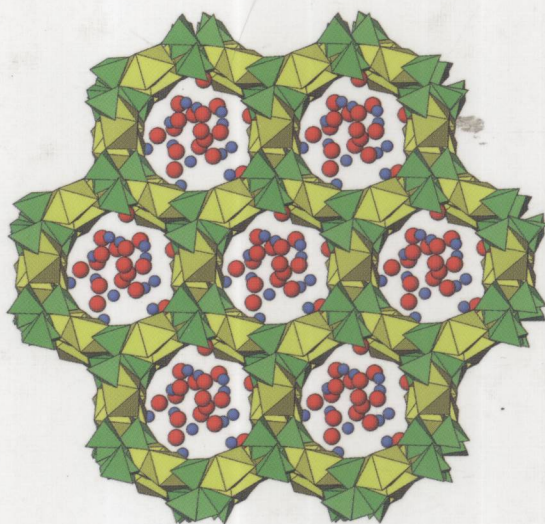


Structural Chemistry of Inorganic Actinide Compounds

Editors: Sergey V. Krivovichev,
Peter C. Burns and Ivan G. Tananaev



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STRUCTURAL CHEMISTRY OF INORGANIC ACTINIDE COMPOUNDS

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STRUCTURAL CHEMISTRY OF INORGANIC ACTINIDE COMPOUNDS

Foreword

This book is a series of reviews of recent results on the state-of-art of structural and crystal chemistry of uranium and transuranium element compounds.

Investigations into crystal structures of neptunium and plutonium compounds were already of great importance at the time of the Second World War. In the 1950s, these studies were extended to include americium, curium and berkelium as well. The first structure determinations of compounds of the new-born elements were carried out at a time when their worldwide quantities were only at the level of micrograms which caused many problems, in particular, in the interpretation of powder X-ray diffraction patterns. Much easier were experiments with uranium and thorium which were in good supply. Despite all the difficulties, the investigations into solid compounds of uranium and transuranium elements were extremely important for the emerging technologies of nuclear fuels reprocessing, the determination of speciation of actinides in the environment, the search for new radioactive waste forms, etc. As a consequence, a large number of reports, papers, reviews and monographs have been published in the field of crystal chemistry of actinide elements. The modern state of science and, in particular, the essential amount of experimental data and development of new methods of structural characterization, allows for the large-scale development of crystal chemistry of actinide compounds. However, not so many books have been published in this area; for instance, the last monograph of this kind in Russia was published more than 20 years ago by M.P. Mefod'eva and N.N. Krot ('Compounds of Transuranium Elements', Moscow, Nauka, 1984). There is no doubt that the enormous amount of accumulated data needs serious systematization and analysis. This book is intended to fulfill this purpose, at least partially. Due to the extensive participation of Russian authors, the book contains many ideas and approaches traditional in Russian science but less well known in the West.

I hope that this book will be another example of a productive and successful international collaboration that transcends the borders of the present world.

Academician Prof. B.F. Myasoedov
Moscow

Preface

This book is a collection of reviews concerning the structural and coordination chemistry of actinide compounds. Over the past decade, these compounds have attracted considerable attention because of their importance for radioactive waste management, catalysis, ion-exchange and absorption applications, and various other applications. Synthetic and natural actinide compounds form as a result of alteration of spent nuclear fuel and radioactive waste under Earth surface conditions, during burn-up of nuclear fuel in reactors, and as oxidation products of uranium mines and mine tailings. Soils and sediments contaminated by actinides often contain such phases as well. Actinide compounds are also of considerable interest to materials scientists owing to the unique electronic properties of actinides which give rise to interesting physical properties that are controlled by the structural architecture of the respective compounds.

The structural chemistry of actinides is very diverse due to the possibility of different oxidation states and the richness of actinide coordination geometries. Whereas actinides in lower oxidation states sometimes mimic rare earth elements, actinides in higher oxidation states possess unique coordination chemistry, due to the tendency to form linear actinyl ions. The reviews in this book are written by specialists in their fields and the subjects range from low-valence actinide compounds to actinide-based metal-organic frameworks. The active participation of Russian authors provides overviews of some activities undertaken by scientists in the former Soviet Union. Their results are sometimes not well known to 'western' readers because of the relatively closed nature of works in this field during the Cold War years.

The book begins with two chapters (by Burns and Serezhkin) concerning the basic structural chemical features of uranium oxocompounds, as these are the most studied actinide compounds in general. Chapter 3, written by Tananaev, describes research results on hydrated oxides, hydroxides and peroxides of transuranium elements and contains some instances of infrared structural features for poorly crystallized compounds from spectroscopic data. The next five chapters are devoted to particular classes of actinide compounds that are characterized by specific structural principles. Krivovichev and Burns (Chapter 4) review structures of over 300 actinide compounds containing hexavalent cations of the VI group elements (S, Se, Mo, Cr, W). In Chapter 5, Sykora, Shvareva and Albrecht-Schmitt describe structural trends observed for actinide compounds with heavy oxoanions containing a stereochemically active lone-pair of electrons (e.g., those formed by Sb(III), Bi(III), Se(IV), Te(IV), Br(V), and I(V)). Chapter 6, written by Locock, provides an overview of actinide phosphates and arsenates that are of great mineralogical and environmental importance. Chapter 7 by Abraham and Obbade presents a systematic overview of the structural diversity of uranyl vanadates. Chemistry and structural chemistry of anhydrous tri- and tetravalent actinide orthophosphates is the topic of Chapter 8 by Orlova. In Chapter 9, Pope describes actinide complexes of polymolybdates and polytungstates, and also discusses solution studies of equilibria between actinide cations and polyoxometalate anions.

Grigory Andreev, Nina Budantseva and Alexander Fedoseev review the current state of the art in research on the interaction of the transuranium elements (TRUE) with N-donor ligands (Chapter 10). Chapter 11 is devoted to a 'hot' topic: U(VI)-containing metal-organic frameworks and coordination polymers and is written by Christopher Cahill and Lauren Borkowski. A short introduction concerning nanostructured actinide compounds is provided in Chapter 12. Finally, Chapter 13, written by Sergey Yudintsev, Sergey Stefanovsky and Rodney Ewing, examines actinide host phases as radioactive waste forms.

In total, the book provides an overview of the structural features of more than two thousand actinide compounds and contains about fifteen hundred references. We are well aware that the reviews gathered in this book do not cover all aspects of research concerning the structures of inorganic actinide compounds. However, we hope that it will be useful for those seeking detailed and updated basic research data concerning actinide compounds as well as those who are seeking a clue in the solution of some important practical problems such as immobilization of radionuclides, utilization of depleted uranium, and safe disposal of nuclear waste.

Sergey V. Krivovichev

Peter C. Burns

Ivan G. Tananaev

May 2006

St. Petersburg – Notre Dame – Moscow

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Chapter 1

Crystal chemistry of uranium oxocompounds: an overview

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1. Introduction

Crystals containing U^{6+} have been the focus of considerable research over several decades. The introduction of CCD-based detectors of X-rays and their application to crystal structure analysis [1] helped facilitate recent studies that have revealed many novel and fascinating crystal structures. A decade ago, the structures of about 180 inorganic compounds containing U^{6+} were known [2], and by 2006 the number of known structures has more than doubled [3]. The majority of these structures correspond to synthetic compounds, but about 90 are for minerals, the special subset of inorganic compounds that are stable for geological times, and that are consistent with geochemical conditions.

Current research concerning the crystal chemistry of U^{6+} oxocompounds is driven by the search for novel solids with important materials properties [4-10], as well as the importance of U^{6+} compounds in the environment [11-16], in geological U deposits [17], and in nuclear waste disposal [18]. The quantity of new structures becoming available is dramatically impacting the state of knowledge of the crystal chemistry of U^{6+} . Relative to a decade ago, dramatically more is known about the structures of uranyl molybdates, sulfates, selenates, selenites, iodates, phosphates, arsenates, oxyhydrates, and peroxides, and significant advances have also been made in the cases of uranyl carbonates, chromates, and silicates. Many of the newer structures follow earlier-established trends, such as the dominance of layered structures, but recent

research has also revealed the remarkable ability of U^{6+} structures to adopt curvature, resulting in nano-scale tubules and spheres [8-10].

The purpose of this chapter is to discuss the specifics of U^{6+} crystal chemistry in terms of the geometries of the coordination polyhedra and their linkages into extended structures. Approaches to understanding and classifying structures containing U^{6+} are examined. Specific coverage is provided for the structures of uranyl oxyhydrates, uranyl silicates, and uranyl carbonates. U^{6+} compounds containing iodate, selenite and tellurite are examined in Chapter 6, sulfates, selenates, molybdates, chromates, and tungstates are in Chapter 7, phosphates and arsenates are in Chapter 8, and uranyl vanadates are covered in Chapter 10.

2. Coordination Polyhedra and Polyhedral Linkages

Actinide cations in higher oxidation states (V and VI) almost invariably form two double bonds to two atoms of oxygen, resulting in an $O=An=O$ (An : actinide cation) ion that is linear or nearly so. The U^{6+} cation conforms to this trend, forming a $(UO_2)^{2+}$ ion in most cases. The U^{6+} -O bond lengths are short because of the double bond, and are typically in the range of 1.78 to 1.82 Å. These short bonds come close to satisfying the bonding requirement of the O atoms, and correspond to about 1.6 to 1.7 valence units [19].

The formal valence of the uranyl ion is 2+, and the ion is always coordinated by multiple ligands in a crystal structure. These ligands are usually located within or near a plane oriented perpendicular to the uranyl ion, passing through the U^{6+} cation. In the case of oxocompounds, four, five or six O, OH or H_2O ligands coordinate the uranyl ion, and are located in the equatorial positions of square, pentagonal and hexagonal bipyramids. In each case, the O atoms of the uranyl ions are located at the two apical positions of the bipyramids (Fig. 1).

The distribution of bond lengths about U^{6+} cations in well-refined structures, as summarized by Burns [3], is presented in Figure 2. The distributions for both pentagonal bipyramids and hexagonal bipyramids are completely bimodal, reflecting the presence of a uranyl ion in each of these polyhedra. The average U-O bond lengths in the uranyl ion are 1.793(35) and 1.783(30) Å for pentagonal and hexagonal bipyramids, respectively. Bond lengths to the equatorial ligands are significantly longer, and show more dispersion: 2.368(100) and 2.460(107) Å for pentagonal and hexagonal bipyramids, respectively.

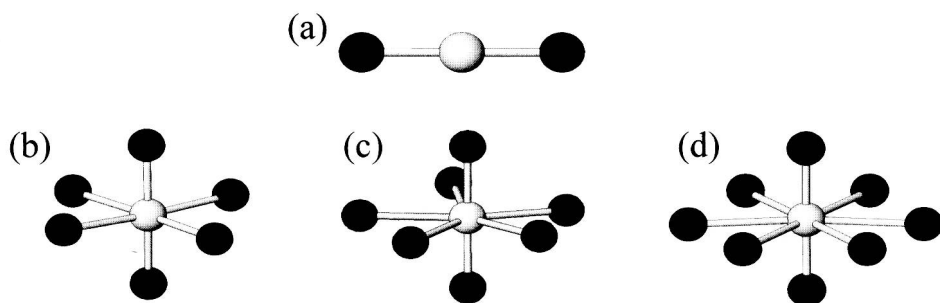


Figure 1. U^{6+} coordination polyhedra. (a) uranyl ion, (b) square bipyramid, (c) pentagonal bipyramid, (d) hexagonal bipyramid.

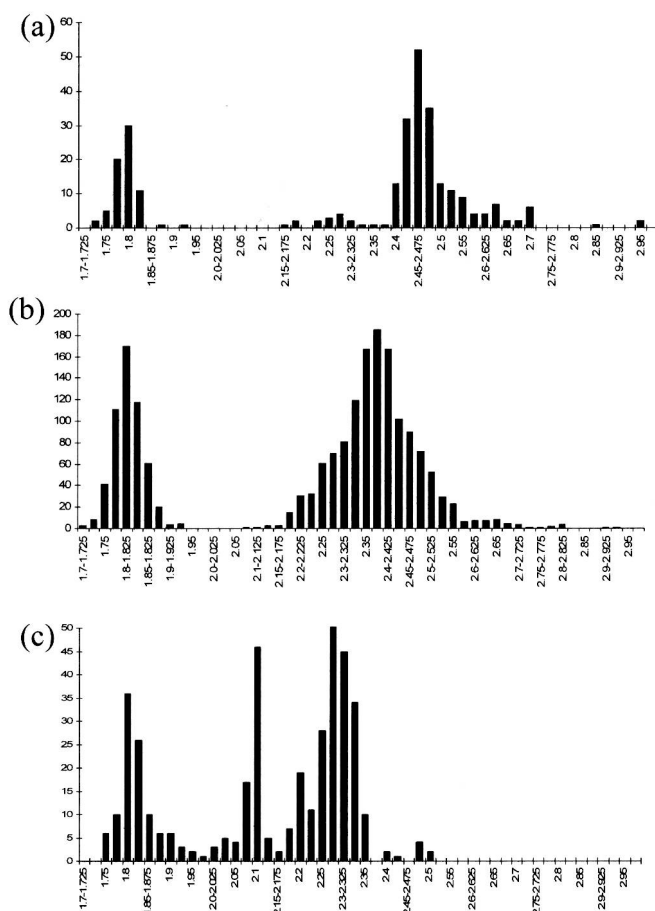


Figure 2. Bond-length distribution for polyhedra containing U^{6+} . (a) hexagonal bipyramids, (b) pentagonal bipyramids, (c) square bipyramids. From [3], reproduced with permission.

Only some of the structures that contain U^{6+} coordinated by six atoms of O exhibit uranyl ions. In the others, the U^{6+} cation is at the center of an octahedron, with a bond-length of about 2.08 Å. It is also interesting to note that various coordination polyhedra intermediate between uranyl square bipyramids and holosymmetric octahedra are present in structures. Where a uranyl ion is present in a square bipyramidal polyhedron, the average uranyl ion and equatorial bond lengths are 1.816(50) and 2.264(64) Å, respectively.

The uranyl ion bond length is weakly dependent upon the number of coordinating ligands, with the shortest bond lengths occurring for hexagonal bipyramids and the longest for square bipyramids. The bond lengths to the equatorial ligands are 0.2 Å longer in the hexagonal bipyramid than in the square bipyramid, and those of the pentagonal bipyramid are intermediate in this range. The corresponding bond-valences associated with the bonds from the U^{6+} cation to the equatorial ligands are 0.71 valence units for the square bipyramid, 0.53 valence units for the pentagonal bipyramid, and 0.44 valence units for the hexagonal bipyramid. Satisfaction of the remaining bond-valence requirements must be achieved if a stable structure is to result. Where H_2O coordinates the uranyl ion, the O atom of the H_2O does not require additional bonds, as the H atoms contribute the required bond valance. Although it may be common in solution, coordination of uranyl ions by H_2O groups is rare in crystal structures, and of the uranyl minerals, is only observed in a few species such as soddyite [20] and uranopilite [21].

Where the equatorial ligands of uranyl bipyramids are O or OH, these O atoms must participate in significant additional bonding to form a stable structure. To meet these bonding requirements, the uranyl polyhedra share equatorial vertices or edges with other polyhedra containing higher-valence cations. Often, such linkages are only between uranyl polyhedra. In these cases, O or OH groups are shared between uranyl ions and the sharing of equatorial edges is common between the polyhedra. As these linkages are almost invariably between equatorial ligands, sheets of uranyl polyhedra are the result. In such sheets, O atoms are almost always bonded to three uranyl ions, but OH groups can bond to either two or three uranyl ions. Where the OH group is linked to three uranyl ions, the bond length is about 0.2 Å longer than the case where O is bonded to three uranyl ions.

It is also common for uranyl polyhedra to share their equatorial vertices with polyhedra containing other types of cations of higher valence. Where this is the case, the types of linkage are dependent upon both the size of the second polyhedron, and the charge of the central cation. For example, borate and

carbonate triangles that are small and contain trivalent or quadravalent cations usually share edges with uranyl hexagonal bipyramids, which presents the shortest equatorial edge length of any of the three types of uranyl bipyramids. In comparison, tetrahedra containing hexavalent cations usually share single vertices with uranyl polyhedra, so as to minimize the repulsion between the cations. Tetrahedra containing pentavalent cations, such as phosphate or arsenate, link to uranyl polyhedra both by sharing edges and only vertices, in roughly equal proportions.

3. Structural Hierarchy of Inorganic Uranyl Compounds

With the substantial growth in the number of known structures containing uranyl polyhedra, a hierarchical arrangement of structures that facilitates comparison and that highlights underlying structural relationships is desirable. The goal of a structural hierarchy is to organize a wealth of complex and diverse structures into a cohesive framework. Structural hierarchies are usually based upon the connectivity of polyhedra in the structures, and thus carry a great deal of information concerning the crystal chemistry of the target group. The intent is to recognize structural trends within large groups of compounds, as such trends are usually obscured by the complexity of individual structures.

Burns et al. [2] developed a detailed structural hierarchy for inorganic uranyl compounds, and included both minerals and synthetic phases. At that time, 180 structures were available for inclusion. Burns [22] expanded the structural hierarchy and updated it in the case of minerals only. Burns [3] further developed the entire hierarchy and included coverage of 368 mineral and synthetic phases. The structural hierarchy is based upon the linkages of those polyhedra that contain higher-valence cations. In every case this includes polyhedra with U^{6+} , and often it includes one or more other types of cation polyhedra. For the purposes of the hierarchy, bonds to low-valence cations and H bonds are ignored (although these bonds are important for the stability of the entire structure).

Structures containing U^{6+} fall into five categories corresponding to isolated polyhedra (8), finite clusters of polyhedra (43), chains of polyhedra (57), sheets of polyhedra (204), and frameworks of polyhedra (56). The numbers in parenthesis indicate the frequency of each type of structure in Burns [3]. Note that linkages through equatorial vertices of uranyl bipyramids results in dominance of sheets of polyhedra, which account for about 55% of known structures.

Burns [3] adopted two different approaches to arranging the structures within the structural classes. In the cases of finite clusters of polyhedra, chains of polyhedra, and sheets of polyhedra that are dominated by the sharing of polyhedra vertices rather than edges, a graphical representation of the structural units was adopted.

Graphical representations are powerful because they reduce the structural complexity and allow recognition of underlying relationships amongst groups of structures. The graph is obtained from a structure by representing each distinct type of polyhedron with a colored circle, and the number of vertices shared between adjacent polyhedra are shown by connectors between the colored circles. Consider for example the clusters and their graphs shown in Figure 3. The graph corresponding to the cluster in Figure 3a has two black circles and eight white circles, the number of uranyl polyhedra and tetrahedra in the cluster. There are two types of white circles; those that are connected to two black circles, and those that are linked to only one. These two types of white circles correspond to the two- and one-connected tetrahedra of the cluster, respectively. The graph also indicates that all linkages in the cluster are by the sharing of vertices, without any sharing of edges that would have been shown by double connectors in the graph. This may be compared to the graph shown in Figure 3b, which has three types of white circles; those that are connected to a single black circle by a single connector, those that are connected to two black circles by single connectors, and those that are connected to a single black circle by two connectors. In the latter case, the two connectors extending between the black and white circle indicate that an edge is shared between the uranyl polyhedron and the corresponding tetrahedron.

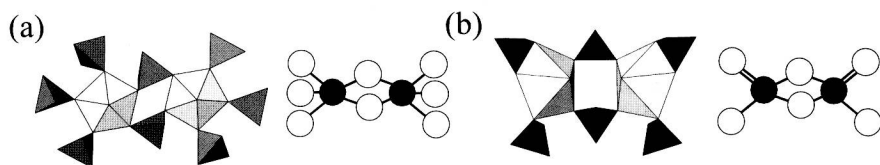


Figure 3. Examples of clusters of uranyl polyhedra and tetrahedra and their corresponding graphs.

Krivovichev & Burns [23] developed a graphical approach for the analysis of sheets that are dominated by the sharing of vertices, Krivovichev [24] greatly expanded this approach, and Burns (2005) analyzed such structures in the same way. This approach is especially powerful because it permits recognition of parent graphs from which many other graphs may be derived. Chapter 7

presents uranyl structures containing sulfate, molybdate, chromate, and selenate using this approach.

Where linkages between polyhedra of higher bond valence within sheets are largely through the sharing of edges, the topological arrangement of anions within the sheets are a powerful means of arranging the structures [2, 3, 22]. In this approach, the connectivity of the sheet of polyhedra is analyzed and only those anions that are bonded to two or more cations within the sheet are considered. Those that are separated by less than about 3.5 Å are connected by lines, all atoms are removed from further consideration, and the resulting representation is projected onto a plane. The resulting two-dimensional tiling of space represents the topological arrangement of anions within the sheet, and is designated the sheet anion-topology. The utility of this approach is that sheets of polyhedra with little obvious resemblance often have the same underlying sheet anion-topology. As shown by Miller et al. [25] and Burns [22], it is possible to create most of the sheet anion-topologies by stacking a small number of distinct chains of polygons. These chains, and their corresponding designations, are presented in Figure 4. This provides a useful means of further comparing sheet anion-topologies, as well as a simple shorthand notation for the topologies. As shown by Miller et al. [25], this also permits derivation of as-yet unknown topologies. Burns [26, 27] showed that it is possible to use this approach to demonstrate that extraordinarily complex sheets in some minerals are composed of modules of simpler sheets found in other minerals or synthetic compounds.

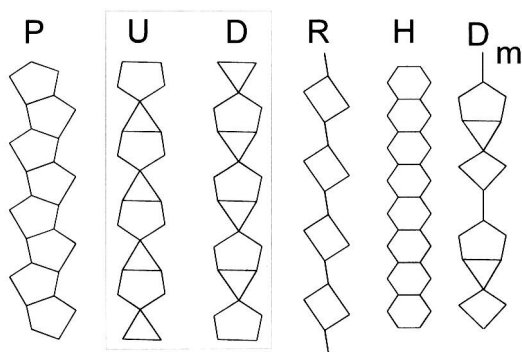


Figure 4. Chains of polygons used to generate sheet anion-topologies.

4. Bond-Valence Approach to Uranyl Structures

The bond-valence approach [28] has proven to be a powerful tool for the prediction and interpretation of bond lengths in solids. Burns et al. [19] presented revised bond-valence parameters derived from uranyl polyhedra in well-refined structures. These parameters facilitate calculations in the case of U^{6+} , as previously proposed parameters generally performed poorly. Burns et al. [19] provided bond valence parameters that were optimized over all uranyl polyhedra, as well as those that are coordination specific. The coordination specific parameters for six-coordinated U^{6+} are $R_{ij} = 2.074 \text{ \AA}$, $b = 0.554 \text{ \AA}$; for seven-coordinated U^{6+} $R_{ij} = 2.045 \text{ \AA}$, $b = 0.510 \text{ \AA}$; for eight-coordinated U^{6+} $R_{ij} = 2.042 \text{ \AA}$, $b = 0.506 \text{ \AA}$. Optimal parameters for all types of U^{6+} polyhedra are $R_{ij} = 2.051 \text{ \AA}$, $b = 0.519 \text{ \AA}$.

Schindler and Hawthorne [29] presented novel insights into the chemical composition and occurrence of uranyl oxide hydrates using a combined binary representation and bond-valence approach. In essence, this approach looks for conditions of overlap of the bonding requirements emanating from the structural unit and interstitial components. The outcome is a series of predicted compositions and mineral stabilities.

5. Uranyl Oxide Hydrates

The most recent compilation of uranyl structures [3] included 29 uranyl oxide hydrates. These structures contain uranyl bipyramids that are invariably linked by the sharing of their equatorial vertices or edges. Most contain interstitial H_2O , and all but six contain low-valence cations that provide linkages between the structural units. Of the 29 uranyl oxide hydrates that have known structures, 17 are minerals. These minerals often form as alteration products of uraninite, UO_{2+x} , in the oxidized portions of U deposits [30]. They are typically the first uranyl minerals to form at the onset of alteration, and although they can persist for geologically significant times. Continued alteration often results in their replacement by other uranyl minerals such as uranyl silicates or phosphates. Uranyl oxide hydrates have also received considerable attention because they form when spent nuclear fuel is altered in a moist, oxidizing environment [31, 32]. It has been suggested that these phases may significantly impact the future fate of a variety of radionuclides during evolution of the repository, as they may incorporate radionuclides such as Cs, Sr, and Np upon crystallization [16].

The linkage of uranyl bipyramids through their equatorial vertices results in the dominance of sheets of polyhedra within this structural class: of the 29 known