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Alfred Werner Revisited: The Coordination Chemistry of Anions

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ABSTRACT
A series of macrocyclic receptors were designed to probe the influence of four factors, hydrogen bonding, charge, dimensionality, and topology, on anion binding. Monocyclic and bicyclic polyammonium and polyamide receptors were synthesized from either 2,2′-diaminodiethylamine derivatives (dien) or 2,2′,2″-aminoethylamine (tren) building blocks, plus aromatic or heterocyclic spacers. Supramolecular complexes of these hosts with three simple anion topologies were probed: spherical (halides), trigonal planar (nitrate), and tetrahedral (sulfate). Results indicate a number of corollaries with transition-metal coordination chemistry in terms of binding concepts such as the chelate effect and dual valencies, as well as geometries for anion complexes that are strikingly similar to those observed in transition-metal coordination chemistry.

Introduction

In the late 19th century, Alfred Werner unraveled the mystery behind the “double salts”, as transition-metal complexes were then called. At that time, a basic understanding had emerged of the bonding around the carbon atom in organic compounds, which was predicated on relatively simple rules relating to the carbon valence. Even this achievement was incredible considering the absence of modern-day X-ray crystallography. However, bonding in the so-called “molecular compounds”, which included transition metals, was still elusive. The puzzling aspect surrounding transition-metal compounds was that they appeared to have higher valences than necessary. Thus, while neutrality principles were satisfied by additional negative ions, often times other species appeared to be associated with the metals, giving rise to more complex stoichiometries such as $CoCl_2 \cdot 6NH_3$, i.e., double salts.

The solution to bonding in transition metals was brilliantly proposed by Alfred Werner, who received the Nobel Prize in 1913 in recognition of his insight. Werner’s discovery provided the foundation for the field of transition-metal coordination chemistry, which has had a major impact on many aspects of modern day society. In addition to a “primary” valence of appropriately charged counterions, Werner invoked a secondary valence for transition-metal compounds: “Even when they are saturated in the sense of the older theory of valence, the elementary atoms still possess sufficient chemical affinity to bind other seemingly also saturated atoms and groups of atoms, under generation of clearly defined atomic bonds.”[1] Therein was born the concept of a double valence for transition-metal ions, a primary valence, satisfying principles of neutrality, plus a secondary valence, providing a “coordination number”, often consisting of additional species beyond those necessary to satisfy the charge.

One-half century later came the intriguing discovery by Park and Simmons that diprotonated bicyclic katapinands could encapsulate halide ions as a result of hydrogen-bonding interactions,[2] a finding that heralded the field of anion coordination chemistry. Although the chemistry of anion recognition advanced somewhat slowly at first, in the mid-1970s, Lehn and co-workers provided significant contributions with the report of macrotricyclic hosts, which could encapsulate halides.[3] The study of the host−guest chemistry of anions slowly gained momentum until a number of other researchers joined the cause in the 1980s.[4,5]

Definition of Anion Coordination Chemistry

Unlike transition-metal coordination, the binding of anions with synthetic receptors falls into the realm of “supramolecular chemistry”, i.e., interactions between molecular or ionic species in the absence of covalent bond formation. Binding affinities between anions and their hosts are mostly attributed to hydrogen-bonding and/or electrostatic interactions, with the former being the more influential in promoting selective binding through topological complementarity. As Moyer and Bonnesen point out, however, it is important to understand the factors influencing anion recognition in the traditional analytical sense, where simple physical properties such as size and hydrophilicity tend to govern selective exchange of one anion over another. They introduce the term *bias* for this type of phenomenon and deduce that truly selective anion receptors must involve some elements of strategic design, including appropriately positioned hydrogen-bond coordination sites.[6]

The introduction of multiple hydrogen-bonding sites along with the resulting topological considerations in anion receptors leads to the concept of double valence for anions as well as for transition-metal ions. For anions, however, the primary valence is the negative charge on the anion and the secondary valence is provided by hydrogen bonds to the anion. Werner postulated that the atoms coordinated via the secondary valence in transition-metal complexes would be arranged in symmetrical shapes around the central metal.[1] Over the years, this insight to the structure of transition-metal complexes has

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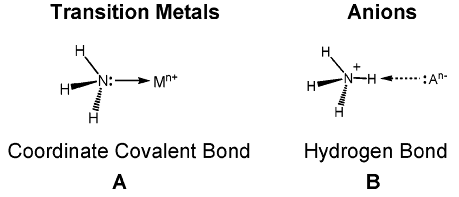


FIGURE 1. Comparison of (A) the coordinate covalent binding mode of transition metals with (B) the hydrogen-bond binding mode of anions.

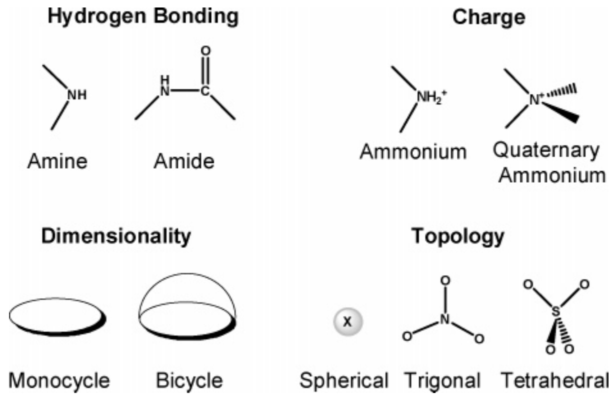


FIGURE 2. Four factors influencing binding in anions.

been verified with a myriad of solid-state crystal structures. After examining the structures of a number of anion complexes, we observe that a similar symmetrical bonding pattern also occurs quite frequently for anions.

Many researchers in the area of the anion recognition already refer to the field as "anion coordination chemistry", as first proposed by Jean-Marie Lehn as early as 1978.[7,8] Before the same concepts can be formally adopted for anions, however, some modifications to the terminology of transition-metal coordination chemistry are in order. For example, the term ligand as applied to transition-metal receptors is defined as a Lewis base that donates a pair (or pairs) of electrons to the metal via a coordinate covalent bond (Figure 1A). In anion coordination, the lone pair of electrons is donated in the reverse fashion, from the anion to a hydrogen atom on the ligand, resulting in hydrogen-bond formation (Figure 1B). Hence, where anion coordination is invoked, the definition of the term "ligand" should be understood to refer to Lewis acid capability and the term "coordination" refers to hydrogen bonds as opposed to coordinate covalent bonds.

Factors Influencing Anion Binding

A number of factors influence the strength, selectivity, and structures observed in the binding between anions and ligands. For the purposes of this Account, however, just four will be considered: hydrogen bonding, topology, dimensionality, and charge (or electrostatic interactions) (Figure 2). A simple set of ligands based on similar carbon frameworks was designed and synthesized to explore these factors (Figure 3).

Hydrogen Bonding. Hydrogen bonding is a major structure-defining aspect of the secondary valence in anion coordination. Two types of hydrogen-bond donors were examined, amines and amides. The polyamine ligands, **1**, **4**, and **5**, are readily obtained by simple Schiff

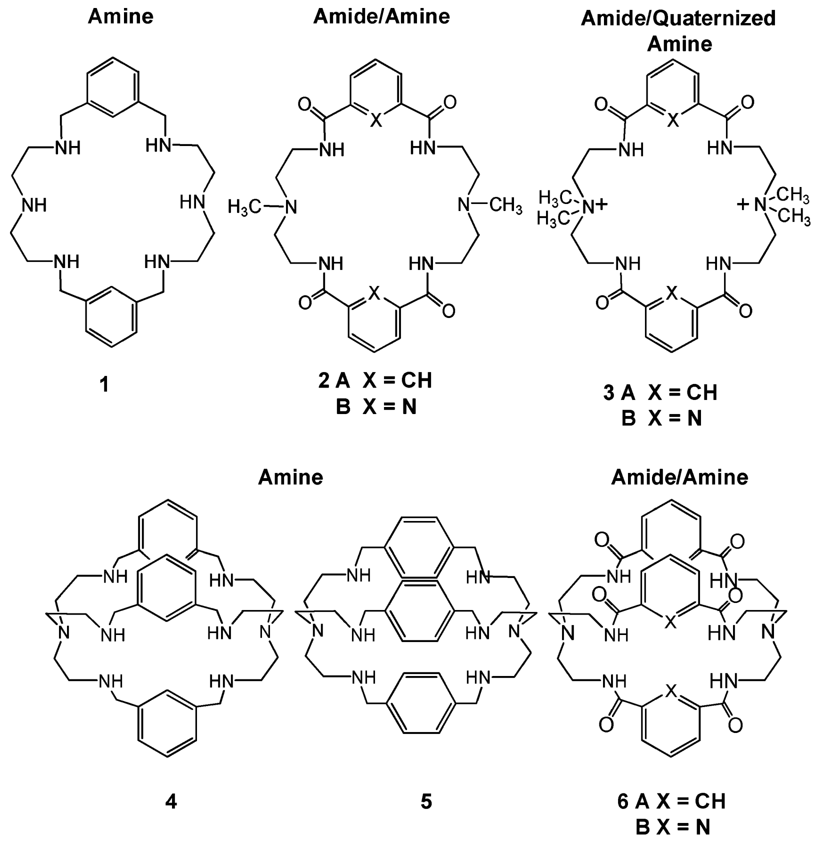


FIGURE 3. Basic series of mono- and bicyclic ligands used to explore anion binding.

base condensations of either 2,2′-diaminodiethylamine (dien) or 2,2′,2″-triaminotriethylamine (tren) with aromatic or heterocyclic dialdehydes followed by borohydride reduction. These ligands have been popular with us as well as other anion chemists.[4,5,9,10] Because anion receptors in Nature often involve amide linkages as hydrogen-bond donors, the amide-based macrocycles, **2** and **6**, were synthesized maintaining the same framework structure of the amines.[11,12] These too are relatively straightforward synthetic procedures using *N*′-methyl-2,2′-diaminodiethylamine (Medien) or tren with the diacid chlorides of the aromatic spacers.

Charge. Electrostatic interactions between a negatively charged anion and a positively charged ligand can influence and enhance binding. Polyammonium ligands are normally polyprotonated when they bind anions, with significant binding usually commencing after several protons are added to the macrocycle.[13] The two amine functionalities of the amide-based monocycle, **2**,[11] provided sites for charge addition via quaternization to yield the dicationic ligand **3**.[14] Hence, as illustrated in the seminal studies by Schmidtchen with another class of anion receptors,[15] a direct evaluation of the effect of positive charge in the absence of additional hydrogen bonding can be evaluated by comparing the two closely related classes of ligands, **2** and **3**.

Dimensionality. Studies comparing monocyclic versus bicyclic binding of anions in polyammonium systems utilized dien and tren as receptor frameworks of monocycles such as **1** and bicycles such as **4** and **5**, respectively.[4,5,7,8,16,17] We used the same strategy to expand the tetraamido framework of **2** to the hexaamido cryptands, **6**.[12,18,19]

Topology. Last, it is important to consider topology in the placement of hydrogen-bond acceptors in the ligands, to overcome "bias"[6] and achieve selective recognition. While there are a number of potential topologies for anions, this Account will focus on just three, spherical (halides), trigonal planar (nitrate), and tetrahedral (sulfate). As a result of the strategic placement of hydrogen-bonding sites on ligands, a number of common geometries and multiple hydrogen-bond interactions can be observed crystallographically for host/guest anion complexes. This points to the tantamount importance of design in anion recognition as discussed in more detail below.

Coordination Numbers and Geometries

Examination of the structural results for anion complexes of the ligands depicted in Figure 3 reveals amazing analogies between anion coordination and transition-metal coordination. These similarities include multidentate binding, known as chelation in the transition-metal chemistry realm, as well as structural motifs such as cascade and sandwich complexes. Furthermore, we have isolated and characterized complexes with coordination numbers from the trivial one coordinate to nine coordinate, with many of the multiply bound anions exhibiting the same regular geometries observed for transition-metal complexes. It should be clearly understood that to date there are no quantum mechanical or orbital explanations such as the simplistic crystal field theory for these observations. In most of these instances, however, as in many transition-metal complexes, the geometrical patterns can be explained as the result of simple charge repulsion phenomena as described for transition metals in the 1970s and 1980s by Kepert.[20] Hence, at this point, these findings are merely structural observations, to perhaps become more grounded in theoretical treatments at a later date. Structural aspects of the multifaceted influences of hydrogen bonding, charge, dimensionality, and topology in terms of coordination numbers and geometries are provided below.

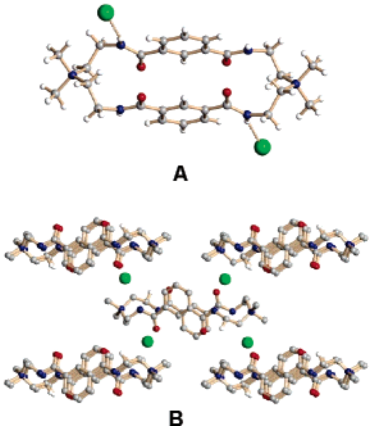
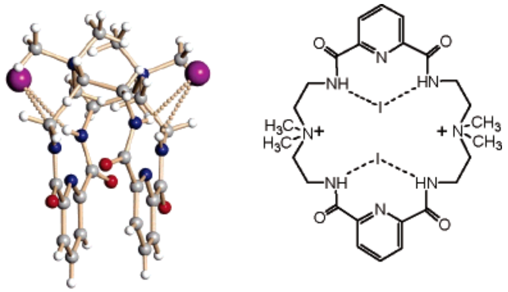


FIGURE 4. Monodentate binding of chloride with **3A**: (A) view of a single molecule and (B) packing diagram showing alternating chloride and macrocycle layers.

One Coordinate (Monodentate). Many two-dimensional macrocycles (monocycles) form simple one-coordinate species with anions, particularly if their binding functionalities are not "preorganized" for multidentate binding. As a result, these structures tend to crystallize with layers of alternating anions and cations as shown in Figure 4 for the chloride complex with the quaternized amide **3A**.[14]

Two Coordinate. Two-coordinate complexes can result from bidentate or chelate formation with donors in the same receptor or ligand. Such binding modes are prevalent in transition-metal coordination chemistry and are responsible for the enhanced thermodynamic stabilities of complexes containing chelating ligands compared with their monodentate analogues. Crystallographic results for ligands containing pyridine spacers almost always indicate internal hydrogen bonding between the pyridine and both adjacent amide hydrogens, while in the *m*-xylyl analogues, structures indicate a more random orientation of the hydrogens either in or outside of the cavity as seen for **3A** (Figure 4). These findings indicate a preorganization of the key binding moieties implemented by the pyridine lone pair. The result is a chelation effect as seen for the structure of **3B** with iodide (Figure 5).[14]

Binding studies also show enhanced binding of both **2B** and **3B**, containing pyridine spacers, over the *m*-xylyl analogues, **2A** and **3A**, indicating the favorable effect of



3B(I)$_2$

FIGURE 5. Bidentate binding of iodide with **3B**.

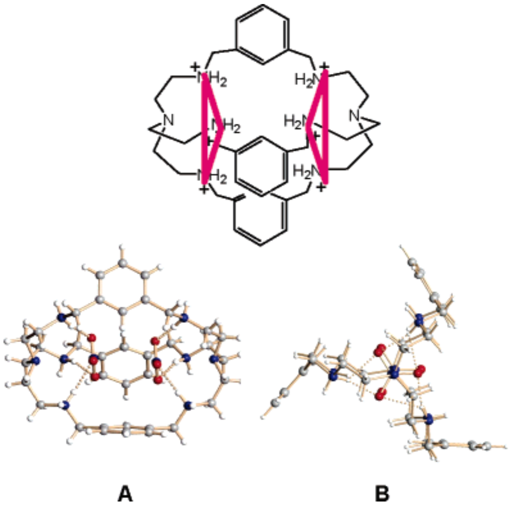


FIGURE 6. Ditopic tridentate trigonal planar coordination of nitrate in H_6**4**$^{6+}$: (A) side view and (B) view down the pseudo-3-fold axis.

preorganization on binding.[14] Furthermore, the quaternized ligands **3** exhibit a higher affinity for almost all anions compared to their neutral counterparts. For example, for dihydrogen phosphate, the affinities determined by NMR are log $K = 2.92$ (**2A**), 4.06 (**3A**), 4.04 (**2B**), and >5 (**3B**) in DMSO-d_6. Thus, a comparison of these four ligands has enabled some insight on the influence of both preorganization (resulting in chelation) as well as charge on anion binding.

Three Coordinate. The 3-fold symmetry of the bicyclic ligand **4** provides a perfect framework for trigonal recognition, as seen in the structure of the ditopic nitrate complex (Figure 6).[16,21] The trigonally arrayed amines are ideally situated to accommodate the trigonal planar nitrates. Each of the nitrate oxygens is held by two hydrogen bonds with adjacent ammonium hydrogens, with one being normal (~2.8−2.9 Å) and one slightly longer (~3.0−3.1 Å). The result is trigonal planar coordination around each of the nitrates. Because this was such an unanticipated mode of binding, the structure was redetermined by Nelson and co-workers, who further confirmed ditopic binding.[22]

The multiple binding observed for the nitrate oxygens is in agreement with a study by Hay and co-workers, who determined the attractive electrostatic potential (ESP) for nitrate and sulfate oxygen atoms using DFT calculations. Their results for nitrate indicated two minima on either side of each nitrate oxygen, as would be anticipated for sp^2 hybridization.[23]

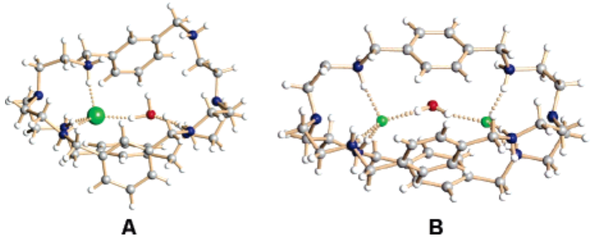


FIGURE 7. (A) Ditopic tetrahedral coordination of fluoride and water in H_6**4**$^{6+}$ and (B) tritopic cascade complex of two chlorides and water in H_6**5**$^{6+}$.

Four Coordinate. As in transition metals, tetradentate is a very common coordination number for anions, especially for the halides. Four-coordinate tetrahedral geometries are observed in fluoride complexes with the two azacryptands, **4** and **5** (Figure 7).[17,24−26] In **4**, the complex is ditopic, with one fluoride and water molecule encapsulated in the ligand (Figure 7A). However, by just a slight expansion of the cavity with a *p*-xylyl spacer, a tritopic complex is obtained with two fluorides and a bridging water molecule in the cryptand (Figure 7B). The chloride complex of **5**, however, contains only a single chloride and water molecule as seen in the fluoride complex of **4**, indicating the influence of anion size as well as cavity size on topicity.[26] Burns has observed that solvent inclusion in a picket-fence porphyrin cavity enhances anion binding and concludes that solvent interaction can exert a positive influence on overall binding energy.[27]

A noteworthy aspect of the fluoride structure, in addition to its tritopic nature, is that it is reminiscent of a class of transition-metal complexes, dubbed as "cascade complexes" by Lehn and co-workers in the late 1970s.[28] Cascade complexes were defined as ditopic transition-metal complexes with a bridging anion (Figure 8A). In the fluoride complex with **5**, however, the ligand is hexaprotonated and two anions are bridged by a "cascading" water molecule (Figure 8B). The structure provides yet another analogy, in addition to the chelate effect, with transition-metal coordination chemistry.

The observation of tetrahedral coordination for fluoride led us to speculate about the possibility of another four-coordinate geometry that is observed frequently in transition-metal complexes, square planar coordination. We have observed such a geometry for fluoride in a sandwich complex with a small urea-derived macrocycle, **7**, the one "outlier" to our targeted set of ligands (Figure 9).[29] The deviation observed for the fluoride from the mean plane formed by the four urea nitrogen atoms is 0.126 Å in this unanticipated structure. The finding is interesting in view of the fact that one would anticipate sp^3 hybridization and tetrahedral orientation as the preferred binding geometry for fluoride. Nonetheless, the results provide yet another geometry for anion binding that correlates with that observed in transition-metal chemistry.

In terms of binding affinities, the possibility of encapsulation appears to enhance binding for the polyammonium cryptands **4** and **5** compared to their monocyclic counterparts. For example, the monoanionic nitrate and fluoride ions show only very weak binding with hexapro-

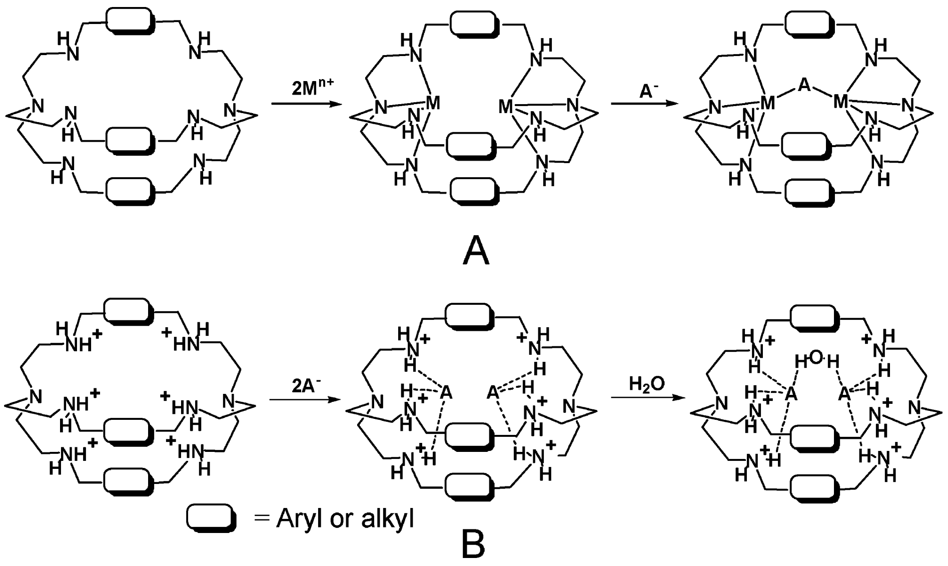


FIGURE 8. Cascade complexes for (A) transition-metal complexes and (B) anion complexes.

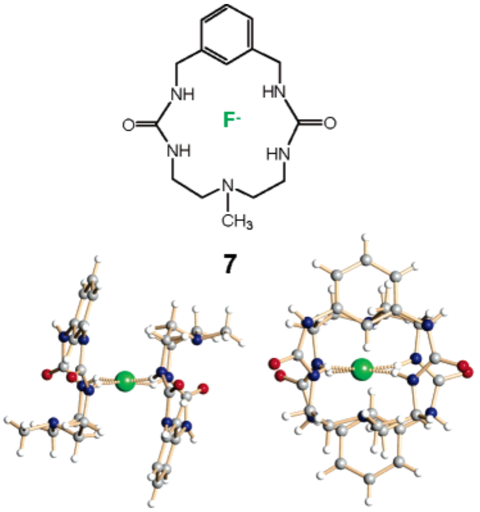


FIGURE 9. Two views of the fluoride square planar sandwich complex with **7**.

tonated $H_6\mathbf{1}^{6+}$ (log $K \leq 2$), while log K of the dianionic sulfate is >4.[16,17] The hexaprotonated cryptand corollary, $H_6\mathbf{4}^{6+}$, however, binds strongly with all three anions: log K = 3.11,[16] 3.56,[17] and 4.36[16] for nitrate, fluoride, and sulfate, respectively. These studies were all performed using potentiometric techniques in aqueous solution with potassium tosylate as the electrolyte.

Five Coordinate. Pentacoordination is observed for a complex between sulfate and the azacryptand **4** (Figure 10).[19] In this structure, all eight of the cryptand amines are protonated and the sulfate is encapsulated in the cavity. However, none of the secondary amines on the left or "west" side of the macrocycle as pictured is hydrogen-bonded with the internal sulfate, which bonds only to the two axial tertiary amines and the three secondary amines on the "east" side of the macrocycle. In terms of coordination geometry, in transition-metal chemistry, the two commonly occurring five-coordinate geometries are square pyramidal and trigonal bipyramidal. In the sulfate structure with $H_8\mathbf{4}^{8+}$, the coordination can best be described as a (very) distorted trigonal bipyramid. The coordination

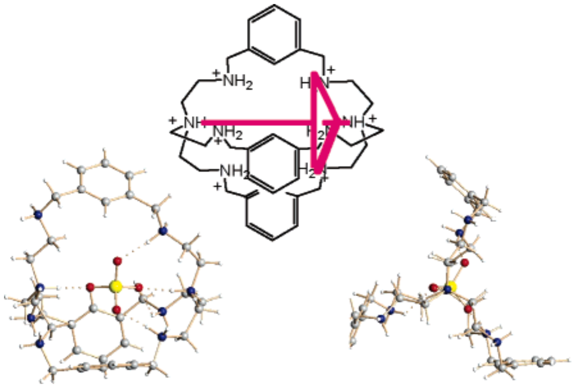


FIGURE 10. Pentadentate trigonal bipyramidal coordination of sulfate in $H_8\mathbf{4}^{8+}$.

assignment is based on the topology of the nitrogen atoms associated with the sulfate via hydrogen bonds, as illustrated on the ChemDraw structure in Figure 10. The three secondary amines form the trigonal plane, while the protonated bridgehead amines provide the axial sites, making **4** a pentadentate ligand.

Six Coordinate. Six-coordinate complexes are quite common in transition-metal chemistry, where geometries vary from octahedral to the more rare trigonal prism. In anion coordination, halides are structurally the closest analogues to the spherical transition metals, and it is with the halides that we have our examples of octahedral geometry. In the fluoride complex with the hexaamide cryptand **6B**, the fluoride forms hydrogen bonds with all six of the amide hydrogens (Figure 11A).[12] The geometry is intermediate between trigonal prism and octahedral, with a trigonal twist angle of 37°. While the distances are all within hydrogen-bonding values, they are somewhat longer than the usual fluoride hydrogen bonds, averaging around 3 Å as opposed to the 2.6–2.7 Å observed for the tetrahedral fluoride complexes in **4** and **5** (Figure 7). Furthermore, it is interesting that, despite very similar ligand topologies, only one fluoride lies in the cavity of **6B**, as opposed to multiple guests in the amine corollary **4**. It is possible that the sp^2 hybridized carbon adjacent

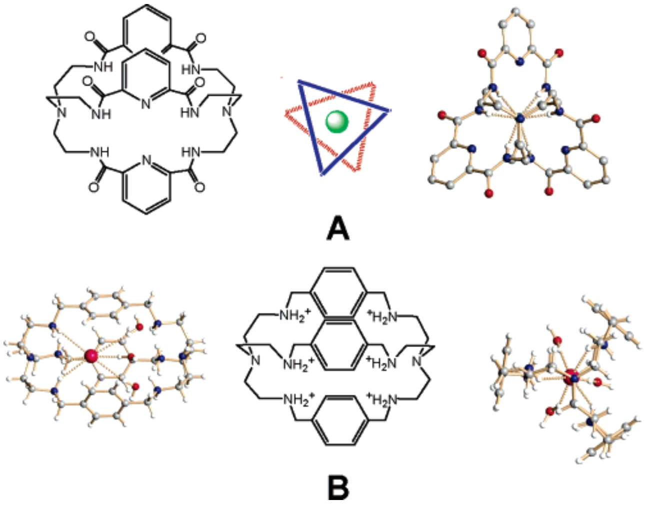


FIGURE 11. Hexadentate coordination (A) for fluoride in **6B** and (B) for bromide in H_6**5**$^{6+}$.

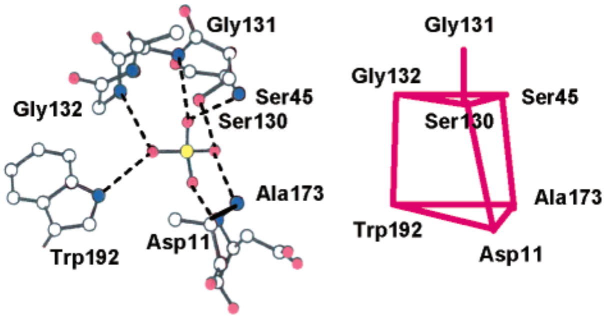


FIGURE 12. Monocapped distorted trigonal prismatic seven-coordinate structure of the sulfate-binding protein.

to the aromatic spacer in the amides plays a role in this observation. Clearly, however, the proximity of the amide hydrogens to the fluoride in **6B** is more heavily influenced by the structural constraints of the cryptand cavity as opposed to the directionality of the lone pairs on the fluoride. Nonetheless, the ^{19}F NMR finding of a symmetrical coupling pattern of the fluoride with all six of the amide protons indicates that interactions are taking place even in solution.[12]

We have also observed pseudo-octahedral coordination in another halide complex. In this case, the complex is the hexaprotonated $[H_6$**5**$]^{6+}$ with bromide. Two independent cryptands with encapsulated bromide occupy the unit cell in this structure. In one cryptand, the bromide is tetrahedrally coordinated with three of the ammonium hydrogens and an internal water molecule much like the fluoride structure with **4**.[17,24] In the second independent unit, the bromide is coordinated to three of the internal amines on one side of the macrocycle and three water molecules located between the cryptand arms on the other side, resulting in pseudo-octahedral coordination (Figure 11B).[26]

Seven Coordinate. Unfortunately, we found no seven-coordinate anion in our own stockpile of crystal structures. However, a highly cited seven-coordinate anion complex is that of the sulfate-binding protein. The structure is depicted schematically in Figure 12 based on the crystal structure coordinates.[30] In terms of geometries in transition-metal complexes, those commonly observed for seven-coordinate complexes are pentagonal bipyramidal and capped octahedron.[31] In the sulfate-binding protein, the closest approximation appears to be the capped octahedron, with the two trigonal planes being formed by Trp 192, Ala 173, and Asp 11 for one trigonal edge and Gly 132, Ser 45, and the γ hydroxide of Ser 130 for the other. The NH of Gly 131 provides the axial cap. All of the sulfate oxygen atoms except one have two hydrogen bonds linking them to the protein.

Eight Coordinate. Octacoordination is usually found for some of the larger transition metals or lanthanides and actinides. It also makes sense therefore that larger, multiatomic anions might prefer higher coordination numbers such as seven and eight. As seen in both the nitrate complex[16,21] (Figure 6) and the sulfate-binding protein[30] (Figure 12), the oxygen atoms in oxo anions are often held by two hydrogen bonds, in these cases possibly relating to the directionality of the oxygen lone pairs. Hence, sulfate with its four oxygen atoms is a perfect candidate for octacoordination. Common polyhedra for octahedral coordination are square prism, square antiprism, dodecahedron, and bicapped trigonal prism.[31] We have now observed two of these geometries in separate crystal structures obtained for sulfate complexes with our amide-based ligands.

The first structure consists of a sandwich complex of the sulfate dianion with **2A**, the monocyclic tetramide.[11] In this structure (Figure 13A), each oxygen atom is bound by two amide hydrogens adjacent to a common *m*-xylyl group. The "top" and "bottom" macrocycles are rotated by 90° to accommodate the S_4 axis of the sulfate. This affords a slightly twisted rhombohedral prism (a variation of square prism) coordination as seen in the overhead and ChemDraw depictions in Figure 13A.

A second eight-coordinate structure obtained with the hexaamide-based cryptand **6B** indicates encapsulated sulfate (Figure 13B).[19] The bridgehead amines of **6B** are protonated and therefore also capable of hydrogen bonding with the sulfate, providing charge complementarity in addition to the multiple hydrogen-bonding network. The hydrogen-bond placement in the diprotonated H_2**6B**$^{2+}$ results in a bicapped trigonal prism geometry. The amide hydrogens form the vertexes of the trigonal prism, while the two axial amines provide the two caps. Although the sulfate is slightly displaced from the center of the cavity, the almost perfect trigonal prism can be seen in the view down the pseudo-3-fold axis on the right in Figure 13B. As in the structure with the monocycle **2A**, each oxygen atom is held by two hydrogen bonds. In Hay's study, as noted earlier, the ESP results indicated a torus around the oxygens such that each oxygen could be involved in as many as three hydrogen bonds, resulting in potentially 12-coordinate binding.[23] While we do not commonly observe three hydrogen bonds to oxygens in our sulfate complexes, many of our structures indicate two hydrogen bonds per oxygen.

Interestingly, in terms of anion binding with the amide-based ligands, the dramatic increase in binding with an

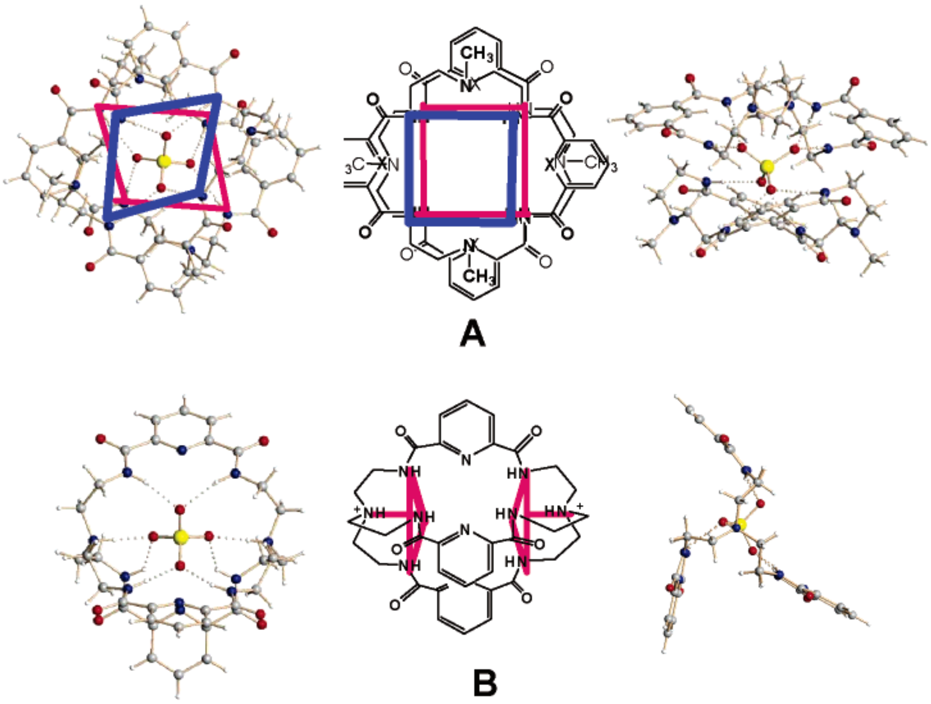


FIGURE 13. Eight-coordinate sulfate structures: (A) square rhombohedral structure with **2A** and (B) bicapped trigonal prism with H_2**6B**$^{2+}$.

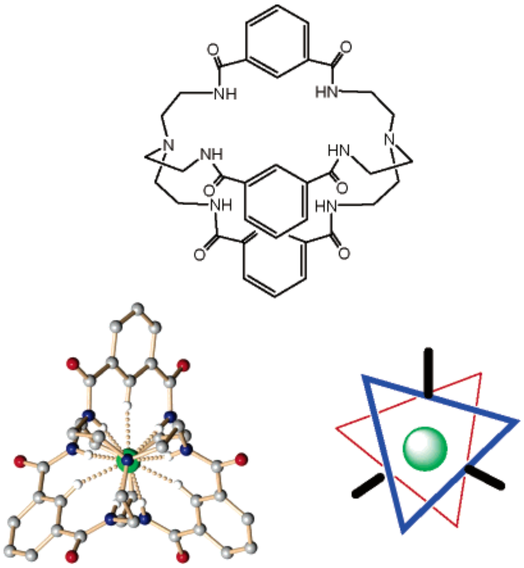


FIGURE 14. Nine-coordinate tricapped trigonal prismatic structure of fluoride in **6A**.

increase in dimensionality is not observed as for the polyammonium ligands. In fact, the binding of sulfate, obtained by NMR in DMSO-d_6, with **2A**, the tetraamide monocycle, is about 10-fold higher (log $K \sim 3$),[11] compared to the hexaamide cryptand, **6B** (log $K \sim 2$).[19] Hence, other factors, possibly structural and related to the possibility of internal coordination between the amide oxygen atoms and the amide NH groups, could be involved. Similar intramolecular hydrogen bonds have been observed for tren-based lipophilic amides in our group.[32]

Nine Coordinate. Surprisingly, it is the smallest anion, fluoride, which was found to have the highest coordination number in this group of structures, that being nine coordinate with the amide-based cryptand **6A**, the *m*-xylyl analogue of **6B** (Figure 14).[18] The additional three hydrogen bonds, compared to the six observed with **6B** (Figure 11A), are between the fluoride and the *m*-xylyl hydrogen atoms that point into the cavity. The hydrogen bonds for these interactions average 3.05 Å and fall approximately within the same range for both the amide and *m*-xylyl hydrogens. As in the structure with **6B**,[12] these are relatively long hydrogen bonds for fluoride, most likely because of multiple potential donors as well as cavity size. While again it is unrealistic to invoke the directionality of the valence shell electrons of fluoride for hydrogen-bond formation, ^{19}F NMR spectroscopy indicates coupling of the encapsulated fluoride with all nine hydrogens.[18]

Conclusions

We have now observed a number of corollaries between the supramolecular chemistry of anions and the traditional coordination chemistry of transition metals. Furthermore, through a systematic investigation of the influence of dimensionality, hydrogen-bond donors, preorganization effects, and charge complementarity, we have established a foundation for understanding the roles that these aspects play in anion binding and selectivity. Obvious similarities with transition-metal chemistry include the chelate and macrocyclic effects, as well as the formation of sandwich and cascade complexes. Furthermore, there appears to be an exciting structural pattern quite analogous to Werner's predictions a century ago: (1) that transition-metal complexes have two valences, a *primary valence* corresponding to the charge on the metal and a *secondary valence* that is satisfied by coordination to a certain number of ligands and (2) that the ligands making up the secondary valence should be arranged in common polyhedra, or "groupings about a metal center".[1] Anion coordination chemistry has now progressed to the level that the same observations can be made: (1) that there are two valences, the charge on the anion and a secondary valence denoted by a "coordination number", in this case satisfied by hydrogen bonding with a "ligand" and (2) that these "ligands" will arrange according to common polyhedra about an *anion* "center".

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