92]. A convenient route to numerous uranium(III) complexes involves the direct treatment of uranium(III) solutions in organic solvents with the appropriate ligands, e.g. $NH_4UCl_4{\cdot}5H_2O$ with a variety of neutral oxygen donor ligands [93], $U(BH_4)_3(THF)_x$ with numerous crown ethers and phosphine ligands [94] and $UCl_3(THF)_x$ with compounds of the $K[H_nBL_{4-n}]$ type (where L = pyrazole or 3,5-dimethylpyrazole [2,95]. A convenient and increasingly widely used method for the synthesis of numerous uranium(III) complex compounds with organic ligands involves the use of $UI_3(THF)_4$ as the starting material. The compound was obtained by reaction of an excess of oxide free amalgamated uranium metal turnings with elemental iodine in dry THF [2,96].

6. Characterization of the compounds

6.1. Uranium trifluoride and uranium(III) fluoro complexes

6.1.1. Uranium trifluoride

A convenient and commonly used method for the preparation of Uranium trifluoride, is the reduction of UF_4 with metallic aluminum [97] or finely powdered uranium [98]. Other metals such as Be, Mg, Ti or Zr, as well as UN or U_2N_3, at 900–950 °C have also been employed. The application of UN or U_2N prevents the formation of corrosive by-products. The reduction with Li, Na, Cs, Mg, Ca, Sr and Ba leads to metallic uranium. Ultra-pure UF_3 can be obtained by reduction of UF_4 with hydrogen at 1020 to 1050 ± 20 °C [99].

A good quality absorption spectrum of UF_3 in chlorinated naphthalene at 4.2 K was recently obtained by Drożdżyński et al. [100] and applied for a crystal-field analysis. There is a large shift of the L′J′S′ multiplets towards higher wave numbers, when compared with other U^{III} low temperature spectra. The magnetic susceptibility of UF_3 was measured between 2 and 300 K [101] and between 293 and 723 K [102]. Available physical data of the compound are summarized in Table 1.

6.1.2. Uranium(III) fluoride monohydrate

A green gelatinous precipitate of $UF_3{\cdot}H_2O$ was obtained by addition of ammonium fluoride to an uranium(III) solution in 1 M HCl or anhydrous methanol [103]. The precipitate turns brown after drying and is immediately oxidized in air, giving a pale green uranium(IV) compound. The reported magnetic susceptibility data may not be fully reliable.

6.1.3. Uranium(III) fluoro complexes

The synthesis and characterization of uranium(III) fluoro complexes were reviewed by Bacher and Jacob [87]. The fluorouranates KUF_4, K_2UF_5, K_3UF_6, Rb_3UF_6 and Cs_3UF_6, were prepared by heating together UF_4, metallic uranium and the appropriate alkali fluoride at 1000 °C [104]. Some other fluoro complexes, such as $NaUF_4$ and Na_2UF_5, were identified from analyses of the binary fused-salt system NaF-UF_3. A number of these complex fluorides were characterized by X-ray powder diffraction investigations (Table 1) but more detailed information is still not available. The reduction of a mixture of UF_4 and ZrF_4, either with metallic zirconium or with metallic uranium at about 800 °C leads to $UZrF_7$. A systematic study of the $UZrF_7$–ZrF_4 binary system enabled also the identification of UZr_2F_{11} [105]. Both are unstable and slowly oxidize even at room temperature. The compounds were characterized by magnetic susceptibility measurements in the 100–300 K range and by X-ray powder diffraction analyses.

Karbowiak et al. [32] have obtained and characterized an uranium(III) fluoro complex of the formula $K_5Li_2UF_{10}$. The observed crystal-field levels were assigned and fitted to parameters of the simplified angular overlap model (AOM) as well as to those of a semi-empirical Hamiltonian, which represented the combined atomic and one-electron crystal-field interactions. The starting values of the AOM parameters were obtained from ab initio calculations. The determined effective magnetic moment amounts to about $2.60\mu_B$ and is much below the value of $3.55\mu_B$, calculated by applying the van Vleck formula for the f^3 configuration and

parameters obtained from the fitting of the spectroscopic data.

6.2. Uranium trichloride and uranium(III) chloro complexes

6.2.1. Uranium trichloride

The best method for the preparation of UCl_3 is the action of gaseous hydrogen chloride on uranium hydride or the reduction of uranium tetrachloride with zinc, metallic uranium or uranium hydride [86,1]. Small amounts of pure UCl_3 may most conveniently prepared by thermal vacuum decomposition of $NH_4UCl_4{\cdot}4H_2O$ [1,84]. The compound obtained by the latter method is reactive and tractable for synthetic purposes, in contrast to that obtained by the first one. UCl_3 possesses hexagonal symmetry with the space group $P6_3/m$. The structure was refined by a number of authors (see Table 1).

High resolution absorption spectra of U^{3+} doped $LaCl_3$ single crystals and UCl_3 polycrystalline samples were reported by Karbowiak et al. [21] and Sobczyk et al. [30] and applied for crystal-field analyses. The so far most complete band intensity analysis of U^{3+} ions was based on the electronic wave functions and a room temperature absorption spectrum of UCl_3 [49].

The magnetic properties of uranium trichloride have been the subject of extensive investigation [1,106]. Neutron diffraction studies revealed the existence of three-dimensional long-range antiferromagnetic ordering below the Néel temperature $T_N = 6.5$ K [62,107]. A number of fused-salt systems containing UCl_3 have also been reported [86]. A large amount of significant physical data, available for UCl_3 are summarized in Table 1.

6.2.2. Uranium trichloride hepta- and hexahydrate

Drożdżyński has synthezised $UCl_3{\cdot}7H_2O$ by reduction of a UCl_4 solution consisting of acetonitrile, propionic acid and water with liquid zinc amalgam [69]. X-ray powder diffraction data shows no qualitative differences between the structures of $LaCl_3{\cdot}7H_2O$ (space group $P\bar{1}$) and $UCl_3{\cdot}7H_2O$ [69]. Recently X-ray single crystal analyses of the heptahydrate as well as of the less hydrated $UCl_3{\cdot}6H_2O$ have also been reported [70] (see Table 1). The presence of water molecules in the inner coordination sphere was supported by an analysis of the solid-state absorption spectrum of $UCl_3{\cdot}7H_2O$, which is very similar to that of the U^{3+} aquo ion [45]. The magnetic moment of $\mu_{eff.} = 2.95$ B.M. is much lower than the "free ion" value of ca. 3.7 B.M. for which the crystal-field of the water molecules is held responsible [69]. A crystal-field level analysis, based on a high quality low temperature spectrum, was reported by Karbowiak et al. [31].

6.2.3. Hydrated uranium(III) chloro complexes

The synthesis and characterization of numerous hydrated complex chlorides of the formulae $MUCl_4{\cdot}5H_2O$ [92], $MUCl_4{\cdot}4H_2O$ (M = K, Rb or NH_4) [7,71], $MUCl_4{\cdot}3H_2O$ (M = Cs, K, Rb or NH_4) [76], and $UCl_3{\cdot}CH_3CN{\cdot}nH_2O$ ($n = 2$ or 5) [70,72] have been reported (see Table 1). The pentahydrates were prepared by shaking a U^{III} solution in 11 M HCl with the appropriate alkali halide MCl (M = K, Rb or NH_4) at 0 °C. whereas the tetrahydrates were obtained using the general route reported by Drożdżyński [68,71]. Apart from some expected similarities between the tetra- and pentahydrates, one can also note some differences, e.g. in the resistance to oxidation in air, solubility in organic solvents as well as in the absorption spectra and magnetic susceptibilities. $(NH_4)_2UCl_4{\cdot}4H_2O$ is an excellent starting material for the preparation of UCl_3 and numerous other uranium(III) compounds [1,6].

The $MUCl_4{\cdot}3H_2O$ series has also been obtained by reduction of appropriate acetonitrile solutions of UCl_4 and MCl (where M = K, Rb, Cs or NH_4) with liquid zinc amalgam, but by using somewhat different conditions than those used for the preparation of the tetrahydrates [76]. In contrast to the deep purple-red colors of the penta- and tetrahydrates the latter ones show green to brown colors caused by a shift of the first broad and strong $5f^3 \rightarrow 5f^26d^1$ bands to wave numbers higher than 21 000 cm^{-1}.

Single crystal X-ray analyses are available for $NH_4UCl_4{\cdot}4H_2O$ [8], $CsUCl_4{\cdot}4H_2O$ [75] and $UCl_3{\cdot}CH_3CN{\cdot}2H_2O$ [70] (Table 1). X-ray powder diffraction analysis shows that the members of the $MUCl_4{\cdot}4H_2O$ and $MUCl_4{\cdot}3H_2O$ series could be indexed on the basis of a monoclinic cell and are, inside of the series, isostructural. The formation of the pentahydrates and $UCl_3{\cdot}CH_3CN{\cdot}5H_2O$ has not been confirmed by X-ray analyzes [70].

A red shift of the $5f^3 \rightarrow 5f^26d^1$ bands observed in the spectra of the tetrahydrates was attributed to the formation of inner sphere complexes with some of the uranium to ligand bond lengths of a markedly more covalent character than those of U^{3+} in $UCl_3{\cdot}7H_2O$ or the $MUCl_4{\cdot}3H_2O$ series [1,7]. The magnetic susceptibility constants from the Curie–Weiss law as well as some other physical data are listed in Table 1.

6.2.4. Anhydrous uranium(III) chloro complexes

The largest group of well characterized uranium(III) compounds form chloro complexes of the formulae $CsUCl_4$ [90], M_2UCl_5 (M = K, Rb, Cs or NH_4) [73,108], $SrUCl_5$ [78], $[(CH_3)_3N]_3UCl_6$ [53], MU_2Cl_7 (M = K, Rb, Ph_4As or Ph_4P) [1,54,68], Ba_2UCl_7 [78], M_2NaUCl_6 (M = K, Rb or Cs) [89] and Cs_2LiUCl_6 [90]. Most of the compounds can be conveniently prepared by heating together the required quantities of the component halides in graphite coated quartz tubes. The $(NH_4)_2UCl_5$, $[(CH_3)_3N]_3UCl_6$, $Ph_4AsU_2Cl_7$ and $Ph_4PU_2Cl_7$ complex halides were obtained by reduction of appropriate uranium tetrachloride solutions in acetonitrile with liquid zinc amalgam [1,53,68,73]. Complexes with the general formulae M_2UCl_5 and MU_2Cl_7 can also be obtained in this way [68]. The syntheses were carried at high vacuum or in an inert gas atmosphere. The formation of a number of uranium(III) chlorocomplexes has also been observed during investigation of binary and ternary phase systems [86]. The complexes display a variety of colors and are readily soluble

in numerous polar organic solvents. All of them are hygroscopic but are to some extent resistant to oxidation in dry air. Extensive physical data are summarized in Table 1.

X-ray powder diffraction data were reported for numerous uranium(III) complex chlorides but only a few X-ray single-crystal analyses are accessible (see Table 1). Cs_2NaUCl_6 crystallizes with the ideal elpasolite arrangement [109] whereas K_2UCl_5 and Rb_2UCl_5 are isotypical with the K_2PrCl_5/Y_2HfS_5 orthorhombic structures [60]. The relatively short U^{3+}–U^{3+} distance through the common edge, equal to 455.6 pm, is assumed to be responsible for antiferromagnetic transitions at 8.6–13.2 K.

The effective magnetic moments range from 3.47 B.M. for $(NH_4)_2UCl_5$ to 3.99 B.M. for K_2UCl_5 [73]. High quality, low temperature absorption spectra are available for almost all complex chlorides. The spectra exhibit characteristic features of uranium(3+) complex anions with strong $5f^3 \rightarrow 5f^26d^1$ bands starting at ca. 18 000 cm^{-1}. Several extensive analyses of the optical spectra were reported by Karbowiak et al. [13,22–24,27]. The far-IR spectra of the pentachlorides exhibit very similar far-IR spectra with one broad and a not well resolved band in the 100–240 cm^{-1} region, assigned to U–Cl stretching modes. An analysis of magnetic phase transitions and crystal-field splitting in the K_2UX_5 (X = Cl, Br or I) series of complex halides was reported by Keller et al. [57].

The formation of a reduced metallic uranium chloride, formulated as NaU_2Cl_6 or $(Na^+)(U^{3+})_2(e^-)(Cl^-)_6$ was reported by Schleid and Meyer [110]. The extra electrons provided by the incorporation of the sodium atom are supposed to occupy the 6d band of uranium. Extensive physical data of uranium(III) complex chlorides are listed in Table 1.

6.3. Uranium tribromide and uranium(III) bromo complexes

6.3.1. Uranium tribromide

The most satisfactory large scale preparation of UBr_3 involves the action of gaseous hydrogen bromide on uranium hydride at 300 °C [86]. Attractive alternative procedures involve the reduction of UBr_4 by metallic zinc or finely divided uranium at about 600 °C. It may be readily obtained by thermal vacuum decomposition of $NH_4UBr_4{\cdot}5CH_3CN{\cdot}6H_2O$ in gram quantities [85]. Other preparation methods, such as the direct combination of the elements or the reaction between uranium oxalate and gaseous hydrogen bromide were reported to be less convenient [86]. Uranium tribromide is isostructural with UCl_3. Extensive crystal-field analyses of low-temperature, high-resolution absorption and fluorescence of UBr_3 and U^{3+}:$LaBr_3$ were reported by Sobczyk et al. [28,30]. A wide set of available physical data is listed in Table 1.

6.3.2. Uranium tribromide hexahydrate

UBr_3 may be converted to a red-colored hexahydrate by controlled exposure to oxygen-free water vapour [111]. Prolonged pumping led to a compound of an approximate composition $UBr_3{\cdot}H_2O$, which may be completely dehydrated with a slow and gradual increase of the temperature to about 100 °C. The X-ray powder diffraction pattern shows that $UBr_3{\cdot}6H_2O$ is isostructural with the monoclinic lanthanide trihalide hexahydrates. Further information is not available.

6.3.3. Anhydrous uranium(III) bromo complexes

A number of bromouranates(III) of the M_2UBr_5 and M_3UBr_6 (M = K, Rb or Cs) composition were identified during investigations of the binary fused-salt systems [88,112]. The pentabromouranates(III) have also been prepared by fusion of the appropriate component bromides whereas complexes of the M_3UBr_6 type are high-temperature phases and decompose on cooling into the alkali bromide and the corresponding pentabromouranate(III). The melting points and regions of existence of the hexabromouranates(III) increase with an increase of the atomic number of the alkali metal. An opposite tendency was observed in the series of pentabromouranates(III) [112]. The thermodynamic properties of some of the bromo complexes were reported by Suglobova and Chirkst [113].

X-ray powder diffraction analyses have shown that the pentabromouranates(III) are isostructural with the orthorhombic structure of Tl_2AlF_5 and that the hexabromouranates(III) possess a face-centered cubic symmetry. On this basis [113] the structure of the pentabromouranates(III) is supposed to contain distorted UBr_6 octahedra, which are connected in parallel chains through common vertices. An extensive analysis of the absorption and luminescence spectra of U^{3+}:K_2LaBr_5 and U^{3+}:Cs_2NaYBr_6 and U^{3+}:$CsCdBr_3$ single crystals were reported by Karbowiak et al. [13,25,26]. A number of physical data for uranium(III) complex bromides are also available (Table 1).

6.4. Uranium triiodide and uranium(III) iodo complexes

6.4.1. Uranium triiodide

For the preparation of UI_3 one may most conveniently employ the action of iodine vapor on finely divided uranium metal, either in sealed or flow systems at 570 and 525 °C, respectively. In flow systems, high purity black crystals of UI_3 were collected in the 375–450 °C zone of an apparatus first reported by Gregory [114]. Attractive alternative methods involve the reduction of uranium tetraiodide with zinc metal or finely divided uranium metal, reaction between uranium hydride and methyl iodide, and vacuum thermal decomposition of UI_4 at 225 to 235 °C [86]. Diffuse reflectance spectra were recorded in the 4000–30 000 cm^{-1} range at room temperature and 90 K [103]. In the series of UX_3 (X = F, Cl, Br or I) halides one may observe a pronounced red shift of the first $5f^3$–$5f^26d^1$ transition from about 23000 cm^{-1} in the spectrum of UF_3 to about 13 400 cm^{-1} for UI_3.

Magnetic susceptibility reveals an antiferromagnetic transition at $T_N = 3.4 \pm 0.2$ K as well as a second susceptibility

maximum at 1.5 K. Uranium triiodide shows a first order magnetic phase transition. The compound orders antiferromagnetically at $T_N = 2.6$ K resulting in the appearance of a magnetic sublattice. Neutron scattering reveals a hysteresis of the integrated neutron intensity of the magnetic reflections versus temperature, which confirms that the phase transition is of the first order [63].

6.5. Uranium(III) oxide halides and mixed halides

The UOCl, UOBr and UOI oxide halides were prepared by heating together stoichiometric amounts of UO_2X_2 ($X \equiv Cl$, Br or I), UO_2 and U or UX_4 (X = CI, Br or I), U_3O_8 and U, for 24 h at 700 °C [115]. Chemical properties of UOCl, UOBr and UOI have not been reported. X-ray powder diffraction patterns of the compounds are consistent with the tetragonal PbFCl-type of structure (*P4/nmm*). The structure was refined by single-crystal X-ray analysis and the atomic positions were determined [116]. The oxide halides are weak ferromagnets with nearly the same transition temperatures ranging from 190 to 183 K. Some IR and magnetic susceptibility data are listed in Table 1 [115].

The preparation of number of uranium(III) mixed halides with the general formulae UXY_2 and UX_2Y where X = Cl or Br and Y = Cl or I were reported by Gregory [114] but very little information about their properties is available. $UClBr_2$ was obtained by reduction of UCl_3Br with hydrogen at 400 °C. For the preparation of UCl_2Br the fusion of a 2:1 molar ratio of UCl_3 and UBr_3 at 850 °C was applied and for that of $UClI_2$ the solid-state reaction between UCl_3 and UI_3. The remaining mixed halides, i.e., UCI_2I, UBr_2I and $UBrI_2$ were obtained by thermal decomposition of UCl_2I_2 and UBr_2I_2 at 400 °C, and of $UBrI_3$ at 375 °C.

6.6. Uranium(III) sulfate hydrates and sulfato complexes

An octahydrated uranium(III) sulfate was obtained by addition of cold ethanol to an aqueous uranium(III) solution at 0 °C. [117]. The X-ray powder diffraction data are similar to those of orthorhombic $Ce_2(SO_4)_3{\cdot}8H_2O$. The compound is relatively stable towards oxidation by dry air and may be partially dehydrated in vacuum at about 100 °C to an orange coloured dihydrate via a green-brown pentahydrate. The diffuse reflectance spectrum exhibits the characteristic features of the U^{3+} aquo-ion. Some magnetic susceptibility and infrared data are also available.

Barnard et al. [91] synthesized a series of hydrated uranium(III) sulfato complexes such as the dark brown $K_2U(SO_4)_4{\cdot}H_2O$, as well as the olive green $KU(SO_4)_2{\cdot}5H_2O$, $RbU(SO_4)_2{\cdot}4H_2O$, $CsU(SO_4)_2{\cdot}5.5\,H_2O$, $(NH_4)U(SO_4)_2{\cdot}4H_2O$, $(N_2H_5)U(SO_4)_2{\cdot}2H_2O$ and $NaU(SO_4)_2{\cdot}2H_2O$. A further series of sulfato complexes with the general formula $M_3U(SO_4)_3{\cdot}2H_2O$ (M = K, Rb or Cs) was reported by Vyatkina and Serebrenikov [118]. The compounds precipitate as well defined crystalline solids, being relatively stable in air. The $RbU(SO_4)_2{\cdot}4H_2O$ and $NH_4U(SO_4)_2{\cdot}4H_2O$ compounds are reported to be completely dehydrated in a hydrogen atmosphere at 200 °C [117]. Those with the composition $M_3U(SO_4)_3{\cdot}2H_2O$ may also be converted to anhydrous salts by thermal dehydration. The isolation of an anhydrous sulfato complex of composition $K_5U(SO_4)_4$ was reported by Peretrukhin et al. [119]. Most of the compounds were characterized by IR and diffuse reflectance spectra as well as by magnetic susceptibility measurements in the 87–300 K range. An X-ray single crystal structure investigation of $NH_4U(SO_4)_2{\cdot}4H_2O$ [120] showed it is isostructural with the analogous La–Tb (except for Pr) sulfato complexes and possesses the space group $P2_1/c$ of monoclinic symmetry. Some available crystallographic data of sulfato complexes are listed in Table 1.

6.7. Uranium(III) compounds with organic acids

Drożdżyński et al. [81,82] characterized the olive-green $U(HCOO)_3$ which is, so far the only known U^{III} compound of an organic acids. The compound is isotypic with the neptunium analogue reported by Schwochau and Drożdżyński [21] and crystallizes in the rhombohedral lattice of $Gd(HCOO)_3$ in which the central atoms are surrounded by nine formate oxygen atoms. High quality, low temperature absorption spectra of thin mulls of the compound in chlorinated naphthalene were applied [15] for an analysis of band intensities and identification of the "free ion" levels [15] as well as for a crystal field analysis [29] (see Table 1). The IR spectrum is almost identical with those of the Nd(III) and Np(III) formates [121] and exhibits all six fundamental bands of the formate ligand. At lower temperatures the inverse magnetic susceptibilities exhibit an antiferromagnetic transition with a Néel temperature of 12 K.

6.8. Uranium(III) coordination compounds with organic ligands

6.8.1. Nitriles

The simple $UCl_3{\cdot}CH_3CN$ adduct was reported but the synthesis could not be confirmed. Zych and Drożdżyński characterized $UCl_3{\cdot}CH_3CN{\cdot}5H_2O$ [72] as dark red needles, which may be converted to UCl_3 by carefully controlled vacuum thermal decomposition. Some structural, magnetic and spectroscopic data are listed in Table 1. Coordination through the nitrogen atom is indicated by the ν[U–NC(CH_3)] frequencies in the 200–240 cm^{-1} spectroscopic range as well as by an increase in the ν(C≡N) stretching frequency. The appearance of strong f–d bands in the 16 000–24 000 cm^{-1} is indicative for an inner sphere complex. At temperatures below 65 K the $1/\chi'_M$ plot curves below the Curie–Weiss line and shows an antiferromagnetic transition at $T_N = 12$ K. Recently the synthesis of single crystals of the composition $UCl_3{\cdot}CH_3CN{\cdot}2H_2O$ together with an X-ray analysis were reported by Mech et al. [70] (Table 1).

The method of preparation of uranium(3+) compounds from solutions reported by Drożdżyński [68]

has also been successfully applied for the syntheses of $K_2UBr_5{\cdot}2CH_3CN{\cdot}6H_2O$, $Rb_2UBr_5{\cdot}CH_3CN{\cdot}6H_2O$ and $(NH_4)[UBr_2(CH_3CN)_2(H_2O)_5]Br_2{\cdot}6H_2O$ [9,79,80]. All compounds are well characterized by various physical methods (Table 1) but single crystal X-ray data are available only for $(NH_4)[UBr_2(CH_3CN)_2H_2O)_5]Br_2{\cdot}6H_2O$ [9].

The synthesis, structural and spectroscopic properties of tetra(tetraethylammonium) hepta-isothiocyanato uranate(III) were reported by Karbowiak et al. [53]. The compound crystallizes in the tetragonal system, space group *I*4/*mmm* and is isomorphic with its neodymium analogue. Single crystal measurements were performed for the latter. The assignments of the IR and Raman frequencies were based on theoretical considerations. Drożdżyński and du Preez have reported [122] the dark brown $UI_3{\cdot}4CH_3CN$ compound. X-ray powder diffraction, magnetic susceptibility data as well as a solid state reflectance spectrum are also available.

6.8.2. Ammonia adducts

$UCl_3{\cdot}7NH_3$ and $UBr_3{\cdot}6NH_3$ adducts with some loosely bound ammonia were prepared by treatment of the uranium halides with gaseous ammonia at room temperature and a pressure of 1013 hPa [123–125]. Heating in a stream of nitrogen up to 45 °C led to a relatively stable $UCl_3{\cdot}3NH_3$ complex. At higher temperatures the adduct decomposes into $UCl_3{\cdot}NH_3$, which is stable up to 300 °C.

6.8.3. Amide ligands

The reaction of bis(trimethylsilyl)sodium amide with $UCl_3(THF)_x$ or $UI_3(THF)_3$ in a THF solution results in the formation of $U[N(SiMe_3)_2]_3$ [2,126] The effective magnetic moment as well as a low energy 5f ionization band observed by photoelectron spectroscopy are consistent with a $5f^3$ electronic configuration [127]. For crystallographic data of the compound [128] see Table 1.

A variety of adducts of $N[CH_2CH_2N(Si(Bu^t)Me_2)]_3U$ were reported by Roussel et al. [129]. The purple complex may be obtained by fractional sublimation of a bimetallic U^{III}/U^{IV} complex [130] or by reduction of $N[CH_2CH_2N(Si(Bu^t)Me_2]_3UI$ with potassium in pentane. This compound is reported to bind N_2 with the formation of $\{N[CH_2CH_2N(Si(t\text{-}Bu)Me_2)U\}_2(\mu^2\text{-}\eta{:}\eta^2\text{-}N_2)$. The complex is reported to be best formulated as a U^{III} species and was crystallographically characterized [130] (Table 1).

Complexes of the formula $U(NRAr)_3(THF)$ (where $R = Bu^t$, adamantyl; $Ar = 3,5\text{-}MeC_6H_3$) were prepared by reduction of the uranium(IV) iodide complex with sodium amalgam [131]. An alternative approach to the stabilization of tervalent uranium amides is reported to be the generation of anionic "ate" type of complexes such as, e.g., the anionic complex $[K(THF)_2]_2[U(NHAr)_5]$ which was synthesized by reaction of $UI_3(THF)_4$ with an excess of KHNAr (where $Ar = 2,6,\text{-}Pr^i_2C_6H_3$). Some crystallographic data [132] are listed in Table 1.

6.8.4. Polypyrazolylborate ligands

The majority of investigations with the $B(pz)_4^-$, $HB(pz)_3^-$ and $H_2B(pz)_2^-$ (where pz = pyrazol-1-yl) with poly(pyrazolyl)borate ligands involves the substituted ligand $HB(3,5\text{-}Me_2pz)_3^-$ [2]. Reactions of $UCl_3(THF)_x$ with different stoichiometries of KH_nBL_{4-n} (where $n = 1$ or 3, and $L \equiv$ 3,5-dimethylpyrazolyl) generate $UCl_2H_2BL_2$ and UCl_2HBL_3 [133].

The treatment of $UI_3(THF)_4$ with $M[HB(3,5\text{-}Me_2pz)_3]$ (where M = Na or K) in a 1:1 and 1:2 ratio generates the $U[HB(3,5\text{-}Me_2pz)_3]I_2(THF)_2$ and $U[HB(3,5\text{-}Me_2pz)_3]_2I$ complexes [134,135]. In other preparation procedures the treatment of $UI_3(THF)_4$ with bis(pyrazolyl)borate ligands results in the formation of $U[H_2B(3,5\text{-}Me_2pz)_2]_3$ and $U[H_2B(pz)_2]_3(THF)$ [136,137]. The interaction with the potassium salt of the tris[3-[2-pyridyl)-pyrazol-1-yl]-borate ligand (^{py}Tp) yields $[^{py}Tp_2U]I$ and in the presence of $NaBPh_4$ leads to the separation of $[^{py}Tp_2U][BPh_4]$ [138]. Structural data of some of the polypyrazolyl borate complexes are listed in Table 1.

6.8.5. Alkoxide complexes

Alcoholysis of $U[N(SiMe_3)_2]_3$ in a hexane solution with three equivalents of HO-2,6-$Bu^t_2C_6H_3$ or HO-2,6-$Pr^i_2C_6H_3$ generate dark green and purple solutions from which homoleptic complexes of the formulae $[U(O\text{-}2,6\text{-}Bu^t_2C_6H_3)_3]$ and $[U(O\text{-}2,6\text{-}Pr^i_2C_6H_3)_3]_2$ were isolated, respectively [139]. The uranium trisaryloxides form a number of adducts with Lewis bases such as THF, EtCN and Ph_3O [139,140]. The molecular structure of $[U(O\text{-}2,6\text{-}Pr^i_2C_6H_3)_3]_2$ is composed of a centrosymmetric bis-η^6 arene – bridged dimer (Table 1).

6.8.6. Complexes with sulfur donor and triflate ligands

Interaction between the bis(2-mercapto-1-methylimidazolyl)borate ligand, $[H(R)B(tim^{Me})_2]^-$, $UI_3(THF)_4$ and $Tl(BPh_4)$ yields the cationic U(III) complexes $[U\{H(R)B(tim^{Me})_2\}_2(THF)_3][BPh_4]$ (where R = H or Ph). The tridentate ligand coordinates with the uranium center through two thione sulfur atoms and one agostic hydrogen atom [141] (Table 1). The tervalent uranium triflate complex, $U(OTf)_3$ (where OTf^- = triflate), was obtained by action of triflic acid with UH_3 [142]. The Lewis base adduct of the compound, $[U(OTf)_2(OPPh_3)_4[OTf]$, was crystallographically characterized (see Table 1).

6.8.7. Heterocyclic ligands, ethers, cyclic ethers and aromatic amines

A purple adduct of the composition $UCl_3(THF)_x$ was obtained by reduction of a UCl_4 solution in tetrahydrofuran with stoichiometric amounts NaH or an excess of Na_2C_2. The compound as well as the purple solution of $UCl_3(THF)_x$ is reported to be a useful starting material for the synthesis of numerous uranium(III) complexes [94,143,144]. Avens et al. [96] have reported the synthesis of organic-solvent-soluble Lewis base adducts, a dark

purple $UI_3(THF)_4$, purple $UI_3(dme)_4$ and black $UI_3(py)_4$ (where THF ≡ tetrahydrofuran, dme ≡ 1,2-dimethoxyethane py ≡ pyridine). The adducts were obtained by reaction of elemental iodine with an excess of oxide-free uranium metal turnings at 0 °C in the appropriate coordinating solvent. $UI_3(THF)_4$ is presently commonly used as one of the key starting materials for the preparation of a variety of uranium(III) complexes [2], e.g. [U(tpa)I_3] I (pyridine)$_3$ (where tpa = tris[(2-pyridyl)-amine) methyl]) [145], U(Mentb)$_2$]I_3 (where Ment*b* = tris(*N*-methylbenzimidazol-2ylmethyl)amine) [145], [UI_2(tbpa)I_2]I(pyridine) (where tbpa = tris[(2,2′-bypirydin-6-yl)methyl]amine [146] or $UI_3(bipy)_2(py)\cdot py$ (where bipy = 2,2′-bipyridine) [147]. Single crystal X-ray diffraction data of $UI_3(THF)_4$ show that the compound is mononuclear with a pentagonal bipyramidal coordination geometry about the uranium ion. Structural characterizations of some of the compounds are presented in Table 1. In addition, a royal-blue $UBr_3(THF)_4$ adduct was obtained by the gentle dissolution of uranium metal turnings in tetrahydrofuran (THF) containing elemental bromine, at about 0 °C [96].

Numerous air sensitive uranium(III) complexes with some cyclic polyethers and aromatic diamines were obtained by reduction of acetonitrile or acetonitrile/propionic acid solutions of UCl_4 and the appropriate ligand by liquid zinc amalgam [1,148], e.g. $(UCl_3)_3$(benzo-15-crown-5)$_2\cdot$1.5 CH_3CN, $(UCl_3)_3$(benzo-15-crown-5)$_2$, UCl_3 (cyclohexyl-15-crown-5), $(UCl_3)_3$(18-crown-6)$_2$, $(UCl_3)_5$(dibenzo-18-crown-6)$_3$, $(UCl_3)_5$(cis-syn-cis-dicyclohexyl-18-crown-6)$_3$, UCl_3(1,10 phenantroline)$_2$, UCl_3(2,2′-bipyridile)$_2$. The complexes are insoluble or react with common organic solvents. Other procedures involve $UCl_3(THF)_x$ as the starting material, e.g. for the synthesis of UCl_3(15-crown-5), UCl_3(18-crown-6), UCl_3(benzo-15-crown-5) [94,144] as well as $(UCl_3)_3$(18-crown-6)$_2$, $(UCl_3)_2$(2,2′bipyridine)$_3$ and $(UCl_3)_2$(dimethoxyethane)$_3$ [94]. The complexes are hygroscopic and are more or less rapidly oxidized by atmospheric air. The absorption spectra exhibit some characteristic features of the U^{3+} ion with very intense f–d transitions in the visible and/or ultraviolet region. Infrared data are indicative of coordination through the ligand nitrogen or oxygen atoms. Some of the complexes have also been characterized by magnetic susceptibility measurements at 298 K (Table 1).

6.8.8. Carbamides

Bullock et al. [149] have reported the synthesis and some characterization of numerous air-sensitive uranium(III) tetrakis complexes with bidendate amides of the general formulae $R_2NCO(CH_2)_nCONR_2$ or $R_2NCOCH_2C(CH_3)_2CH_2CONR_2$ (where R = CH_3 or CH_3CH_2 and n = 1–4). The complexes were formed in ethanolic solutions by adding stoichiometric quantities of sodium tetraphenylborate or ammonium hexafluorophosphate to a solution obtained on mixing $NH_4UCl_4\cdot 5H_2O$ with the appropriate *NNN′N′*-tetralkylamide. In a similar manner a number of subsequent uranium(III) complexes with various oxygen donor ligands and hexacyanoferrates(III) has also been prepared [92,93]. The bands observed between 14 000 and 24 000 cm^{-1} in the spectra of the tetrakis complexes with bidentate amides were attributed to $5f^3 \rightarrow 5f^26d^1$ transitions, those between 20 000 and 24 000 cm^{-1} to metal to ligand transitions ($f \rightarrow \pi^*$) and above 30 000 cm^{-1} to internal ligand $n \rightarrow \pi^*$ transitions. Magnetic susceptibility measurements were performed only in the 70–298 K range [93]. In addition, the syntheses of hexathiocyanatochromate complexes of uranium(III) with antipyrine, amidopyrine, pyridine and dimethylformamide were also reported [150].

6.9. Uranium(III) complexes with borohydride ligands

Thermal decomposition of $U(BH_4)_4$ at 100 °C leads to the formation of $U(BH_4)_3$ [2,151]. Due to the explosive properties of the compound in contact with air, much more information is available about its derivatives. $U(BH_4)_3(THF)_3$ is a useful reagent for the synthesis of base adducts of uranium(III) tetrahydridoborate. The compound was obtained by treating UH_3 with a diborane solution in tetrahydrofuran [152]. The addition of the appropriate ligand to a solution of $U(BH_4)_3\cdot(THF)_3$ in tetrahydrofuran (THF) results in the formation of $U(BH_4)_3\cdot(dmpe)_2\cdot 1/2C_6H_6$ [dmpe = $M_2PCH_2CH_2PMe_2$] [153] and $U(BH_4)_3\cdot(ph_2Ppy)_2$ [ph_2Ppy = 2-(diphenylphosphino)-pyridine] [154]. Crystals suitable for X-ray investigations were grown from ether or toluene solutions.

Borohydride Lewis base adducts of tervalent uranium have also been prepared by reduction of their tetravalent analogues. For example, the tertiary phosphine complex of the formula $(CH_3BH_3)_3U[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$ was obtained by heating a solution of dimethylphosphinoethane with $U(BH_3CH_3)_4\cdot$dmpe in toluene to about 80 °C for several hours [155] and the $U(BH_4)_3L_2$ adducts (where L = PEt_3 or PEt_2Ph) [156] can be achieved by reduction of $U(BH_4)_4$ in the presence of these phosphines. The molecular structures of the $U(BH_4)_3$ derivatives, determined by single crystal X-ray diffraction analyses are summarized in Table 1.

Moody et al. [157] have prepared an orange compound of the composition $U(BH_4)_3\cdot$(18-crown-6) by treating UCl_3(18-crown-6) with $NaBH_4$ in a THF solution. In selected cases the reduction of $U(BH_4)_4$ in the presence of crown ether ligands, such as (18-crown-6) and dicyclohexyl-(18-crown-6) yield complexes of the general formula $U_3(BH_4)_9$(crown-6)$_2$ [158]. Two further compounds with the formulae $UCl_2\cdot H_2BPz_2\cdot$THF and $UCl_2\cdot H_2BPz_3\cdot$THF (where Pz = pyrazole) were obtained from a tetrahydrofuran solution by treating $UCl_3(THF)_x$ with KH_2BPz_2 and $KHBPz_3$, respectively, followed by vacuum evaporation [95]. Protonation of $U(BH_4)_3(THF)_3$ with [NEt_3H][BPh_4] yields a cationic complex of the formula [$U(BH_4)_2(THF)_5$][BPh_4] [159] whereas the reaction of $U(BH_4)_3(THF)_3$ with $NaBH_4$ in the presence of 18-crown-6 leads to the isolation of the anionic complex [Na(18-crown-6)][$U(BH_4)_4$] [160].

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