

Pentauranium(V) Chloride Dodecaoxide $U_5O_{12}Cl$

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The structure of a new uranium oxide chloride $U_5O_{12}Cl$ was determined by X-ray diffraction. It is orthorhombic, $Pbmm$, $a = 7.111(9)$, $b = 19.625(12)$, $c = 4.130(2)$ Å, $Z = 2$, $D_m = 7.83$, $D_x = 8.17$ Mg m^{-3} . The final $R = 0.036$. The structure is strongly reminiscent of that of $\alpha-U_3O_8$. It consists of layers of composition U_3O_7Cl , alternating with layers of composition O_5 . One U atom has a pentagonal bipyramidal oxygen coordination like in U_3O_8 , the others have a rather more distorted coordination with six O atoms and one Cl atom. This latter atom covers a range of about 1.7 Å along z . The enthalpy of formation of $U_5O_{12}Cl$ has been determined via its enthalpy of solution in a $\{H_2SO_4 + Ce(SO_4)_2\}$ solution. The value $\Delta H_f^\circ(298.15\text{ K}) = -5854.4 \pm 8.6$ kJ $mole^{-1}$ has been obtained. Its thermochemical stability is compared with the other uranium oxide chlorides. © 1985 Academic Press, Inc.

Introduction

In the system U–O–Cl several oxide chlorides have been described, in which the formal uranium valency varies from 3 to 6. An assessment of the system has been published recently (1). In addition to the phases described in that paper, we here present another oxide chloride of composition $U_5O_{12}Cl$, the preparation and properties of which have not been described before.

Preparation of Single Crystals

The title compound can be prepared by a solid-state reaction when a mixture of UO_2Cl_2 , UO_3 , and UO_2 in the molar ratio 1:2:3 is heated in a closed, evacuated sil-

ica ampoule at about 650°C for 20 hr. A grey-violet powder is obtained which is insoluble in water.

In the given molar ratio of the starting materials the reaction product is always slightly contaminated with a water-soluble oxide chloride. However, when the molar ratio is only slightly changed the reaction product contains either U_3O_8 or UO_2Cl_2 . After washing with dilute sulfuric acid and drying at 120°C, chemical analyses yielded the following results: U(total) = 83.68 ± 0.05 wt% (calc: 83.96%), U(VI) = 42.86 ± 0.04 wt% (calc: 41.98%), and Cl = 2.44 ± 0.03 wt% (calc: 2.50%).

The density was determined in water with a pycnometer (Table I).

When the oxide chloride is heated above 725°C partial decomposition occurs during

TABLE I
CRYSTAL DATA AND COLLECTION OF X-RAY DATA

Crystal system	Orthorhombic
<i>a</i> (Å)	7.111(9)
<i>b</i> (Å)	19.625(12)
<i>c</i> (Å)	4.130(2)
<i>V</i> (Å ³)	576.4
<i>Z</i>	2
Reflection condition	0 <i>kl</i> , <i>k</i> = 2 <i>n</i>
Space group	<i>Pbmm</i>
<i>D_v</i> (Mg m ⁻³)	8.17
<i>D_m</i> (Mg m ⁻³)	7.83
Crystal size (mm)	0.125 × 0.01 × 1.0
Radiation (graphite monochromated)	MoKα (λ = 0.71069 Å)
Scan	θ - 2θ
μ (MoKα) (mm ⁻¹)	66.79
Number of reflections measured	2052
Number of unobserved refl. (<i>I</i> < 3σ(<i>I</i>))	1197
Number of independent reflections	404

which black crystalline blocks of U₃O₈ are formed. From the faces of these crystals the title compound grows as black fragile needles along *c*. These needles have a very notable tendency to cleave along the needle axis: even the very tiny sample used in the investigation (Table I) consisted of two approximately equal parts. One of these was singled out for intensity measurements on a Nonius CAD-4 diffractometer.

Structure Determination

Details of crystal data and intensity collection are given in Table I. Cell dimensions were obtained by least-squares fitting of 24 reflections. Reference reflections for intensity and orientation remained constant during data collection. Refinement based on *F* was carried out with 404 unique reflections obtained by averaging multiple measurements. They were corrected for Lorentz and polarization effects.

Atomic scattering data were taken from (2), dispersion factors for U and Cl from (3). No extinction corrections were applied. Absorption corrections were performed by means of the program DIFABS (4), applied to the structure factors before averaging.

Strong low-order reflections are found for indices which obey the relation $h + k/5 = 2n$, indicating the presence of a U₃O₈-like subcell (5) of dimensions *a*, *b*/5, *c*. Fitting the corresponding pattern of the U positions in accordance with the symmetry requirements of *Pbmm* led to a trial structure which readily converged on least-squares refinement. Positions of O and Cl were found from difference maps. Subsequent least-squares refinement led to the positions given in Table II for all atoms except Cl.

Putting Cl at 0,0,0 a high isotropic temperature factor ($B = 5.8 \text{ \AA}^2$) results. From difference maps and geometrical considerations it was clear that this was due to elongation of the electron density along *z*. Splitting the atom in two halves above and below the plane $z = 0$ gave some improvement ($B = 4.2 \text{ \AA}^2$), but now the difference map exhibited a positive peak at 0,0,0 of 4.4 electrons \AA^{-3} , interpreted to indicate that Cl is distributed over some range along *z* with a distribution function peaking at $z = 0$. This was approximated by introducing half a Cl atom at 0,0,0 and two quarter at-

TABLE II

FINAL COORDINATES AND TEMPERATURE FACTORS
FRACTIONAL ATOMIC COORDINATES ($\times 10^4$ FOR U,
 $\times 10^3$ FOR O AND Cl) AND U_{iso} ($\times 10^2$) WITH e.s.d.'s
IN PARENTHESES. Cl(1) AND Cl(2) ARE FRACTIONS
OF ONE Cl ATOM, SEE TEXT.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B_{\text{iso}}$ (Å ²)
U(1)	2339(4)	2500(-)	0(-)	0.47(11) ^a
U(2)	3296(3)	686(1)	0(-)	0.59(7) ^a
U(3)	2116(3)	6457(1)	0(-)	0.47(6) ^a
O(1)	470(4)	326(1)	0(-)	-0.9(5)
O(2)	627(6)	454(2)	0(-)	1.5(8)
O(3)	96(6)	356(2)	0(-)	2.1(9)
O(4)	877(6)	250(-)	0(-)	-0.1(8)
O(5)	231(7)	250(-)	500(-)	0.5(9)
O(6)	321(6)	71(2)	500(-)	2.5(9)
O(7)	208(6)	646(2)	500(-)	1.4(7)
Cl(1)	0(-)	0(-)	0(-)	1.9(8)
Cl(2)	0(-)	0(-)	203(13)	1.0(9)

^a $U_{\text{eq}} = (1/3) \sum U_{ii}$.

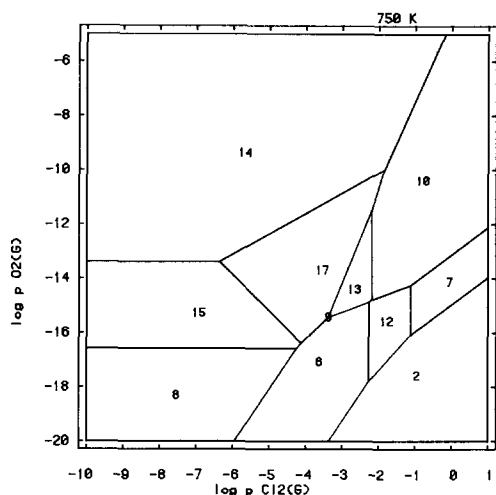


Fig. 1. Part of a section of the U-O-Cl phase diagram at 750 K. 2. UCl_4 6. UOCl_2 7. UOCl_3 8. UO_2 9. UO_2Cl 10. UO_2Cl_2 12. $\text{U}_2\text{O}_2\text{Cl}_5$ 13. $(\text{UO}_2)_2\text{Cl}_3$ 14. U_3O_8 15. U_4O_9 17. $\text{U}_5\text{O}_{12}\text{Cl}$

oms at $\pm 0,0,z$. Refinement yielded the data given in Table II (anisotropic temperature factors for U, isotropic for O and Cl). The resulting z parameter of 0.203 for Cl(2) indicates a distribution with a full width at half maximum of about 1.7 Å. This model to describe the fuzzy electron distribution is arbitrary: the Cl atom can be split in other fractions without significant changes in the agreement. The 1:2:1 split has been adapted because it affords a simple description.

In the final difference Fourier the minimum and maximum height were -5.8 and $+6.6 \text{ Å}^{-3}$ in the plane $z = 0$ near the U positions. As might be expected, there is an indication of some systematic error in the intensity measurements.

The Enthalpy of Formation; Thermochemical Stability

The enthalpy of solution of $\text{U}_5\text{O}_{12}\text{Cl}$ in $\{1.505 \text{ mole dm}^{-3} \text{H}_2\text{SO}_4 + 0.035 \text{ mole dm}^{-3} \text{Ce}(\text{SO}_4)_2\}$ solution has been measured in a calorimeter as described before (6). From the value obtained, $\Delta H^\circ(\text{soln}) = -709.25 \pm 4.3 \text{ kJ mole}^{-1}$, the enthalpy of formation has

been derived, using the auxiliary thermodynamic data, as given in a previous paper (7). The value $\Delta H_f^\circ(298.15 \text{ K}) = -5854.4 \pm 8.6 \text{ kJ mole}^{-1}$ has been obtained.

The value $S^\circ(298 \text{ K}) = 465 \text{ J K}^{-1} \text{ mole}^{-1}$ for the entropy of $\text{U}_5\text{O}_{12}\text{Cl}$ has been estimated by comparison with the other uranium oxide chlorides (1). This enables us to compare the thermochemical stability of $\text{U}_5\text{O}_{12}\text{Cl}$ with that of the other oxide chlorides. In Fig. 1 part of the phase diagram of the U-O-Cl system at 750 K is given, illustrating the phase relationships. It appears that the phase field of UO_2Cl , the other possible pentavalent oxide chloride of which the existence had been assumed in our previous paper (1), has disappeared and, instead, a broad phase field of $\text{U}_5\text{O}_{12}\text{Cl}$ has grown. Apparently, $\text{U}_5\text{O}_{12}\text{Cl}$ is thermochemically stable with respect to UO_2Cl .

Discussion

The structure of the new uranium oxide chloride is strongly reminiscent of that of U_3O_8 . It consists of layers of composition $\text{U}_5\text{O}_7\text{Cl}$ alternating with layers of composi-

TABLE III
SELECTED BOND LENGTHS (Å)

U(1)-O(5)	2.067(2)
-O(1)	2.19(3)
-O(3)	2.34(4)
-O(4)	2.61(4)
U(2)-O(6)	2.067(2)
-O(2)	2.16(4)
-O(3)	2.22(4)
-O(2)	2.27(4)
-O(1)	2.29(3)
-Cl(1)	2.70(12) ^a
U(3)-O(7)	2.065(1)
-O(4)	2.14(1)
-O(3)	2.19(4)
-O(2)	2.27(4)
-O(1)	2.33(3)
-Cl(1)	3.23(11) ^a

^a ESD is difference between U-Cl(1) and U-Cl(2).

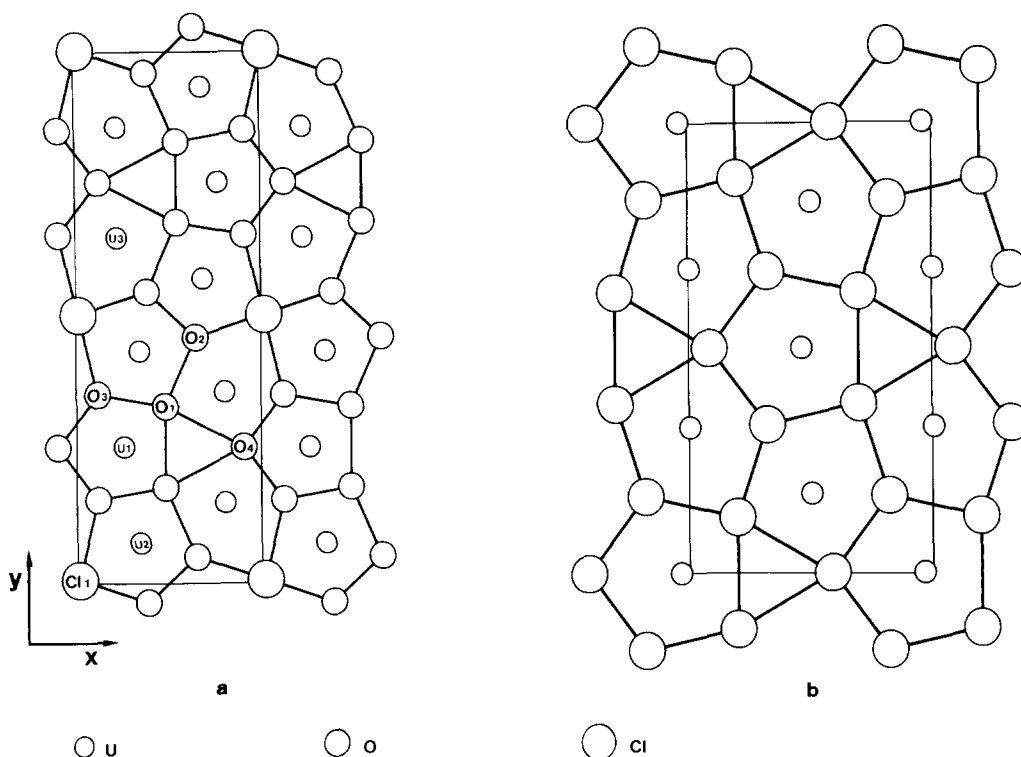


FIG. 2. Projections of $U_5O_{12}Cl$ and $\alpha-U_3O_8$ along C axis. (a) $U_5O_{12}Cl$; in this projection O_5 , O_6 , O_7 coincides with U_1 , U_2 , U_3 . (b) $\alpha-U_3O_8$.

tion O_5 . The composition $U_5O_{12}Cl$ is in accord with the chemical analysis, apart from the fact that probably some oxidation of U(V) to U(VI) has occurred during dissolution of the sample.

Table III lists some bond lengths. For the U–Cl distances the spread is based on the difference between the U–Cl(1) and U–Cl(2) bonds. U(1) has a normal 7-coordination, completely comparable to that in $\alpha-U_3O_8$ (5). U(2) and U(3) are coordinated by 2 “uranyl” O atoms at $z = \pm 0.5$ and 4 O atoms in the $z = 0$ plane. The U(3)–Cl bond is long, 3.23 Å, indicating that bonding is weak, but the Cl definitely plays a role in the coordination. For U(2)–Cl(1) a distance of 2.70 Å is found, slightly less than usual: 2.73 Å in UO_2Cl_2 (8), 2.729–2.742 Å in $U_2O_2Cl_5$ (9), and 2.748, 2.754 Å in $UO_3 \cdot HCl \cdot H_2O$ (10). Due to the influence of

the Cl atom, the coordination polyhedron around U(2) and U(3) is much less regular than that around U(1).

Figure 2a shows a projection of the structure along the c axis. For comparison, Fig. 2b shows the corresponding projection for $\alpha-U_3O_8$. It is clear that the two are related and that $U_5O_{12}Cl$ is the more irregular of the two.

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