Tetrahedral Oxyanions in Halogen-Bonded Coordination Networks

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S *Supporting Information*

ABSTRACT: The deliberate construction of (6,3) networks via halogen bond-driven self-assembly of tetra-*n*-butylammonium perchlorate, periodate, and perrhenate with 1,4-diiodotetra-fluorobenzene is reported. The mononegative oxyanions sit at network nodes and work as tridentate halogen bond (XB) acceptors, the diiodobenzene derivative spaces the nodes and function as a bidentate XB donor, while the ammonium cations occupy the space encircled by the supramolecular (6,3) frames. Mixed crystals wherein two different oxyanions statistically occupy the network nodes have also been obtained and show geometrical parameters intermediate to the corresponding pure crystals containing only one of the two oxyanions. Mononegative tetrahedral oxyanions are thus demonstrated to behave as general and effective tectons in anion coordination and anion-templated assembly driven by halogen bonding.
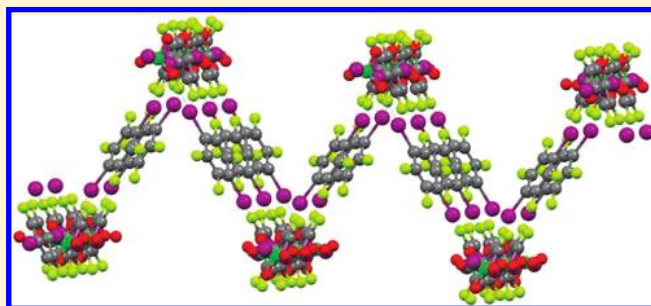
■ INTRODUCTION

The selective binding, extraction, and separation of anions are frequently invoked as potential solutions to a number of fundamental and applicative problems. As far as inorganic oxyanions is concerned, their complexation is actually a major challenge in supramolecular chemistry and impacts in environmental, industrial, and health-related areas.[1]

Similar to what happens for cations, the number of coordinated ligands which surround anions and form their coordination sphere is usually greater that the anion charge, both in the solid state and in solution. Coordination to the cation, electrostatic interactions, hydrogen bonding, "anion-π" interactions, and combinations of these interactions commonly participate in the construction of the anion coordination sphere.[2] Halogen bond (XB), any noncovalent interaction involving halogens as the electrophilic species,[3] has recently emerged as a new item in the toolbox for anion coordination and anion-templated assembly.[4] Halides have been by far the anions most studied in XB-based self-assembly processes;[5] in the solid state the formation of a variety of zero-, one-, two-, and three-dimensional (0D, 1D, 2D, and 3D) networks has been reported, and recognition phenomena in solution have also been studied.[6] Attention has also been paid to the XB-driven binding of some rather uncommon anions (e.g., polycyano- and polyhalometallates),[7] but surprisingly poor attention, if any, has been given to XB-based coordination of oxygen-centered anions. Oxyanions are the most frequently

Scheme 1. Schematic Representation of the Self-Assembly of Tetra-*n*-butylammonium Salts 1a—d with 1,4-Diiodotetra-fluorobenzene (2) To Give (6,3) Networks 3a—d
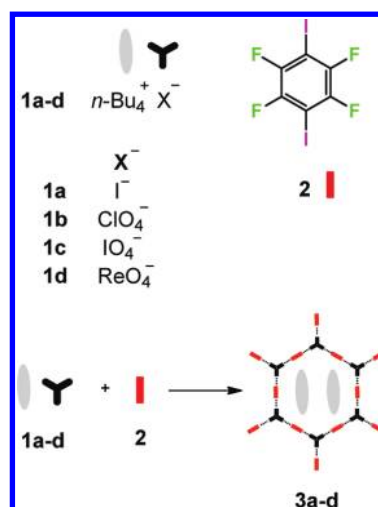
Scheme 2. Self-Assembly of Tetra-n-butylammonium Salts 1b−d with 1,4-Diiodotetrafluorobenzene (2) Affords the Honeycomb Anionic Networks 3b−h
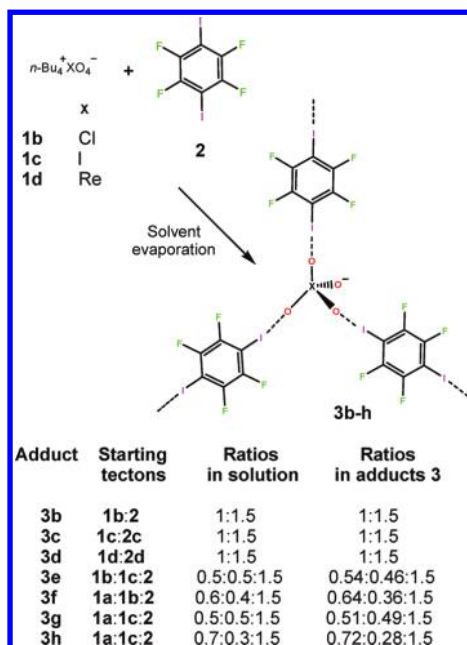
occurring anions in organic chemistry,[8] and we thus decided to study their potential in directing the self-assembly of anion coordination networks under XB control. A search in the Cambridge Structure Database shows that the perchlorate anion affords the most numerous group of serendipitously formed adducts with halocarbons.[9] In these adducts, perchlorate anions form one, two, or four XBs as a function of the available partners. We started our study of the potential of oxyanions as XB acceptors, by investigating the behavior of perchlorate and of two other mononegative tetrahedral oxyanions (namely, the periodate and perrhenate anions).

In the ion pairs given by the ClO_4^-, IO_4^-, and ReO_4^- anions, if one oxygen atom is preferentially bound to the cation, when the three remaining oxygen atoms work as coordinating sites, it may impart to the system a trigonal binding geometry. The use of nodes with a trigonal geometry favors the formation of (6,3) networks.[10,11] In fact, if the interaction driving the self-assembly is directional, the 3-fold symmetry of the nodes (molecular symmetry) is straightforwardly translated into the (6,3) network of the crystal packing (supramolecular symmetry). We thus pursued the ion pairs of ClO_4^-, IO_4^-, and ReO_4^- as tridentate nodes of (6,3) networks.

It is known that there are difficulties in increasing the number of XBs formed by a single XB donor molecule[12] wherein the XB donor sites are conjugated. This difficulty comes from the fact

Table 1. Crystallographic and Structural Data for Adducts 3b−d

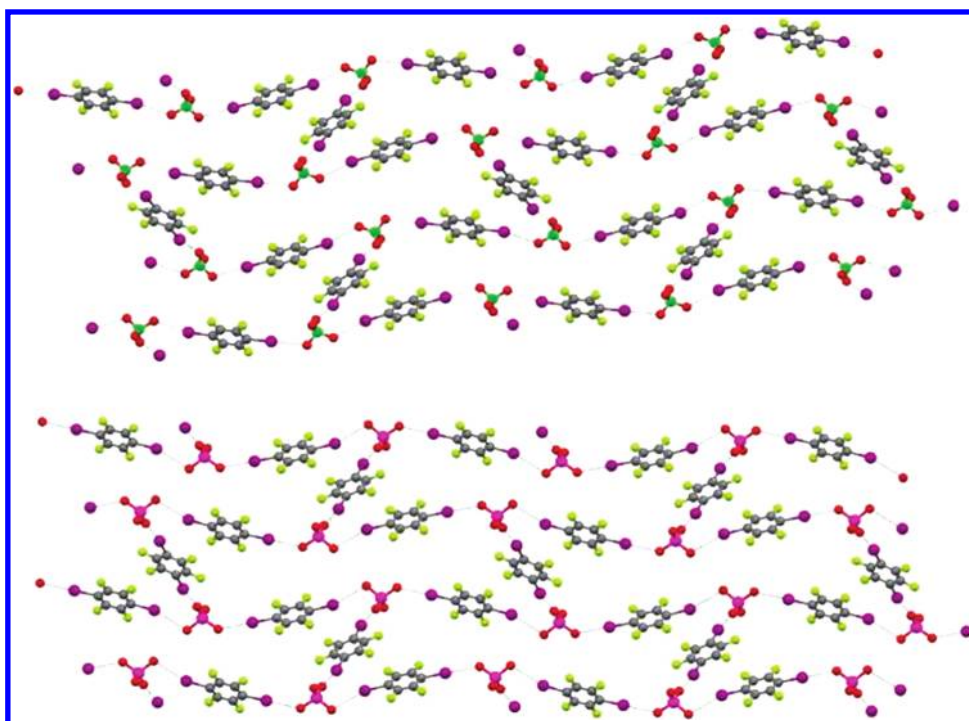|	3b	3c	3d
formula	$(C_{16}H_{36}N)^+ClO_4^- \cdot 1.5(C_6F_4I_2)$	$(C_{16}H_{36}N)^+IO_4^- \cdot 1.5(C_6F_4I_2)$	$(C_{16}H_{36}N)^+ReO_4^- \cdot 1.5(C_6F_4I_2)$
fw	944.70	1036.15	1095.45
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	10.0206(8)	9.9803(9)	10.0350(10)
b [Å]	13.3414(12)	14.0182(12)	13.6797(14)
c [Å]	25.180(2)	24.690(2)	26.195(3)
β [deg]	99.551(7)	97.405(7)	100.285(10)
V [Å^3]	3319.6(5)	3425.5(5)	3538.2(6)
T (K)	123	123	room temp
Z	4	4	4
F(000)	1820	1964	2052
ρ_{calcd} [Mg m^{-3}]	1.890	2.009	2.056
μ [mm^{-1}]	2.969	3.700	6.111
T_{min}, T_{max}	0.6144, 0.7460	0.6071, 0.7458	0.4812, 0.7454
crystal size [mm^3]	0.18 × 0.30 × 0.40	0.10 × 0.20 × 0.34	0.05 × 0.12 × 0.36
$\theta_{completeness}$ [°]	30.00	30.00	25.00
no. refln collected	44484	70325	30854
R_{ave}	0.0242	0.0265	0.0317
no. unique	9679	13779	6224
no. with $I > 2\sigma(I)$	8783	10692	4563
refined parameters	494	505	383
restraints	906	906	135
R_1 [$I > 2\sigma(I)$]	0.0212	0.0240	0.0389
wR_2 [$I > 2\sigma(I)$]	0.0477	0.0462	0.0927
R_1 [all data]	0.0253	0.0418	0.0604
wR_2 [all data]	0.0497	0.0515	0.1063
$\Delta\rho$ [e Å^{-3}]	−0.72 ↔ 1.07	−0.85 ↔ 1.08	−1.33 ↔ 1.37
CCDC number	830750	830751	830752

Figure 1. Ball and stick representation of one supramolecular anionic layer of **3b** (top) and **3d** (bottom) approximately along the *a* axis. Cations have been omitted for simplicity. XBs have been indicated as dotted lines. Color code: gray, carbon; light green, fluorine; violet, iodine; red, oxygen; green, chlorine; pink, rhenium.

that newly formed XBs weaken when electron-donor moieties are already bound to the XB donor.[13] Moreover, the higher the number of XBs formed by a given tecton is,[14] the higher the dimensionality of the resulting network is, namely, the more demanding the space filling requirements are in the overall crystal packing. We were expecting to encounter similar difficulties and demanding requirements as we were pursuing the expression of the polydentate potential of conjugated XB acceptors. Specifically, when an oxygen atom of a polyoxyanion is binding a halocarbon, the propensity of other oxygen atoms to form XBs is expected to decrease as a consequence of the decreased overall electron density on the anion (due to possible polarization phenomena associated with XB formation).

When involved in XB, I^- can function as a mono-, bi-, tri-, and even tetradentate electron-donor,[15] but on crystallization of its tetra-*n*-butylammonium salt **1a** with 1,4-diiodotetrafluorobenzene (**2**, XB donor partner), the tricoordinating ability of this anion is selectively elicited and the (6,3) network **3a** is formed[11c] wherein iodide anions are the nodes and diiodotetrafluorobenzene rings bridge the nodes (Scheme 1). We reasoned that the crystallization of tetra-*n*-butylammonium perchlorate, periodate, and perrhenate with the same XB donor could result is a similar self-assembly process and elicit the potential of these mononegative tetrahedral oxyanions to function as tridentate XB acceptors by overcoming both the electronic and the steric problems described above.

In this paper we describe how crystallization of *n*-Bu$_4$NClO$_4$ (**1b**), *n*-Bu$_4$NIO$_4$ (**1c**), and *n*-Bu$_4$NReO$_4$ (**1d**) in the presence of 1,4-diiodotetrafluorobenzene (**2**) affords the undulated (6,3) networks **3b**, **3c**, and **3d** (Scheme 2) wherein anions function as tridentate XB acceptors, the diiodotetrafluorobenzene rings function as bidentate XB donors, and the ammonium cations occupy the space encircled by the (6,3) frames.

■ EXPERIMENTAL SECTION

Materials and Methods. All reagents were purchased from commercial suppliers (Apollo and Sigma Aldrich) and used without further purification. IR spectra were obtained using a Nicolet Nexus FTIR spectrometer equipment with a U-ATR device. The values were given in wave numbers and were rounded to 1 cm^{-1} upon automatic assignment. Melting points were determined with differential scanning calorimetry (DSC) analyses using a Mettler Toledo DSC 823e.

Synthesis of (*n*-C$_4$H$_9$)$_4$N$^+$ClO$_4^-$ · 1.5(C$_6$F$_4$I$_2$) (3b). Colorless crystals of **3b** were obtained by slow evaporation, at room temperature, of a methanol solution of tetra-*n*-butylammonium perchlorate (**1b**, 1.00 mmol) and 1,4-diiodo-2,3,5,6-tetrafluoro-benzene (**2**, 1.50 mmol). Filtration of the formed crystalline solid gave **3b** in 84% yield; ^{1}H and ^{19}F NMR of mother liquor showed starting compounds **1b** and **2** had remained unchanged in solution. Mp 113−115 °C. IR, ν_{max} (selected peaks): 2969, 1739, 1462, 1430, 1355, 1215, 1082, 942, 758 cm^{-1}.

Synthesis of (*n*-C$_4$H$_9$)$_4$N$^+$IO$_4^-$ · 1.5(C$_6$F$_4$I$_2$) (3c). The procedure described above for **3b** was used, but chloroform, instead of methanol, was employed as a solvent. Filtration of the formed crystalline solid gave **3c** in 88% yield; ^{1}H and ^{19}F NMR of mother liquor showed starting compounds **1c** and **2** had remained unchanged in solution. Mp 115−118 °C. IR, ν_{max} (selected peaks): 2961, 1462, 1430, 1356, 1214, 944, 839, 760, 740 cm^{-1}.

Synthesis of (*n*-C$_4$H$_9$)$_4$N$^+$ReO$_4^-$ · 1.5(C$_6$F$_4$I$_2$) (3d). The procedure described above for **3b** was used. Filtration of the formed crystalline solid gave **3d** in 85% yield; ^{1}H and ^{19}F NMR of mother liquor showed starting compounds **1d** and **2** had remained unchanged in solution. Mp 127−130 °C. IR, ν_{max} (selected peaks): 2960, 2873, 1462, 1442, 945, 898, 761, 739 cm^{-1}.

Synthesis of Mixed Crystals (*n*-C$_4$H$_9$)$_4$N$^+$ClO$_4^-$/IO$_4^-$/ReO$_4^-$ · 1.5(C$_6$F$_4$I$_2$) (3e−h). The procedure described above for **3b** was used. Filtration of the formed crystalline solids gave **3e−h** in
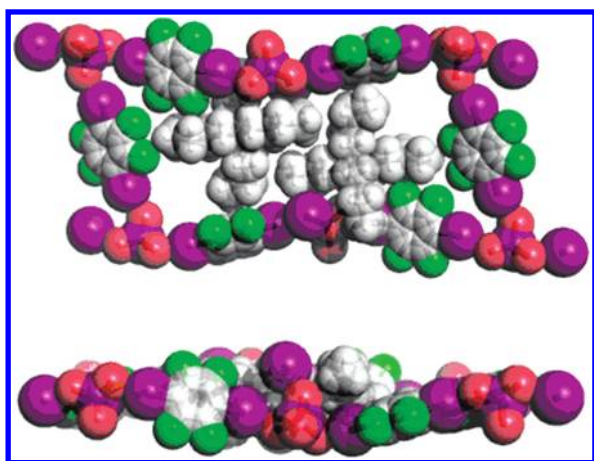
Figure 2. View perpendicular to one (6,3) ring of **3c** (top) and side view of the same ring (bottom) showing how two tetra-*n*-butylammonium cations occupy the space encircled by the supramolecular (6,3) frames. Color code: gray, carbon; light gray, hydrogen; light green, fluorine; violet, iodine; red, oxygen.

75—83% yield; ^{1}H and ^{19}F NMR of mother liquor showed starting compounds **1b**—**d** and **2** had remained unchanged in solution.

X-ray Structure Analyses. *Single Crystal X-ray Diffraction.* Data were collected on a Bruker KAPPA APEX II diffractometer with Mo—Kα radiation (λ = 0.71073) and CCD detector at room temperature (excluding structures **3b** and **3c** which were collected at 123 K using Bruker KRYOFLEX device). The structures were solved by *SIR*2002[16] and refined by *SHELXL*-97[17] programs, respectively. The refinement was carried out by full-matrix least-squares on F^2. Hydrogen atoms were placed using standard geometric models and with their thermal parameters riding on those of their parent atoms. CIF files containing crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray Powder Diffraction. X-ray powder diffraction experiments were carried out on a Bruker D8 Advance diffractometer operating in reflection mode with Ge-monochromated Cu Kα1 radiation (λ = 1.5406 Å) and a linear position-sensitive detector. Powder X-ray diffraction data were recorded at ambient temperature, with a 2θ range 5—40°, a step size 0.016°, exposure time 1.5 s per step.

■ RESULTS AND DISCUSSION

Slow evaporation at room temperature of methanol, or chloroform, solutions containing ammonium salts **1b**—**d** and diiodobenzene derivative **2** in 1:1.5 ratio yields colorless crystals **3b**—**d**. Single crystal X-ray analyses (Table 1) show that the expected honeycomb networks are formed (Figure 1). The X-ray powder diffraction (XRPD) patterns of products (see Supporting Information) revealed the quantitative transformation of the starting materials into the crystalline crystals **3b**—**d**, as corroborated by the absence of characteristic peaks of starting compounds **1b**—**d** and **2**. Moreover, the simulated XRPD from single crystal X-ray analysis and the experimental XRPD patterns of **3b**—**d** show characteristic diffraction peaks indicating that the structures obtained from single crystal X-ray analysis are representative of the bulk polycrystalline sample (see Supporting Information).

The three crystals are in the $P2_1/c$ space group and are isostructural. Interestingly, both their coordination pattern and
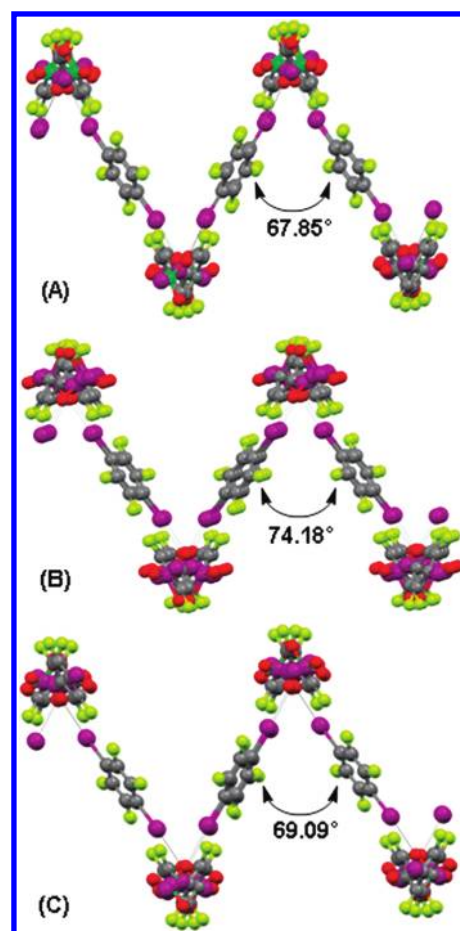

Figure 3. Ball and stick representation of one supramolecular anionic layer of **3b** (A), **3c** (B), and **3f** (C) showing the undulation of the layer. The angle characterizing the "anticline" is reported. Cations have been omitted for simplicity. Color code: gray, carbon; light green, fluorine; violet, iodine; red, oxygen; green, chlorine.

their overall topology are strikingly similar to that of the iodide analogue **3a**, thus proving how effective the use of diiodotetrafluorobenzene and tetra-*n*-butyl ammonium cation is in eliciting the tridentate XB-acceptor potential of mononegative anions which can also be mono-, bi-, and tetradentate. The nodes of the (6,3) nets are the mononegative tetrahedral oxyanions which work as tridentate XB acceptors; the diiodotetrafluorobenzene rings function as node spacers and work as bidentate XB donors. The space encircled in the (6,3) frames is occupied by two ammonium cations which support the (6,3) anionic networks construction from within the cavities by multiple C—H···F—C short contacts pinning the butyl chains to the fluorophenyl rings (Figure 2). While these cations do not contribute with short contact, namely, strong interactions, to the formation of the anionic network, they can be considered to play a templating role by occupying conveniently the space inside the hexagonal framework.

When a supramolecular system is designed to guest nonspherical anions, it is of particular importance to address the specific shape of the targeted anion. The relative geometry and direction of the individual binding sites are critical in the design of coordination systems that rely on directional interactions. The optimization of the requirements deriving from the size and

Table 2. Crystallographic and Structural Data for Adducts 3e−h

	3e	3f	3g	3h
formula	$(C_{16}H_{36}N)^+ \cdot 0.54(ReO_4^-) \cdot$ $0.46(IO_4^-) \cdot 1.5(C_6F_4I_2)$	$(C_{16}H_{36}N)^+ \cdot 0.64(ClO_4^-) \cdot$ $0.36(IO_4^-) \cdot 1.5(C_6F_4I_2)$	$(C_{16}H_{36}N)^+ \cdot 0.51(ClO_4^-) \cdot$ $0.49(ReO_4^-) \cdot 1.5(C_6F_4I_2)$	$(C_{16}H_{36}N)^+ \cdot 0.72(ClO_4^-) \cdot$ $0.28(ReO_4^-) \cdot 1.5(C_6F_4I_2)$
fw	1068.02	977.62	1018.19	986.91
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	10.052(3)	10.115(3))	10.146(8)	10.096(2)
b [Å]	13.827(3)	13.593(3)	13.549(9)	13.473(3)
c [Å]	25.985(7)	13.593(3)	26.484(19)	26.125(5)
β [deg]	99.851(9)	100.44(2)	101.84(4)	100.86(2)
V [Å^3]	3558.5(16)	3515.8(15)	3563(4)	3490.0(12)
T (K)	room temp	room temp	room temp	room temp
Z	4	4	4	4
$F(000)$	2011	1872	1933	1885
ρ_{calcd} [Mg m^{-3}]	1.994	1.847	1.898	1.878
μ [mm^{-1}]	4.914	3.092	4.376	3.768
T_{min}, T_{max}	0.5823, 0.7452	0.5767, 0.7452	0.6382, 0.7452	0.6162, 0.7454
cr size [mm^3]	0.02 × 0.11 × 0.42	0.04 × 0.10 × 0.40	0.02 × 0.11 × 0.46	0.02 × 0.12 × 0.30
$\theta_{completeness}$ [°]	25.00	25.00	25.00	25.00
no. refln collected	33488	30542	25518	184115
R_{ave}	0.0558	0.0431	0.0491	0.0799
no. unique	6230	6156	6234	6124
no. $I > 2\sigma(I)$	3624	3195	3265	3371
ref parameters	384	384	383	383
restraints	165	141	165	165
R_1 [$I > 2\sigma(I)$]	0.0435	0.0440	0.0450	0.0439
wR_2 [$I > 2\sigma(I)$]	0.0928	0.1032	0.1022	0.0974
R_1 [all data]	0.0928	0.1044	0.1084	0.1013
wR_2 [all data]	0.1179	0.1363	0.1299	0.1285
$\Delta\rho$ [e Å^{-3}]	−1.14 ↔ 1.29	−0.61 ↔ 0.83	−0.65 ↔ 0.80	−0.61 ↔ 0.77
CCDC number	830753	830754	830755	830756

shape of anions is thus of key relevance when the halogen-bonded coordination of oxyanions is pursued. The versatility of the described protocol, which gives isostructural architectures starting from mononegative tetrahedral oxyanions of different sizes, proves the robustness of the employed supramolecular synthons.

The I···O$^-$ distances in crystal 3b, 3c, and 3d are within the ranges 294.8−301.0, 286.4−293.1, and 299.4−326.4 pm, respectively, and correspond to quite close, namely, strong, contacts. As an approximate measure of strength of XB, we define "normalized contact" the ratio $N_c = D_{ij}/(r_{vdwi} + r_{ARj})$, where D_{ij} is the distance between the atoms i and j and r_{vdWi} and r_{ARj} are the van der Waals radius of atom i (198 pm for iodine) and ionic radius of anion j (176 and 216 pm for oxygen and iodine). N_c is a useful indicator of the interaction strength, more useful than the distance D_{ij}, because it allows XBs in different halogen/anion supramolecular synthons to be compared. The above-reported I···O$^-$ separations give normalized contacts in the range 0.79−0.80, 0.76−0.78, and 0.78−0.87 for 3b, 3c, and 3d, respectively. The I···I$^-$ separations in iodide-based network 3a correspond to a normalized contact in the range 0.84−0.88. Iodide anions are commonly considered good XB donors, and a comparison of the normalized contact of 3a with those of 3b−d indicates that also mononegative tetrahedral oxyanions function as strong XB donors.

In covalently bonded halogen atoms, the electronic density on the halogen is asymmetrically distributed: the belt-shaped region orthogonal the extension of the covalent bond to the halogen atom is characterized by a negative electrostatic potential, while the region on the extension of the covalent bond is depleted of electronic density, frequently to the point that a positive electrostatic potential is observed. This region, named positive σ-hole,[18] interacts attractively with negative sites and gives rise to XBs which have a remarkable tendency to be linear. In 3b−d the C−I···O$^-$ angles span the range 160.53−172.35°, the greatest deviation from linearity being observed in 3d.

The honeycomb layers in 3b−d are highly corrugated and form undulated layers; the angle formed by the mean square planes of the two intersecting sides of the corrugated layers are 67.85°, 74.18°, and 71.14°, respectively (Figure 3). This arrangement is a likely consequence of the overall crystal packing requirements as the iodide analogue 3a also presents the undulated layers with an angle of 53.38°. The tetrahedral geometry of the employed oxyanions affects this inherent bias for corrugation.

The remarkably close structural similarities among the perchlorate, periodate, and perrhenate networks prompted us to try the synthesis of mixed crystals where the nodes of the anionic network were statistically occupied by two different oxyanions.

We thus slowly evaporated methanol solutions wherein the **1**:**2** ratio was 1:1.5 and the required amount of XB acceptor **1** was obtained by mixing two different salts **1b**–**d** in the same or different ratio (Scheme 2). The mixed crystals **3e**–**h** were obtained and their single crystal X-ray analyses (Table 2) revealed they all were isostructural with **3b**–**d**. They consist of highly corrugated (6,3) networks, and two different anions statistically occupy the nodes with ratios nicely similar to the corresponding ratios in crystallization solution. For instance, in the crystal **3e** the IO_4^-/ReO_4^- ratio was 54:46 which parallels the corresponding 1:1 ratio in crystallization solution; the ClO_4^-/ReO_4^- ratios in crystals **3g** and **3h** were 51:49 and 72:28 while being 1:1 and 7:3 in starting solutions, respectively. Even though the three oxyanions have quite different sizes and are actively involved in the formation of the crystals, they are perfectly switchable as nodes in the (6,3) anionic network construction. This suggests the three anions have similar tendencies to be involved in XB directed self-assembly processes or the overall crystal packing requirements overpower the differences.

Finally, it is interesting to observe that the mixed crystals **3e**–**h** show geometric parameters intermediate to the corresponding pure crystals **3b**–**d**. For instance, the corrugation of **3e**, **3f**, and **3g** is characterized by an angle between the intersecting mean square planes of the "anticline" arrangement of 72.05°, 69.09°, and 68.14°, these values being in between those of the two crystals containing the corresponding pure oxyanions (**3c** and **3d**, **3b** and **3c**, **3b** and **3e** in the order).

CONCLUSIONS

In conclusion, we have reported the deliberate construction of (6,3) networks **3b**–**h** via XB-driven self-assembly of tetra-*n*-butylammonium perchlorate, periodate, and perrhenate **1b**–**d** with 1,4-diiodotetrafluorobenzene (**2**). The oxyanions sit at network nodes and work as tridentate XB acceptors, the diiodobenzene derivative spaces the nodes and function as bidentate XB donor, while the ammonium cations occupy the space encircled by the supramolecular (6,3) frames. The potential of the used anions to function as tridentate XB acceptors was elicited by a judicious choice of the XB donor and of the cation.

The synthesis of crystals **3b**–**h**, their close structural similarities, and the obtainment of crystals wherein two different oxyanions statistically occupy the network nodes, positively show perchlorate, periodate, and perrhenate anions are reliable tectons for the design and synthesis of halogen-bonded supramolecular anions.

We have already reported how the self-assembly of onium halides with 1,3,5-triiodotrifluorobenzene affords (6,3) networks when onium cations of quite a different size and nature are used, and we have also described how mixed (6,3) nets can be synthesized wherein different cations statistically populate the centers of the (6,3) frames.[11c] The formation described here of mixed (6,3) nets wherein different anions statistically occupy the space encircled by the (6,3) frames is even more remarkable as anions are the nodes of the nets and drive the self-assembly by functioning as XB acceptors. Mononegative tetrahedral oxyanions can be expected to develop as general and effective tectons in anion coordination and anion-templated assembly, and this last result proves the remarkable trustworthiness of the developed crystal engineering heuristic principles.

ASSOCIATED CONTENT

ⓢ **Supporting Information.** XRPD and IR of **3b**–**d**, check-CIF/PLATON report for **3b**–**h**, representation of (6,3) nets and their undulation, and single (6,3) rings containing tetra-*n*-butyl ammonium cations. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Gale, P. A.; Quesada, R. *Coord. Chem. Rev.* **2006**, *250*, 3219–3244.(b) Sessler, J. L.; Gale, P. A.; Cho, W. S. *Anion Receptor Chemistry*; RSC: Cambridge, 2006; (c) Keegan, J.; Kruger, P. E.; Nieuwenhuyzen, M.; O'Brien, J.; Martin, N. *Chem. Commun.* **2001**, 2192–2193.

(2) Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671–678.

(3) (a) Metrangolo, P.; Pilati, T.; Resnati, G. *CrystEngComm* **2006**, *8*, 946–947. (b) Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. *Acc. Chem. Res.* **2005**, *38*, 386–395. (c) Metrangolo, P.; Resnati, G. *Chem.—Eur. J.* **2001**, *7*, 2511–2519. (d) Metrangolo, P.; Pilati, T.; Resnati, G.; Stevenazzi, A. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 215–222. (e) Rissanen, K. *CrystEngComm* **2008**, *10*, 1107–1113.

(4) (a) Ghassemzadeh, M.; Harms, K.; Dehnicke, K. *Chem. Ber.* **1996**, *129*, 259–262. (b) Ghassemzadeh, M.; Harms, K.; Dehnicke, K. *Chem. Ber.* **1996**, *129*, 115–120. (c) Rosokha, S. V.; Neretin, I. S.; Rosokha, T. Y.; Hecht, J.; Kochi, J. K. *Heteroat. Chem.* **2006**, *17*, 449–459. (d) Haddad, S.; Awwadi, F.; Willett, R. D. *Cryst. Growth Des.* **2003**, *3*, 501–505. (e) Willett, R. D.; Awwadi, F.; Butcher, R.; Haddad, S.; Twamley, B. *Cryst. Growth Des.* **2003**, *3*, 301–311. (f) Awwadi, F. F.; Willett, R. D.; Twamley, B. *Cryst. Growth Des.* **2007**, *7*, 624–632. (g) Brammer, L.; Espallargas, G. M.; Adams, H. *CrystEngComm* **2003**, *5*, 343–345. (h) Espallargas, G. M.; Brammer, L.; Sherwood, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 435–440.

(5) Metrangolo, P.; Pilati, T.; Terraneo, G.; Biella, S.; Resnati, G. *CrystEngComm* **2009**, *11*, 1187–1196.

(6) (a) du Mont, W.-W.; Stenzel, V.; Jeske, J.; Jones, P. G.; Sebald, A.; Pohl, S.; Saak, W.; Batcher, M. *Inorg. Chem.* **1994**, *33*, 1502–1505. (b) Bock, H.; Holl, S. *Z. Naturforsch., B: Chem. Sci.* **2002**, *57*, 713–725. (c) Shirahata, T.; Kibune, M.; Maesato, M.; Kawashima, T.; Saito, G.; Imakubo, T. *J. Mater. Chem.* **2006**, *16*, 3381–3390. (d) Lindner, H. J.; Kitschke-von Gross, B. *Chem. Ber.* **1976**, *109*, 314–319. (e) Imakubo, T.; Shirahata, T.; Hervé, K.; Ouahab, L. *J. Mater. Chem.* **2006**, *16*, 162–173. (f) Yamamoto, H. M.; Kato, R. *Chem. Lett.* **2000**, 970–971. (g) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1973**, 2664–2669.

(7) (a) Brammer, L.; Espallargas, G. M.; Libri, S. *CrystEngComm* **2008**, *10*, 1712–1727. (b) Bertani, R.; Sgarbossa, P.; Venzo, A.; Lelj, F.; Amati, M.; Resnati, G.; Pilati, T.; Metrangolo, P.; Terraneo, G. *Coord. Chem. Rev.* **2010**, *254*, 677–695.

(8) Cavallo, G.; Metrangolo, P.; Pilati, T.; Resnati, G.; Sansotera, M.; Terraneo, G. *Chem. Soc. Rev.* **2010**, *39*, 3772–3783.

(9) (a) Jensen, T. B.; Scopelliti, R.; Bünzli, J. C. G. *Inorg. Chem.* **2006**, *45*, 7806–7814. (b) Han, X.; An, C.; Zhang, Z. *Appl. Organomet. Chem.* **2008**, *22*, 565–572. (c) Lü, Z.; Yuan, M.; Pan, F.; Gao, S.; Zhang, D.; Zhu, D. *Inorg. Chem.* **2006**, *45*, 3538–3548. (d) Pal, S.; Olmstead, M. M.; Armstrong, W. H. *Inorg. Chem.* **1995**, *34*, 4708–4715. (e) Usón, R.; Forniés, J.; Navarro, R.; Usón, M. A.; Garcia, M. P.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 345–350. (f) Song, R. F.; Xie, Y. B.; Li, J. R.; Bu, X. H. *Dalton Trans.* **2003**, 4742–4748. (g) Bhula, R.; Collier, S.; Robinson, W. T.; Weatherburn, D. C. *Inorg. Chem.* **1990**, *29*, 4027–4032. (h) Wong, E.; Liu, S.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1995**, *34*, 3057–3064. (i) Pal, S.; Olmstead, M. M.; Armstrong, W. H. *Inorg. Chem.* **1995**, *34*, 4708–4715. (j) Vicente, J.; Abad, J. A.; Clemente, R.; López-Serrano, J.; Ramírez de Arellano, M. C.; Jones, P. G.; Bautista, D. *Organometallics* **2003**, *22*, 4248–4259. (k) Abraham, D. J.; Rosenstein, R. D.; Pettit, G. R. *J. Med. Chem.* **1971**, *14*, 1141–1142. (l) Yu, X. Y.; Maekawa, M.; Morita, T.; Chang, H. C.; Kitagawa, S.; Jin, G. X. *Polyhedron* **2002**, *21*, 1613–1620. (m) Comba, P.; Fath, A.; Hambley, T. W.; Kühner, A.; Richens, D. T.; Vielfort, A. *Inorg. Chem.* **1998**, *37*, 4389–4401. (n) Guillemot, M.; Toupet, L.; Simonneaux, G. *Inorg. Chem.* **1996**, *35*, 6334–6336. (o) Shakya, R.; Peng, F.; Liu, J.; Heeg, M. J.; Verani, C. N. *Inorg. Chem.* **2006**, *45*, 6263–6268. (p) Sengottuvelan, N.; Saravanakumar, D.; Kandaswamy, M. *Inorg. Chem. Commun.* **2005**, *8*, 297–300. (q) Ferguson, G.; Lloyd, D.; McNab, H.; Marshall, D. R.; Ruhl, B. L.; Wieckowski, T. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1563–1568. (r) Reim, J.; Krebs, B. *J. Chem. Soc., Dalton Trans.* **1997**, 3793–3804. (s) Bermejo, M. R.; Castiñeiras, A.; Garcia-Monteagudo, J. C.; Rey, M.; Sousa, A.; Watkinson, M.; McAuliffe, C. A.; Pritchard, R. G.; Beddoes, R. L. *J. Chem. Soc., Dalton Trans.* **1996**, 2935–2944.

(10) To represent the connectivity of a certain net, the general symbol (*n*, *p*) is used, where *p* is the number of connections to neighboring nodes that radiate from any node or center, and *n* is the number if nodes in the smallest closed circuits within the net:Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494.

(11) (6,3) Networks are two-dimensional (2D) infinite nets common in organic supramolecular structures and hybrid metal organic coordination networks which have been synthesized through a variety of self-assembly protocols:(a) Liantonio, R.; Metrangolo, P.; Pilati, T.; Resnati, G. *Cryst. Growth Des.* **2003**, *3*, 355–361. (b) Liantonio, R.; Metrangolo, P.; Meyer, F.; Pilati, T.; Navarrini, W.; Resnati, G. *Chem. Commun.* **2006**, 1819–1821. (c) Metrangolo, P.; Meyer, F.; Pilati, T.; Resnati, G.; Terraneo *Chem. Commun.* **2008**, 1635–1637. (d) Barth, J. V.; Costantini, G.; Kern, K. *Nature* **2005**, *43*, 671–679. (e) Wang, Z.; Kravtsov, V. C.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 2877–2880. (f) Ahn, S.; Reddy, P.; Kariuki, B. M.; Chatterjee, S.; Ranganathan, A.; Pedireddi, V. R.; Rao, C. N. R.; Harris, K. D. M *Chem.—Eur. J.* **2005**, *11*, 2433–2439. (g) Bhogala, B. R.; Basavoju, S.; Nangia, A. *Cryst. Growth Des.* **2005**, *5*, 1683–1686. (h) Bushey, M. L.; Nguyen, T.-Q.; Zhang, W.; Horoszewski, D.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5446–5453. (i) Choi, H. J.; Lee, T. S.; Suh, M. P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1405–1408. (j) Staniec, P. A.; Perdigão, L. M. A.; Rogers, B. L.; Champness, N. R.; Beton, P. H. *J. Phys. Chem. C* **2007**, *111*, 886–893. (k) Perdigão, L. M. A.; Champness, N. R.; Beton, P. H. *Chem. Commun.* **2006**, 538–540.

(12) The XB-donor is the electrophilic halogen (Lewis acid) and the XB-acceptor is its nucleophilic partner (Lewis base).

(13) Lucassen, A. C. B.; Karten, A.; Leitus, G.; Shimon, L. J. W.; Martin, J. M. L.; Van der Boom, M. E. *Cryst. Growth Des.* **2007**, *7*, 386–392.

(14) Metrangolo, P.; Resnati, G. Tectons: Definition and Scope. In *Encyclopedia of Supramolecular Chemistry*; Marcel Dekker: New York, 2004; pp 1484−1492.

(15) (a) Cavallo, G.; Biella, S.; Lü, J.; Metrangolo, P.; Pilati, T.; Resnati, G.; Terraneo, G. *J. Fluorine Chem.* **2010**, *131*, 1165–1172. (b) Abate, A.; Brischetto, M.; Cavallo, G.; Lahtinen, M.; Metrangolo, P.; Pilati, T.; Radice, S.; Resnati, G.; Rissanen, K.; Terraneo, G. *Chem. Commun.* **2010**, *46*, 2724–2726. (c) Abate, A.; Biella, S.; Cavallo, G.; Meyer, F.; Neukirch, H.; Metrangolo, P.; Pilati, T.; Resnati, G.; Terraneo, G. *J. Fluorine Chem.* **2010**, *130*, 1171–1177. (d) Casnati, A.; Cavallo, G.; Metrangolo, P.; Resnati, G.; Ugozzoli, F.; Ungaro, R. *Chem.—Eur. J.* **2009**, *15*, 7903–7912. (e) Gattuso, G.; Notti, A.; Pappalardo, S.; Parisi, M. F.; Pilati, T.; Resnati, G.; Terraneo, G. *CrystEngComm* **2009**, *11*, 1204–1206. (f) Biella, S.; Gattuso, G.; Notti, A.; Metrangolo, P.; Pappalardo, S.; Parisi, M. F.; Pilati, T.; Resnati, G.; Terraneo, G. *Supramolecular Chem.* **2009**, *21*, 149–156. (g) Metrangolo, P.; Carcenac, Y.; Lahtinen, M.; Pilati, T.; Rissanen, K.; Vij, A.; Resnati, G. *Science* **2009**, *323*, 1461–1464. (h) Gattuso, G.; Pappalardo, A.; Parisi, M. F.; Pisagatti, I.; Crea, F.; Liantonio, R.; Metrangolo, P.; Navarrini, W.; Resnati, G.; Pilati, T.; Pappalardo, S. *Tetrahedron* **2007**, *63*, 4951–4958. (i) Casnati, A.; Liantonio, R.; Metrangolo, P.; Resnati, G.; Ungaro, R.; Ugozzoli, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 1915–1918. (j) Gattuso, G.; Liantonio, R.; Metrangolo, P.; Meyer, F.; Pappalardo, A.; Parisi, M. F.; Pilati, T.; Pisagatti, I.; Resnati, G. *Supramolecular Chem.* **2006**, *18*, 235–243. (k) Mele, A.; Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. *J. Am. Chem. Soc.* **2005**, *127*, 14972–14973. (l) Logothetis, T. A.; Meyer, F.; Metrangolo, P.; Pilati, T.; Resnati, G. *New. J. Chem.* **2004**, *28*, 760–763. (m) Farina, A.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G.; Vecchio, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2433–2436. Farina, A.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G; Vecchio, G. *Angew. Chem.* **1999**, *111*, 2585–2588.

(16) Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G.; Spagna, R. SIR2002: *J. Appl. Crystallogr.* **2003**, *36*, 1103.

(17) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(18) (a) Politzer, P.; Murray, J. S.; Concha, M. C. *J. Mol. Model.* **2008**, *14*, 659–665. (b) Politzer, P.; Murray, J. S.; Concha, M. C. *J. Mol. Model.* **2007**, *13*, 643–650. (c) Politzer, P.; Murray, J. S.; Lane, P. *Int. J. Quantum Chem.* **2007**, *107*, 3046–3052. (d) Riley, K. E.; Murray, J. S.; Politzer, P.; Concha, M. C.; Hobza, P. *J. Chem. Theor. Comput.* **2009**, *5*, 155–163. (e) Politzer, P.; Murray, J. S.; Clark, T. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7748–7757.