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Crystallographic Evidence for Oxygen Acceptor Directionality in Oxyanion Hydrogen Bonds

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Anion recognition by synthetic hosts is a rapidly emerging field.[1] One of the challenges is the development of receptors that can selectively complex inorganic oxyanions, such as NO_3^-, SO_4^{2-}, and PO_4^{3-}, which are important targets in environmental, industrial, and health-related areas. A successful approach for preparing molecules that coordinate with anions has been to add hydrogen bond donors to an organic scaffold to yield charge-neutral receptors that only interact with anions through hydrogen bonding.[2] Because hydrogen bonds are directional, it should be possible to design hosts with shaped cavities that are capable of differentiating between anionic guests with different geometries, for example, a cavity with D_{3h} symmetry for NO_3^- complexation. The deliberate design of host architecture requires knowledge of the geometric aspects of hydrogen bonding with the guest anion. Yet, for the inorganic oxyanions, little attention has been given to this critical facet of host design.

Studies of hydrogen bonding in a wide variety of systems[3,4] suggest that certain geometric features must be present to attain the optimal hydrogen bonding interaction between a generic donor, D−H, and the oxygen atom acceptor of an oxyanion, O−A. First, for any given hydrogen bond, there is an H$\cdots$O distance that will give the strongest interaction. This distance will depend on the identity of the D−H,O−A pair and can show significant variation. For example, the H$\cdots$O distances observed in crystal structures of salts of protonated oxyanions range in value from 1.3 to 1.8 Å.[5] Second, the D−H$\cdots$O angle should be near 180°; in other words, the D−H vector should point toward the acceptor atom.[3,4] Third, there may be some directionality at the oxygen atom acceptor defined by preferred H$\cdots$O−A angles and H$\cdots$O−A−O dihedral angles. Studies of weak-to-moderate hydrogen bonds with organic oxygen atom acceptors, that is, ketones, aldehydes, ethers, epoxides, and alcohols, show that there is a weak, but definite, preference for the D−H vector to point toward the oxygen atom in directions traditionally associated with the location of electron lone pairs based on sp^2 or sp^3 hybridization.[6] Herein we report results of a survey of crystal structures that establishes for the first time the existence of a significant and general oxygen acceptor directionality in hydrogen-bonded complexes with trigonal planar and tetrahedral oxyanions.

Data for H$\cdots$O−A angles and H$\cdots$O−A−O dihedral angles of intermolecular hydrogen bonds between any D−H donor group and selected oxyanions were retrieved from the Cambridge Structural Database using QUEST and VISTA.[7] For each anion, the search was subject to the following constraints: H$\cdots$O distance between 1.4 and 2.0 Å, anion not coordinated with a metal ion, *R*-factor less than 0.10, no disorder, and error free. Analysis of 2632 hydrogen bonds shows two distinct acceptor directionalities that depend only on the geometry of the central atom of the oxyanion.[8] For trigonal planar oxyanions, HCO_3^- (18 hits), CO_3^{2-} (28 hits), and NO_3^- (861 hits), the average H$\cdots$O−A angle is 115 ± 12° (Figure 1), and there is a clear preference for the hydrogen atom to lie within the plane of the anion (Figure 2).

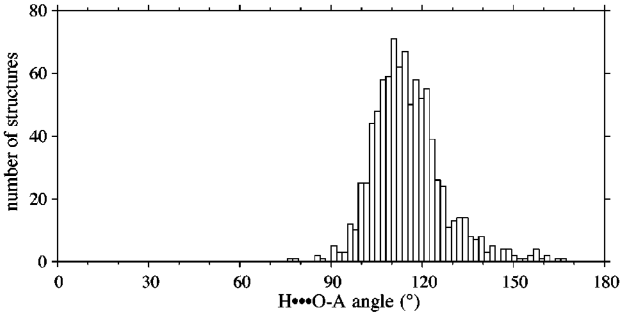

Figure 1. Distribution of H$\cdots$O−A angles for trigonal planar oxyanions. Analysis of 907 hydrogen bonds involving three different oxyanions yields an average value of 115 ± 12°.

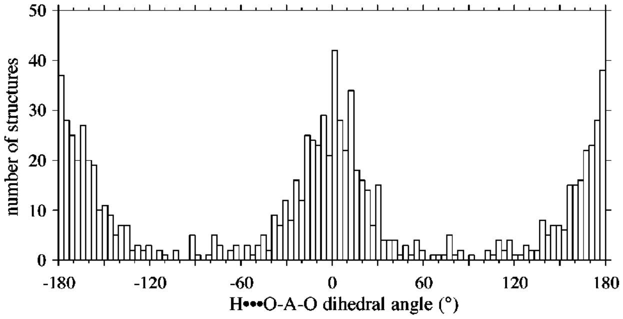

Figure 2. Distribution of H$\cdots$O−A−O angles in trigonal planar oxyanions revealing a clear preference for the hydrogen atom to lie within the plane of the anion.

For tetrahedral oxyanions, $H_2PO_4^-$ (338 hits), HPO_4^{2-} (95 hits), HSO_4^- (48 hits), SO_4^{2-} (761 hits), ClO_4^- (366 hits), $H_2AsO_4^-$ (24 hits), $HAsO_4^{2-}$ (5 hits), AsO_4^{3-} (1 hit), $HSeO_4^-$ (3 hits), SeO_4^{2-} (8 hits), CrO_4^{2-} (9 hits), and MoO_4^{2-} (67 hits), the average H$\cdots$O−A angle is 122 ± 12° (Figure 3), and there is a weak, but observable, preference for the hydrogen atom to adopt an eclipsed conformation with H$\cdots$O−A−O dihedral angles of 0 or ±120° (Figure 4). These distributions are much more pronounced than those previously reported for hydrogen bonds of moderate and weak strength.[6] This observation is consistent with the fact that oxyanions, in general, form stronger hydrogen bonds[3] and, thus, would exhibit stiffer potential wells for distortion from the preferred geometry.

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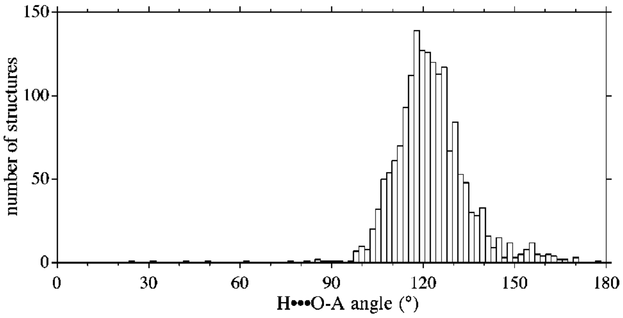

Figure 3. Distribution of H···O−A angles in tetrahedral oxyanions. Analysis of 1725 hydrogen bonds involving 12 different oxyanions yields an average value of 122 ± 12°.

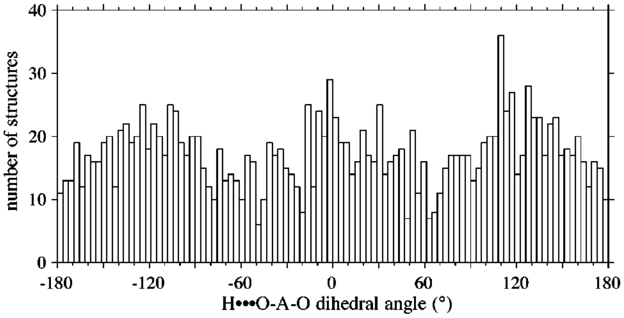

Figure 4. Distribution of H···O−A−O dihedral angles in tetrahedral oxyanions establishes a weak preference for the hydrogen atom to eclipse adjacent oxygen atoms.

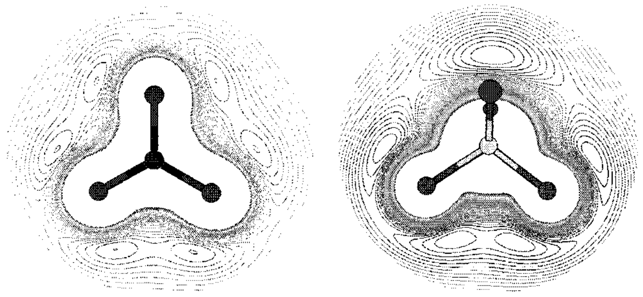

Figure 5. Contour maps of the electrostatic potential surface for a positive point charge in the plane of nitrate, left, and in one of the O−S−O planes of sulfate, right. Contour lines are spaced at 5 kcal/mol intervals. For nitrate, the six equivalent low-energy regions are bound by contours at −165 kcal/mol. For sulfate, the two minimum energy regions (bottom) are bound by contours at −275 kcal/mol and the three other low-energy regions (sides and top) are bound by contours at −270 kcal/mol.

It is possible to rationalize the observed oxygen acceptor directionalities after examination of the attractive portion of the electrostatic potential (ESP) for the oxyanions. ESPs were generated for CO_3^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-, CrO_4^{2-}, and MoO_4^{2-} from DFT calculations. The ESPs for the two trigonal planar anions show comparable structural features. Similarly, the ESPs for the five tetrahedral anions show similar structural features. Representative ESP slices shown for NO_3^- and SO_4^{2-} (Figure 5)[9] reveal the location of minima for the placement of a positive charge that closely correspond to the observed locations of the hydrogen atoms in in the complexes. In the trigonal planar case, there are two minima on either side of each oxygen atom and within the plane of the anion, in other words, at approximately the positions expected for sp^2 hybrid lone pairs. In the tetrahedral case, the nature of the surface is more difficult to visualize. A slice of the ESP through one of the O−A−O planes again reveals two minima on either side of the oxygen atoms, but the minimum energy region that lies between the two in-plane oxygens is deeper. Considering that each oxygen atom resides in three O−A−O planes and each plane exhibits identical surfaces, the minima in tetrahedral oxyanions can be visualized as a torus about each oxygen atom with bulges that would correspond to H···O−A−O dihedral angles of 0 and ±120°.

The results establish that trigonal planar and tetrahedral oxyanions exhibit distinct hydrogen-bond acceptor directionalities that are independent of the central atom, A, and the degree of protonation of the oxyanion. Although both intra- and intermolecular steric factors might be expected to exert some influence, the observed directionalities are also surprisingly independent of the identity of the donor group, D−H. We conclude that achieving structural complementarity between a receptor and an oxyanion must entail a consideration of H···O length, D−H···O angle, *and the directionality at the oxygen acceptor*, that is, the H···O−A angle and the H···O−A−O dihedral angle.

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Supporting Information Available: Electrostatic potential surfaces for selected oxyanions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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