Hydrogen bonding and perhalometallate ions: A supramolecular synthetic strategy for new inorganic materials

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A synthetic strategy for constructing ionic hydrogen-bonded materials by combining perhalometallate anions with cations able to serve as hydrogen bond donors is presented. The approach is based on identification of well defined hydrogen bond acceptor sites on the anions by a combination of experimental and theoretical approaches. Selective population of these sites by hydrogen bond donors has the potential to afford organized crystalline arrays in one, two, or three dimensions. The approach is applicable to a wide range of metal centers.

Molecular synthesis, particularly organic synthesis, encompasses a vast array of specific reactions capable of exerting control over the composition and construction of the final product (1). By contrast, materials synthesis, that is the synthesis of solids, has traditionally lacked this level of control because of the limited number of synthetic strategies available. Such synthetic control would of course be of tremendous value given the intimate link between the microscopic composition and atomic (molecular) arrangement in solids and their macroscopic properties. Thus, greater (microscopic) synthetic control should enhance the ability to tailor macroscopic properties. Given the importance of synthetic materials in areas from electronics and optics through to modern medicine, new or improved synthetic strategies in this area are undoubtedly of considerable value. The present limitations in the synthesis of solids have recently been discussed by Tulsky and Long, who have described one approach with the potential to enhance synthetic control, that of dimensional reduction, in which binary solids are converted to ternary solids of lower dimensionality (2).

A rapidly developing area of chemistry in which synthetic control over crystalline solids is specifically sought is that of crystal engineering (3–6), a field closely allied to supramolecular chemistry (7). While having older roots in organic solid-state photochemistry and solid-state reactions (8), the primary focus of contemporary crystal engineering is the identification or design of molecular level building blocks whose interactions with other building blocks (including self recognition) exhibit some degree of predictability. These building blocks can then, in principle, be assembled systematically to give crystalline solids. Thus, the principles are often those of supramolecular chemistry applied to the construction of infinite solid-state assemblies. The ultimate aim of crystal engineering, of course, is to be able to tailor the macroscopic properties of solids by control of microscopic assembly.

An important concept in crystal engineering is that of the supramolecular synthon (hereafter contracted to synthon; see ref. 9), introduced by Desiraju and typically applied to noncovalent interactions, such as hydrogen bonds. Synthons are the recognition motifs between building blocks that can be used to propagate networks or supramolecular assemblies. The archetypal supramolecular synthon is the hydrogen-bonded dimer formed by carboxyl groups, I (Fig. 1). A related idea conveyed by Yaghi and coworkers is that of the secondary building unit (10), which has been applied to molecular building blocks constructed by using coordination bonds of well defined orientation. This idea is exemplified by the square 4-connected metal carboxylate unit II (Fig. 1), which is known for a variety of divalent transition metals, M\(^{II}\), and has been applied to the synthesis of metal-organic frameworks.

Previously, we have highlighted the fact that halogens coordinated to metal centers are very effective hydrogen bond acceptors (11–13). Furthermore, analysis of many thousands of observed hydrogen bond geometries, D—H···X—M (D = C, N, O; X = F, Cl, Br, I; M = transition metal), using the Cambridge Structural Database (CSD; ref. 14), has revealed distinct directional preferences for terminal halide acceptor groups, namely (D)H···X—M of 90–130° for X = Cl, Br, I, and (D)H···F—M of 120–160° (12, 13). This observation led us to suggest new supramolecular synthons based on these recognition preferences (15) and consequently to develop the synthetic strategy presented in this article, in which these synthons are applied as charge-assisted hydrogen bonds in organic salts of perhalometallate ions. The emphasis in this paper will be on chlorometallate systems, but the extent of applicability to other halometallates will be addressed. The strategy has applications in the crystal engineering of inorganic solids and more broadly in inorganic supramolecular chemistry. However, whereas our immediate focus in this work is on designing tunable solids based on reliable hydrogen bond network propagation in one, two, and ultimately three dimensions, it should be noted that perhalometallate salts have attracted attention as novel materials for various technological purposes, including the possibility of tunable magnetic, optical, and electronic properties (16, 17).

**Methods**

Experimental Data: CSD Searches and Population Density Plots. The program QUEST was used search the CSD to identify close

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Abbreviations: CSD, Cambridge Structural Database; DABCO, 1,4-diazabicyclo[2.2.2]octane.

Data deposition: Crystal structure data for 1,4-diazabicyclo[2.2.2]octane were deposited in the Cambridge Structural Database. Cambridge Crystallographic Data Centre, Cambridge CB2 1EZ, United Kingdom (deposition no. CCDC 174679).

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contacts between N—H groups and three types of anion, square planar [MCl₄]⁻², tetrahedral [MCl₄]²⁻, and octahedral [MCl₆]³⁻. No restriction was placed on the anion charge, although dianions (2⁻) are the most common in each category. The program ISOGEN was then used to combine these observations and display them as fully symmetrized contoured population density plots representing the distribution of hydrogen bond donors in the vicinity of each anion type. Full details are published as supporting information on the PNAS web site (www.pnas.org).

Synthesis and Crystal Structure of (1,4-diazabicyclooctane)H₂[CuCl₄]. See supporting information on the PNAS web site (crystal structure deposition no. CCDC 174679).

Theoretical Methods. Electrostatic potentials were calculated at the Hartree–Fock level with the GAMESS-UK® (18, 19) package, using a compact effective potential (CEP) pseudopotential of Stevens, Basch, Krauss, Jasien, and Cundari (SBKJC), the associated polarized valence double-ζ basis set (SBKJC VDZ ECP) (20) for Pd and Rh, and a Sadlej polarized valence triple-ζ (pVTZ) basis set (ref. 21 and refs. therein) on all other atoms. Geometries for the square planar [PdCl₄]²⁻, tetrahedral [CdCl₄]²⁻, and octahedral [PdCl₆]³⁻ anions, and the cis-PdCl₂(PH₃)₂ and fac-RhCl₃(PH₃)₃ model compounds were obtained by restricted geometry optimization in which all bond lengths were optimized together with torsion angles involving phosphine hydrogen atoms. Interligand angles were not optimized but rather were maintained at angles consistent with the idealized point group of the ion or molecule. All geometry optimizations were conducted at the Hartree–Fock level by using GAMESS-UK® with the following double-ζ basis sets for the metal complexes: SBKJC VDZ ECP (20) for Pd and Rh and Ahlrichs double-ζ with polarization (DZP) (22) for C, H, Cl, and P.

Results and Discussion

Cooperativity Between cis- or fac-Chloride Ligands: Recognition of Hydrogen Bond Donors. We have previously shown that the directional preference for the approach of hydrogen bond donors to terminal metal halides is an electronic effect governed by the electrostatic potential around the halide ligand, which itself is explained in terms of a simple orbital model of metal-halide bonding (13). In the case of metal chlorides, there is a distinct preference for approach of the hydrogen bond donor approximately orthogonal to the metal-chloride bond. This observation led us to surmise that where chloride ligands were located cis to each other (in square planar, tetrahedral, or octahedral metal complexes) or were facially arranged (fac) in octahedral complexes, a cooperative effect might arise wherein the electrostatic potential minima associated with neighboring chloride ligands would reinforce each other. That this is the case is illustrated by the calculated electrostatic potential plots for the model systems cis-PdCl₂(PH₃)₂ and fac-RhCl₃(PH₃)₃ shown in Fig. 2. Thus, a distinct minimum is observed between the chloride ligands in cis-PdCl₂(PH₃)₂ (Fig. 2 a and b) and can be thought of as a binding pocket for hydrogen bond donors (or other positively charged species). The region of negative potential also extends above and below the molecular plane (Fig. 2b). For fac-RhCl₃(PH₃)₃, the region of minimum potential energy similarly lies between the three adjacent chloride ligands (Fig. 2c).

The global minima in fact lie between each pair of chloride ligands (bifurcated site), slightly off the 3-fold axis (trifurcated site) (see Fig. 2d), although the difference in potential is very small [E_min (bifurcated site) = −61.7 kcal/mol; E_min (trifurcated site) = −60.9 kcal/mol]. Overall, the calculations suggest that the hydrogen-bonding arrangements (III–V) depicted in Fig. 3 should be favorable. This result reinforces our prior insight based on a small number of crystal structures that III and IV may serve as novel synthons for the construction of new supramolecular assemblies and network compounds (15).

The situation for tetrahedral metal-halide compounds may be expected to differ slightly from that shown for square planar and octahedral metal coordination environments. The angle between the chloride ligands is 109.47° for an ideally tetrahedral complex, i.e., markedly larger than the 90° interligand angles present in square planar and octahedral systems. Thus, cooperativity between the halide ligands is likely to be less pronounced. This issue will be explored further in the next section.

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*GAMESS-UK®* is a package of *ab initio* programs written by M. F. Guest, J. H. van Lenteke, J. Kendrick, K. Schoeffel, P. Sherrwood, and R. J. Harrison with contributions from R. D. Amos, R. J. Buenker, H. van Dam, M. Dupuis, N. C. Handy, I. H. Hillier, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, A. P. Rendell, V. R. Saunders, A. Stone, and D. Tozer (18). Further details can be found on the Computing for Science, Ltd., web site at www.dl.ac.uk/CFS. The package is derived from the original GAMES code due to Dupuis et al. (19). Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory and funded by the U.S. Department of Energy under contract DE-AC06-76RL1830.

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Fig. 2. Negative electrostatic potential contoured at 10 kcal/mol intervals. Shown for cis-PdCl₂(PH₃)₂ (a) in molecular plane and (b) perpendicular to the molecular plane. For fac-RhCl₃(PH₃)₃ (c) at 1Å from plane of chloride ligands and (d) in the plane perpendicular to that in (c) containing one Rh—Cl bond. Note, the parts of the molecular structures that lie behind the planes are not shown.

Fig. 3. Supramolecular synthons comprised of hydrogen bonding interactions with metal-halide (M—X) acceptor groups.
Interactions of Hydrogen Bond Donors with Perchlorometallate Anions. Having identified the bifurcated (III) and trifurcated (IV) hydrogen-bonded synthons, a systematic way to apply them to supramolecular synthesis was sought, particularly with a view toward designing and preparing new crystalline solids. The intended approach was to use relatively strong charge-enhanced hydrogen bonds linking cationic hydrogen bond donors and perhalometallate anions as hydrogen bond acceptors. With this in mind, the recognition of hydrogen bond donors by mononuclear chlorometallate anions of simple geometries, namely square planar $[\text{MCl}_4]^{n-}$, tetrahedral $[\text{MCl}_4]^{n-}$, and octahedral $[\text{MCl}_6]^{n-}$, has been investigated by using both experimental observations and theoretical calculations.

Searches of the CSD were performed to identify the experimental distribution of N-O-H groups in the vicinity of each of the three anion types in known crystal structures. These distributions are represented in Figs. 4–6 as appropriately symmetrized three-dimensional (3D) contour maps of the hydrogen atom (N-O-H) population density. The distributions are compared with the calculated negative electrostatic potential maps also represented by 3D contours (Figs. 4–6) for the representative anions $[\text{PdCl}_4]^{2-}$ (square planar), $[\text{CdCl}_4]^{2-}$ (tetrahedral), and $[\text{PdCl}_6]^{2-}$ (octahedral).

Fig. 4 shows that the preferred interaction sites for hydrogen bond donors at square planar $[\text{MCl}_4]^{n-}$ anions are the bifurcated sites (see synthon III) that lie on the four edges of the square comprised of the four chloride ligands. From Fig. 5, both experimental and theoretical data show that trifurcated interactions (synthon IV) are not favored in the tetrahedral anions. The experimental distributions (Fig. 5a and b) indicate that the bifurcated sites (synthon III) are preferred. These lie along the six edges of the tetrahedron delimited by the four chloride ligands. However, examination of individual crystal structures suggests that many of these bifurcated interactions are substantially asymmetric, involving a shorter interaction with one of the two chlorides. This observation is reinforced by examination of the theoretical electrostatic potential (Fig.
5c and d), which shows a double minimum along each of the six edges (i.e., 12 minima in total). For the octahedral \([\text{MCl}_6]^{2-}\) anions, the experimental distributions (Fig. 6 a and b) suggest a preference for trifurcated interactions (synthon IV). These interactions occur at the eight triangular faces of the octahedron demarcated by the six chloride ligands. The theoretical results (Fig. 6 c and d) point toward a preference for bifurcated interactions (see V) at the 12 edge sites of the octahedron. However, clearly only a small difference in potential between the face and edge binding sites of the octahedral perchlorometallate ions is found, consistent with the earlier calculations on the neutral \(\text{RhCl}_3(\text{PH}_3)_3\) system (Fig. 2).

### Developing a Supramolecular Synthetic Strategy: (i) Perchlorometallate Anions as Network Nodes.

On the basis of the preferences for the interaction of hydrogen bond donors with the edge sites of square planar anions and tetrahedral anions and the face sites of octahedral anions, a strategy for constructing hydrogen-bonded networks can be envisioned. Thus, perchlorometallate anions can be linked via rigid cationic hydrogen bond donors such that the anions serve as nodes defining the overall topology of the network. Some illustrative examples of possible anion nodes are provided in Fig. 7. The synthetic strategy then resembles that used so effectively in constructing coordination networks, wherein metal centers with well defined coordination geometries have been used as nodes and linked via rigid ditopic ligands such as \(4.4'-\text{bpyridine}\) (5). A further adaptation of the coordination network approach has been to use polytopic ligands capable of connecting more than two metal sites. This approach introduces a second type of node at the ligand site, which may be similar or dissimilar to the metal-based node (6).

#### Table 1. Hydrogen bond acceptor sites per unit charge for perchlorometallate dianions

<table>
<thead>
<tr>
<th>Anion</th>
<th>Charge</th>
<th>Acceptor sites, (N_a)</th>
<th>Acceptor sites per unit charge, (N_{ac})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square planar ([\text{MCl}_4]^2-)</td>
<td>2</td>
<td>4 (edge)*</td>
<td>2*</td>
</tr>
<tr>
<td>Tetrahedral ([\text{MCl}_4]^2-)</td>
<td>2</td>
<td>6 (edge)</td>
<td>3</td>
</tr>
<tr>
<td>Octahedral ([\text{MCl}_6]^2-)</td>
<td>2</td>
<td>8 (face)</td>
<td>4 (face)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12 (edge)</td>
<td>6 (edge)</td>
</tr>
</tbody>
</table>

*If these edge sites are considered able to accept two hydrogen bonds (as illustrated in Fig. 7c), then \(N_a = 8\) and \(N_{ac} = 4\).

### Fig. 7. Examples of proposed nodes of connectivity 2–8 potentially accessible for perchlorometallate anions via interactions with hydrogen bond donors (N–H): (a–c) square planar \([\text{MCl}_4]^2-\); (d) tetrahedral \([\text{MCl}_4]^2-\); (e, f) octahedral \([\text{MCl}_6]^2-\). Anions/acceptors (red), cations/donors (blue), hydrogen bonds (dashed, black). (a) Two of four edges sites occupied: linear 2-connected node. (b) Four of four edge sites occupied: square 4-connected node. (c) Four edge sites each doubly occupied: cubic 8-connected node. (d) Six of six edge sites occupied: octahedral 6-connected node. (e) Four of eight face sites occupied: tetrahedral 4-connected node. (f) Eight of eight face sites occupied: 8-connected cubic node.

### Fig. 8. One-dimensional hydrogen-bonded polymers from the crystal structures of \((\text{DABCO})_2\text{H}[\text{PtCl}_6]\) (15), 1; \((\text{DABCO})_2\text{H}[\text{CuCl}_4]\), 2; \((\text{DABCO})_2\text{H}[\text{PtCl}_4]\) (15), 3. Shown with cations (donors) in blue and anions (acceptors) in red.

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Adopting this nodal approach for construction of hydrogen-bonded networks, one can envisage using in the first instance linear ditopic ligands such as 4,4'-bipyridine and 1,4-diazabicyclooctane (DABCO) that can be protonated at the nitrogen sites to give cationic hydrogen bond donors with the same linear topology as their neutral counterparts. Some examples involving such cations are provided in the next section. Similarly, extensions of this approach could then be made by using polyprotonated polytopic cationic hydrogen bond donors to introduce additional nodes into the final network. We are actively engaged in such efforts.

(ii) Matching Donors and Acceptors: Balancing the Charges. Unlike coordination networks, the number of interactions at the metal-based node (the perchlorometallate anion) is also governed by the need to balance charges between cations and anions, assuming that the overall network is neutral (i.e., there are no other non-network cations or anions present in the final structure). Important parameters in this regard are the number of acceptor sites per unit charge on the anions (NA/C) (Table 1) and the corresponding number of donor sites associated with the cations (ND/C). For the purposes of this analysis, ND/C will be calculated by considering only “strong” donor sites, e.g., N—H or O—H, as these are likely to be of primary importance in forming hydrogen bonds (23). The number of hydrogen-bonded links formed by each anion will in most cases be limited by ND/C, because this will likely be smaller than NA/C. The fraction of anion sites populated by hydrogen bond donors should in principle be given by the quotient ND/C/NA/C.

Applying the Synthetic Strategy. We have applied this strategy to the preparation of a few simple networks. The examples in Fig. 8 show the use of the cation [(DABCO)H₂]²⁺, derived from diprotonation of the diamine DABCO. This cation presents two hydrogen bond donor groups, N—H or O—H, oriented at 180° to each other, and has ND/C = 1 (ND = 2). Combination by salt metathesis reaction of [(DABCO)H₂]²⁺ with dianions [PtCl₆]²⁻ (octahedral) (15), [CuCl₄]²⁻ (tetrahedral) (see also the isostructural [(DABCO)H₂][ZnCl₄] in Viossat et al., ref. 24), and [PtCl₄]²⁻ (square planar) (15) using 1:1 cation/anion stoichiometry yields one-dimensional hydrogen-bonded polymers 1-3, propagated through synthons IV or III, in which ¼, 1/3, and 1/2 (i.e., ND/C/NA/C), respectively, of the anion acceptor sites are used. In each case, two diametrically opposed face or edge sites on the anions are used as hydrogen bond acceptor sites. The flexibility of synthon III is demonstrated in 2 and 3, where zigzag chains are accommodated, presumably to maximize other (weaker) interactions in the solid state. The predominant weaker interaction type is the C—H···Cl hydrogen bond, numerous of which provide the interactions orthogonal to the polymer backbone that give rise to the final three-dimensional structure.

Some examples of two-dimensional (2D) hydrogen-bonded networks (4-5) reported by Orpen and coworkers and consistent with the synthetic strategy outlined herein are shown in Fig. 9. Compound 4, [{(isonicotinic acid)H₂(OH)₂}[PtCl₄]] (25), shows a rectangular grid network in which all four edge sites of the square planar [PtCl₄]²⁻ anions are occupied. In this case, the composite cations, [{(isonicotinic acid)H₂(OH)₂}[PtCl₄]]²⁺, each self assembled from two 4-HO₂CC₅H₄NH⁺ cations and two water molecules, have ND/C = 2, matching the nominal acceptor capability of the anion (NA/C = 2). Thus, ND/C/NA/C = 1. Compound 5, [{(piperazine)H₂}[PtCl₄]] (25), also has ND/C = 2.
matched with the nominal $N_{AC} = 2$, but a different 2D network arises. In this case, only two of the four anion edge sites serve as acceptors, but both are 

**Limitations and Augmentations of the Synthetic Strategy.** The strategy described here is intended to provide a guide for supramolecular synthesis using halometalate salts. These principles may also have applications to assemblies of other metalate salts. However, it should be emphasized that solid-state structures arise from a balance of intermolecular forces. Although stronger forces may dominate and lead to development of synthetic strategies based on this dominance, weaker forces (other hydrogen bonds, other donor-acceptor interactions, and dispersion forces) are important, and accommodation of these forces can modify or may even overwhelm the stronger interactions. In recent work, Orpen and coworkers have also sought to prepare hydrogen-bonded halometalate salts, focusing particularly on the use of synthon III (25–28). Their results show that when the planar 4,4'-bipyridinium dication is combined with square planar $[MCl_4]^{2-}$, tetrahedral $[MCl_4]^{2-}$, and octahedral $[MCl_6]^{2-}$ anions then, in contrast to our use of the $[(DABCO)H_2]^2+ cation (see above), synthon III is specifically adopted only for the polymer generated by using the planar $[MCl_4]^{2-}$ anions, and synthon IV is not adopted at all. Importantly, however, their studies indicate that all of these structures can be rationalized as belonging to a larger homologous family of 4,4'-bipyridinium salts that include chloride and a variety of chlorometallates as counteranions (28). All form structures based on ribbon motifs containing NH...Cl...HN interactions, into which synthon III can be accommodated but is not required.

**Conclusion**

A supramolecular synthetic strategy based on experimental observations supported by ab initio theoretical calculations has been described for the construction of new ionic hydrogen-bonded crystalline materials on the basis of the molecular recognition capabilities of perchlorometallate anions. Initial synthetic applications suggest that this strategy may provide a valuable guide in this area of supramolecular synthesis. Preliminary investigations of other perhalometalates suggest that this strategy should be applicable to bromo- and iodometalates, although fluorometalates may show somewhat different behavior, namely less cooperativity between neighboring fluoride ligands (13). Optimization of synthetic procedures, i.e., solvent, temperature, and pressure conditions for crystal synthesis, has not been the focus of this report but is under active investigation.

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