

Gmelin Handbuch der Anorganischen Chemie

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8th Edition

U **Uranium**

Supplement Volume E1

Coordination Compounds

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Leopold Gmelin

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U Uranium

Supplement Volume E1

Coordination Compounds

With 11 Illustrations

by **Cornelius Keller**

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Preface

The coordination compounds of uranium have been given special consideration during the last twenty years as can be deduced from the vast amount of publications. There are many such compounds for uranyl(VI), fewer for U^{IV} , and only a few for U^{III} or uranyl(V). Besides their scientific interest, many of these compounds have practical importance in the analytical chemistry of uranium and in the extraction processes for the isolation of uranium from minerals or for reprocessing spent nuclear fuel by the PUREX process. In these processes R_3PO ligands, like $(n-C_4H_9O)_3PO$ (= TBP), are used. Therefore it is understandable that coordination compounds with the $>P=O$ group have received greater attention than other similar complexes, such as the compounds with the phosphines. To obtain a good understanding of the bonding in these compounds, systematic changes of the coordinative ligands have been undertaken in many systems.

Despite the vast number of compounds investigated, comprehensive data are lacking for most of them. We have many spectra, some magnetic data, but less structural data. Thermodynamic data or complete phase diagrams are almost always lacking.

Professor Ken Bagnall has gathered the widely distributed contributions on the subject and presented them in a clear, systematic way. The editor thanks him for his wholehearted cooperation during the preparation of this volume. Similar cooperation was encountered with all the staff of the Gmelin Institute, particularly the director, Prof. Dr. M. Becke, and the editor in chief, Dr. K.-C. Buschbeck.

Karlsruhe
June 1979

Cornelius Keller

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1 Complex Compounds of Uranium

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Complex
Com-
pounds
of Uranium

Introduction

Introduction

This chapter covers the isolated complex compounds of uranium with neutral ligands such as NH_3 , alkylamines, or pyridine (this volume), and those with non-neutral ligands including diketones, tropolones, 8-hydroxyquinoline and its derivatives, cupferron, dithiocarbamates, and others ("Uranium" Suppl. Vol. E2, mostly referred to as "vol. E2").

Stability constants and details of the properties and behaviour of solutions in which uranium complexes have been formed are not included in these sections but are given in the separate volume on chemistry in solution. In this respect, the uranium volumes are like those of the Gmelin Handbook transuranium series.

Since the last edition of this work, which appeared in 1936 [1], a number of books and review articles have appeared in which the chemistry of uranium complexes is discussed. The most comprehensive of these is a book which covers the chemistry of complex compounds of uranium in all oxidation states [2], while reviews of the coordination chemistry of uranium(IV) and (VI) [3], the chemistry of uranium(V) [4], the stereochemistry of dioxouranium(VI) compounds [5, 6] and dioxouranium(VI) chelate complexes [7] contain useful information on the complex compounds of this element. The last, [7], includes a discussion of f-orbital involvement in the bonding in these chelate complexes. More scattered, and certainly less comprehensive, information of this kind is available in books on the chemistry of uranium [8, 9] and of the actinides in general [10 to 12], while reviews on the latter [13], on the halides of the actinides [14 to 16], and on actinide chelate complexes [17] are also useful sources of information. An extensive bibliography of the earlier work on uranium chemistry [18] is also available, and a review of the progress and trends in the development of the coordination chemistry of uranium has appeared [19].

Most of the recent literature on the type of uranium chemistry covered in this chapter is concerned with complex uranium(IV) and dioxouranium(VI) (uranyl) compounds formed with nitrogen or oxygen donor ligands, and much less is known about the analogous uranium(III) and uranium(V) systems. With the advent of improved, more rapid methods of X-ray structure determination, there have been many reports describing the detailed molecular structures of a wide variety of uranium complexes, and results of such work are included in the sections that follow, and in the separate chapter on p. 2. Although water is an oxygen donor ligand, the hydrates of otherwise simple uranium compounds are not discussed here, but are included in the sections which deal with the parent anhydrous compound.

In the formulae of the complexes the ligands are mostly written as an abbreviation, L, or as empirical formulae. In many cases the names of the ligands or their linear formulas are given. In cases where non-neutral ligands result from deprotonation of compounds like 1,3-diketones or Schiff bases, the unionised compounds are used in explanation (e.g. H_2L instead of L^{2-}). The complex formulas are preferably written as in the original paper.

For convenience, the complexes of organouranium compounds are described with the parent compounds in Chapter 2 of the volume E2.

The information on complex compounds in the last edition of this work [1] was given in the sections dealing with the parent uranium compounds, whereas in this chapter the complexes formed with specific individual ligands are collected together. For the sake of completeness the complexes which have previously been recorded [1] are listed, without further detail, in the summary tables which are provided in the majority of the following sections.

Abbreviations

In the tables general use is made of the abbreviations d. (= decomposition), b.p. (= boiling point), and m.p. (= melting point). D_{calc} = calculated density, D_{obs} or D_m = observed density.

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Structures and Spectra of the Uranium Complexes

Structures and Spectra of the Uranium Complexes

A very wide range of uranium complexes is discussed in this chapter, the majority of which involve oxygen donor ligands bonded to uranium(IV) or dioxouranium(VI) centres. For many of the complexes the only information that is available concerns the method of preparation and the infrared spectra of the compounds. Relatively few structural studies have been reported.

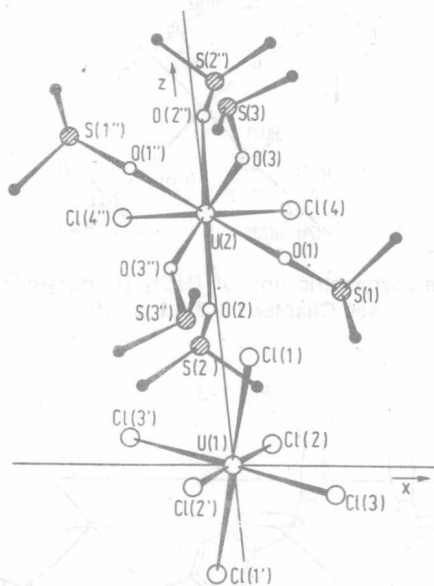
Ionic Radii Coordination Numbers

The radii of the uranium centres in complexes in which the element is formally in the +3, +4, +5 or +6 oxidation state (+6: the dioxouranium cation, UO_2^{2+}) are large relative to those of d transition metal ions in the same oxidation state. For example, the ionic radius of U^{4+} is reported to be 97 pm, as against 74 pm for both Mo^{4+} and W^{4+} [1]. Because of the larger size of the uranium ions the coordination numbers for uranium complexes are higher than those found for complexes in the d transition series. 8-Coordination is, in fact, relatively common in uranium(IV) complex compounds; 6-, 7- and, less commonly, 8-coordination are found for

Literature for "Structures and Spectra" on p. 11

uranium in complexes which contain the UO_2^{2+} ion. In these uranium(VI) complexes the coordination geometry is dictated by the linear $\text{O}=\text{U}=\text{O}$ group, and 7- and 8-coordination is invariably based on pentagonal or hexagonal bipyramidal geometry.

Fig. 1-1



The structure of $[\text{UCl}_2((\text{CH}_3)_2\text{SO})_6][\text{UCl}_6]$ [5]. For a detailed description of the compound, see Chapter 1.1.3.5.1, p. 202/7.

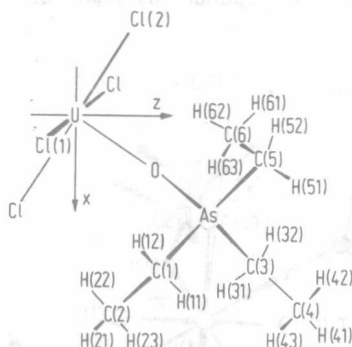
As is commonly the case, the analytical stoichiometry is an unreliable indicator of the coordination number of the central metal atom. One example is the complex of composition $\text{UCl}_4 \cdot 3 (\text{CH}_3)_2\text{SO}$, which appeared to be monomeric from a molecular weight determination [2], but which could also be formulated as an ionic species, either $[\text{UCl}_3((\text{CH}_3)_2\text{SO})_5]^- [\text{UCl}_5((\text{CH}_3)_2\text{SO})]^+$ [3] or $[\text{UCl}_2((\text{CH}_3)_2\text{SO})_6]^{2+} [\text{UCl}_6]^{2-}$, with the latter favoured on lattice energy grounds [4]. The last view is correct, as has been shown by an X-ray crystal structure determination (Fig. 1-1) which revealed that the 8-coordinate uranium atom in the cation is at the centre of a distorted dodecahedron with 6 oxygen and 2 chlorine atoms at the apices [5].

Structures
 U^{IV}

The structures of uranium(IV) complex compounds in which the coordination numbers are 6, 7 or 8 are of considerable interest. In the case of 6-coordination, examples of both *cis* and *trans* octahedral geometry have been recorded for the complexes $[\text{UCl}_4\text{L}_2]$. The complexes $[\text{UCl}_4\{(\text{CH}_3)_2\text{N}\}_3\text{PO}]_2$ [6] and $[\text{UCl}_4\{(\text{C}_2\text{H}_5)_3\text{AsO}\}_2]$ (Fig. 1-2, p. 4) [7] are examples of *trans* octahedral geometry, and *cis* octahedral geometry has been found for the complex $[\text{UCl}_4\{(\text{C}_6\text{H}_5)_3\text{PO}\}_2]$. In this structure (Fig. 1-3, p. 4) two C_6H_5 rings from each molecule of the complex (one from each $(\text{C}_6\text{H}_5)_3\text{PO}$ molecule) are face to face, with the rings from two adjacent molecules at an interplanar distance of 3.52 Å. It is suggested that the strong graphite type interaction is the basis for the preference of *cis* rather than *trans* geometry, because of

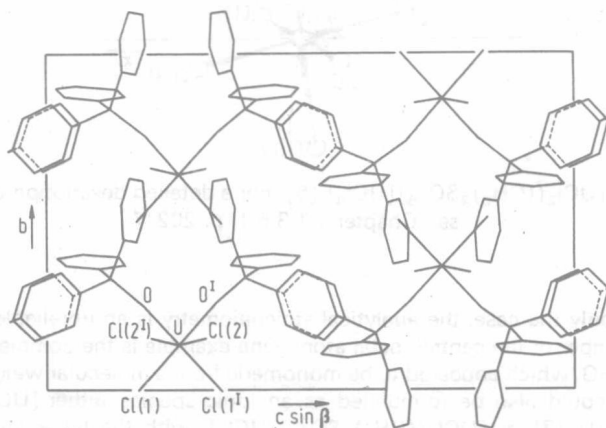
Literature see p. 11

Fig. 1-2



A projection of the asymmetric unit of $[\text{UCl}_4\{(\text{C}_2\text{H}_5)_3\text{AsO}\}_2]$ down y [7], see Chapter 1.1.3.4.1, p. 194.

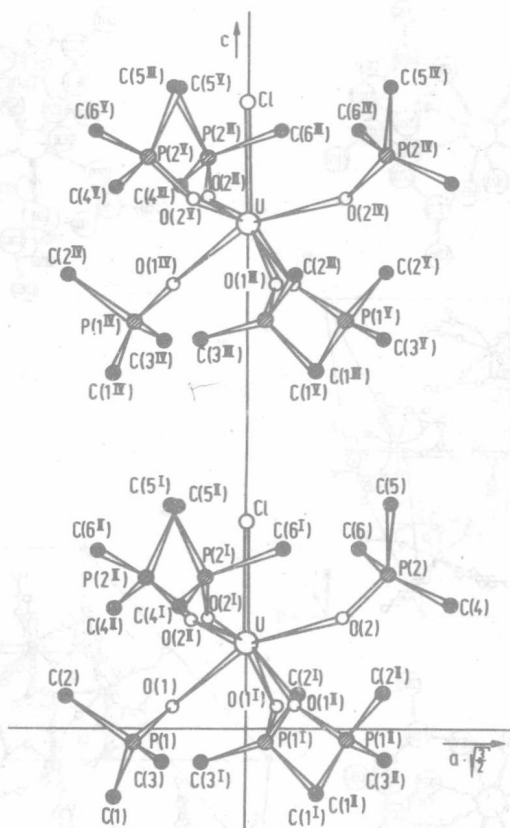
Fig. 1-3



Projection of the structure of $[\text{UCl}_4\{(\text{C}_6\text{H}_5)_3\text{PO}\}_2]$ down the b axis [8], see Chapter 1.1.3.3.1.15, p. 169.

better packing in the crystal [8]. Examples of 7-coordinate in uranium(IV) complexes are uncommon. One example for which the structure has been determined is the complex $\text{UCl}_4 \cdot 6 (\text{CH}_3)_3\text{PO}$, which is ionic, $[\text{UCl}\{(\text{CH}_3)_3\text{PO}\}_6]\text{Cl}_3$. The coordination geometry about the 7-coordinate uranium atom in the cation (Fig. 1-4) can be described as a distorted monocapped antiprism or octahedron [9]. 8-Coordinate uranium(IV) in the α - and β -forms of the acetylacetonate, $\text{U}(\text{acac})_4$, can be described as mainly dodecahedral (α -form) and mainly square antiprismatic (β -form) [10]; the two structures are illustrated in Fig. 1-5, p. 6. These are the two common geometries for 8-coordinate uranium(IV) species.

Fig.1-4



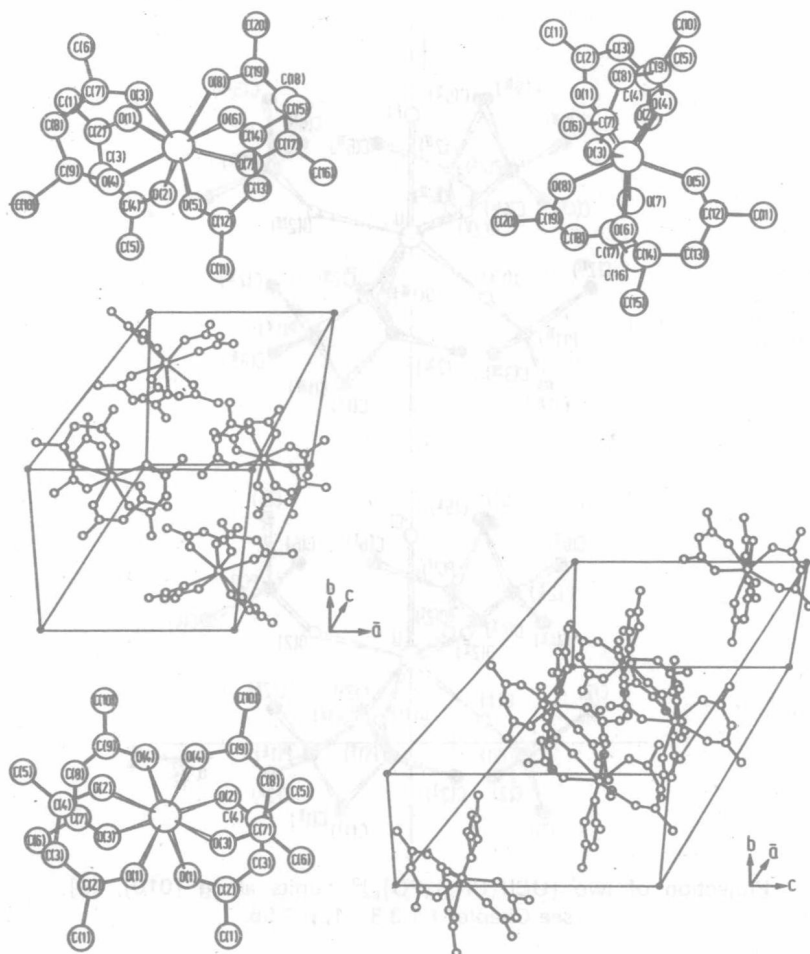
Projection of two $[\text{UCl}\{(\text{CH}_3)_3\text{PO}\}_6]^{3+}$ units along $[010]$, [9], see Chapter 1.1.3.3.1.1, p. 155.

Very few structures are known for uranium(V) complexes with neutral ligands. The 6-coordinate geometry of $[\text{UCl}_5\{(\text{C}_6\text{H}_5)_3\text{PO}\}]$ is a slightly distorted octahedron (Fig. 1-6, p. 7) [11], as might be expected.

In the dioxouranium(VI) complexes, several examples of *trans* octahedral geometry have been reported. The simplest ones are the complexes $[\text{UO}_2\text{Cl}_2\{((\text{H}_3\text{C})_2\text{N})_3\text{PO}\}_2]$ [12] and, in contrast to the complex with UCl_4 , $[\text{UO}_2\text{Cl}_2\{(\text{C}_6\text{H}_5)_3\text{PO}\}_2]$ (Fig. 1-7, p. 7) [13]. Pentagonal bipyramidal 7-coordinate geometry is very common for complexes containing the dioxouranium(VI) ion; this geometry is adopted by the complex $[\text{UO}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2\{(\text{CH}_3)_3\text{NO}\}]$, in which the four sulfur atoms of the dithiocarbamate and the oxygen atom of the amine oxide are in the equatorial plane [14], and by $[\text{UO}_2\text{Cl}_2\{(\text{HOC}_6\text{H}_{10})_2\text{S}\}]$ (Fig. 1-8, p. 8), in which the *bis*(2-hydroxycyclohexyl)sulfide ligand is terdentate, with the oxygen atoms of both OH groups and the sulfur atom bonded to

Literature see p. 11

Fig.1-5



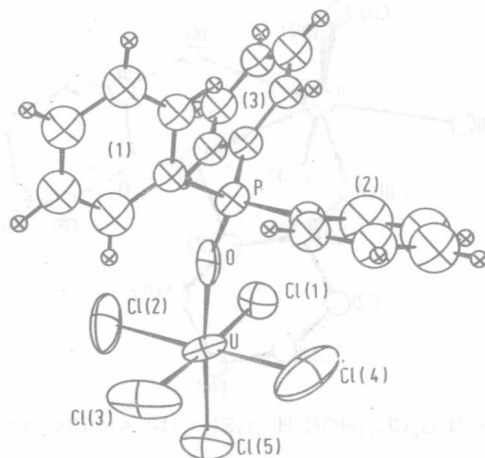
The formula unit and unit cell of α - (top) and β -U(acac)₄ (bottom). The formula unit is viewed from the 8 and 2-axis for the α -form and from the 8-axis for the β -form), [10], see Chapter 1.2.1 in "Uranium" Suppl. Vol. E2.

the uranium atom [15]. Hexagonal bipyramidal 8-coordinate complexes are limited to species containing the smaller bidentate ligands, such as nitrate ion in, for example, the tetrahydrofuran complex $[\text{UO}_2(\text{NO}_3)_2(\text{thf})_2]$ [16] and the dithiocarbamate complexes, such as $(\text{CH}_3)_4\text{N}[\text{UO}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_3]$ (Fig. 1-9, p. 8) [17].

Electronic Spectra

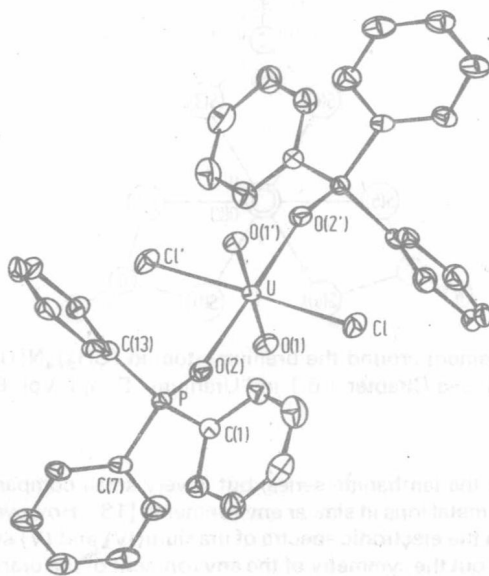
The electronic spectra of uranium(III), (IV) and (V) compounds (f^3 , f^2 and f^1 configurations respectively) can also provide structural information. The splitting caused by spin-orbit interaction for the U^{4+} ion (f^2) in an octahedral field is about twice that observed for the

Fig.1-6



Perspective view of the asymmetric unit in the structure of $[\text{UCl}_5\{(\text{C}_6\text{H}_5)_3\text{PO}\}]$, showing 50% probability vibrational ellipsoids [11], see Chapter 1.1.3.3.1.15, p. 176.

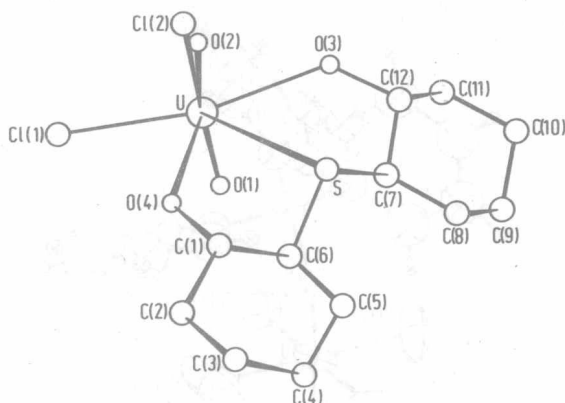
Fig.1-7



Perspective view of the $[\text{UO}_2\text{Cl}_2\{(\text{C}_6\text{H}_5)_3\text{PO}\}_2]$ molecule, showing 50% probability ellipsoids [13], see Chapter 1.1.3.3.1.15, p. 176.

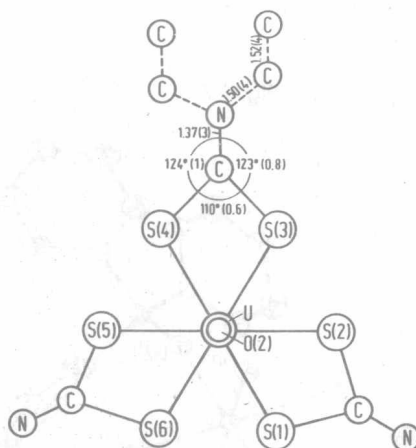
Literature see p. 11

Fig.1-8



The structure of $[\text{UO}_2\text{Cl}_2\{(\text{HOC}_6\text{H}_{10})_2\text{S}\}]$ [15], see Chapter 1.1.4, p. 219.

Fig.1-9



The coordination arrangement around the uranium atom in $(\text{CH}_3)_4\text{N}[\text{UO}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_3]$ [17], see Chapter 1.6.1 in "Uranium" Suppl. Vol. E2.

isoelectronic Pr^{3+} ion in the lanthanide series, but is very small compared with the splitting observed for d transition metal ions in similar environments [18]. However, ligand field effects are certainly detectable in the electronic spectra of uranium(IV) and (V) systems, and although it is very difficult to work out the symmetry of the environment of the uranium ion in a complex from its electronic spectrum, it is possible to use the spectra of complexes of known coordination geometry as "fingerprints" for the identification of unknown coordination geometries [19].