# Secondary bonding as a potential design element for crystal engineering

Letter

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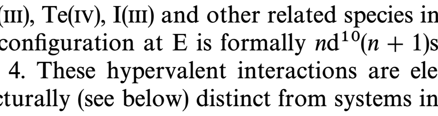
**Crystallographic data imply that intermolecular hypervalent interactions, "secondary bonds", involving heavy p-block elements such as Bi(III), may form robust supramolecular synthons with many features in common with organic hydrogen bonds, including the ability to form polymeric networks in the solid state.**

The synthesis of crystalline solids in which molecular units are arranged in predictable ways—crystal engineering—is a major and a realistic goal for modern chemistry.[1] One means to this end is the identification and application of reliable supramolecular synthons,[2] which control molecular aggregation and lead to crystal structures with at least partly controlled structures, containing sheets, ribbons and other desired motifs. The synthons identified and exploited to date[1–3] have been for the most part taken from organic and biological chemistry and use the directionality of hydrogen bonds to afford the desired control of aggregation. There is a clear need for alternatives to this strategy in order to afford chemical and functional diversity in these solids. Among the areas most profitably explored in this context is that of dative coordinate bonded networks, usually of the late d-block elements (Groups 9–12, see, for example, the work of Robson, Ciani, Iwamoto, Schröder, Zaworotko and others).[4] In this paper we show that secondary bonding,[5] that is, intermolecular hypervalent interactions, has many structural features in common with the hydrogen bond and may afford a reliable new class of supramolecular synthon.

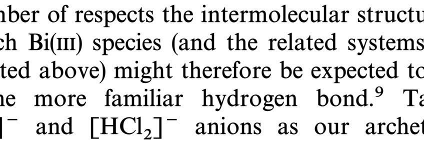
In 1972 Alcock defined secondary bonding in a seminal paper[5a] as involving intermolecular hypervalent interactions of length less than the sum of van der Waals radii between a heavy p-block element (E, say) and an electron pair donor (typically halogen, O, N or S). Such secondary bonding is ubiquitous in the solid state chemistry of the compounds of Pb(II), Bi(III), Te(IV), I(III) and other related species in which the electron configuration at E is formally $nd^{10}(n+1)s^2(n+1)p^x$, $x = 0, 2, 4$. These hypervalent interactions are electronically and structurally (see below) distinct from systems in which the Lewis acid centre has no lone pair [*e.g.*, in aluminium(III) or antimony(V) complexes]. To date there has been no systematic attempt to exploit secondary bonding in the design of crystal structures (but see reference 6 for examples in iodine chemistry).

The description of the hypervalent interactions involved in secondary bonding has attracted controversy and interest for much of the past 40 years. The current consensus is that the best simple bonding model treats such interactions as involving delocalised 3c-4e σ bonds.[7] An archetypal example of such an interaction is the $[BiCl_2Ph_2]^-$ anion[8] {which is formally and practically obtained by addition of $Cl^-$ to the Bi(III) $[5d^{10}6s^2]$ centre in $BiClPh_2$, see Scheme 1}. Here the second Bi–Cl bond is formed *trans* to the Bi–Cl bond in pyramidal $BiClPh_2$, leading to the familiar disphenoidal (equatorially vacant trigonal bipyramidal) $C_{2v}$ symmetric geometry of $[BiCl_2Ph_2]^-$. In this case the Lewis base ($Cl^-$) donates an electron pair into a Bi–Cl σ* orbital, thereby forming the 3c-4e interaction, and a linear or near-linear Cl–Bi–Cl moiety. Many similar species are formed in Bi(III) chemistry [and related systems based on Pb(II), Sb(III), Te(IV), I(III), *etc*.]. Most frequently the σ* orbital is associated with an E–X bond involving an electronegative substituent X [X = halide, alkoxide or other oxygen ligand, *etc*., see Scheme 2(*a*) and 2(*b*)] since this lowers the energy of the σ* orbital, ensures it is mainly bismuth-centred and that the bismuth is more positively charged. In many cases of secondary bonding the incoming Lewis base is the electronegative atom X in an adjacent molecule and the interaction leads to the formation of polymeric or oligomeric structures.



**Scheme 1** Formation of $[BiCl_2Ph_2]^-$ from $BiClPh_2$ and $Cl^-$.

In a number of respects the intermolecular structural chemistry of such Bi(III) species (and the related systems from the p-block noted above) might therefore be expected to resemble that of the more familiar hydrogen bond.[9] Taking the $[BiCl_2Ph_2]^-$ and $[HCl_2]^-$ anions as our archetypes, the replacement of $H^+$ by $[BiPh_2]^+$ (for example) should yield systems with similar structural properties. The similarities in the distribution of angles at hydrogen in O–H···O hydrogen bonds and the Cl–Bi···Cl angles in *trans*-Bi(III)$Cl_2$ fragments [see Scheme 2(*c*); Fig. 1]† is striking. Despite the differences in the details of the 3c-4e bonding[7] in these systems the preference for linearity at the central atom is clear. The bond length variability in O–H···O bonds is familiar from many neutron diffraction studies and is illustrated in Fig. 2(*a*). The two O–H distances are coupled and follow a well-defined hyperbolic curve.[10,11] The corresponding plot for the *trans*-Bi(III)$Cl_2$ system [Fig. 2(*b*)] shows some resemblance in having many points around a similarly curved trajectory. It is noteworthy that similar plots for other Bi(III) and Sb(III) dihalides have essentially identical forms, while those for Sb(V) dihalides have points only very near the symmetrical ($d_1 = d_2$) geometry.[7b,8] The Cl–Bi···Cl plot shows much more scatter perpendicular to the ideal hyperbolic path and somewhat more concentration of points near the symmetrical ($d_1 = d_2$) geometry than



**Scheme 2** (*a*) $BiXZ_2$ moiety (X = uninegative electronegative substituent, Z = X or R, R = uninegative less electronegative substituent. (*b*) Bi–X σ* orbital. (*c*) *trans*-$BiCl_2$ fragment.

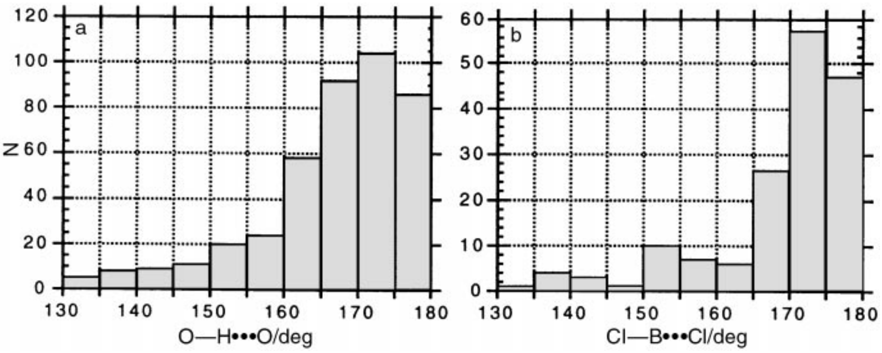


**Fig. 1** Histograms of angles (deg) in (*a*) O–H···O and (*b*) Cl–Bi···Cl 3c-4e systems in the CSD.‡

the O–H···O plot. The former difference may be ascribed to the presence of (and variation in) substituents on the central atom (Bi) *cis* to the 3c-4e system, which are of course not present in the O–H···O hydrogen bonds. We have commented on the mechanisms by which *cis* substituents interact with the geometry of the $BiCl_2$ moiety.[12] Analysis of the second aspect will be addressed in a full paper, but surely relates to the difference in the 3c-4e bonding in the two systems. The third way in which the O–H···O and Cl–Bi···Cl plots differ is metric; the Bi–Cl bonds are much longer (*ca.* 2.7 Å for the symmetrical species, *cf.* *ca.* 1.2 Å for O–H in symmetrical O–H–O bonds).

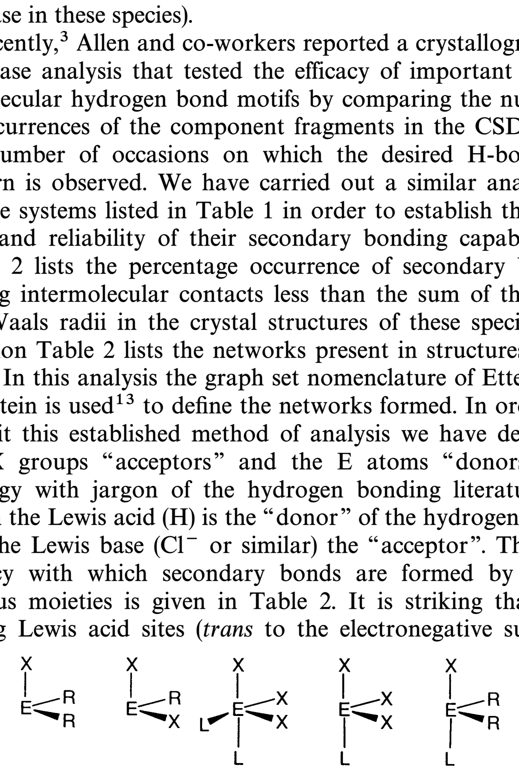
The pyramidal shape of $BiX_3$ and $SbX_3$ molecules and their derivatives and the model given above for hypervalent bonding in these systems allow qualitative predictions of the likely secondary bonding motifs in the solid state structures of such species. A selection of relatively common bismuth or antimony species for which such predictions may be made is given in Table 1. In these species the formula is given by $EX_xR_{3-x}L_y$ (Scheme 3) where E = Sb or Bi; X, as above, is a uninegative ligand with an electronegative contact atom (*e.g.*, halide), R is a uninegative ligand with a less electronegative contact atom (*e.g.*, aryl), and L is a 2e donor ligand (*e.g.*, pyridine, THF, $Cl^-$). Therefore, the coordination number at E is given by $n = 3 + y$; the number of strong Lewis acid sites at E is given by $N_s = x - y$, while there are $N_w$ weak acceptor sites *trans* to the R substituents (assuming the maximum coordination number for E to be 6 as is usually but not universally the case in these species).

**Table 1** Secondary bonding capabilities of bismuth(III) and antimony(III) moieties

| Moiety[a] | $n$[b] | $x$[b] | $y$[b] | $N_s$[c] | $N_w$[c] |
|---|---|---|---|---|---|
| $ER_2X$ | 3 | 1 | 0 | 1 | 2 |
| $ERX_2$ | 3 | 2 | 0 | 2 | 1 |
| $EX_3L_2$ | 5 | 3 | 2 | 1 | 0 |
| $EX_3L$ | 4 | 3 | 1 | 2 | 0 |
| $ER_2XL$ | 4 | 1 | 1 | 0 | 2 |

[a] Moiety formula: E = Sb, Bi; X = halide, alkoxide, *etc.*; L = 2e donor ligand, including cases where $L = X^-$; R = alkyl, aryl, *etc.* [b] $n$ = coordination number of E; $x$ = number of substitutents X; $y$ = number of ligands L. [c] $N_s$ and $N_w$ are the number of strong and weak secondary bonding sites at E, respectively.

Recently,[3] Allen and co-workers reported a crystallographic database analysis that tested the efficacy of important cyclic bimolecular hydrogen bond motifs by comparing the number of occurrences of the component fragments in the CSD with the number of occasions on which the desired H-bonding pattern is observed. We have carried out a similar analysis‡ for the systems listed in Table 1 in order to establish the efficacy and reliability of their secondary bonding capabilities. Table 2 lists the percentage occurrence of secondary bonds having intermolecular contacts less than the sum of the van der Waals radii in the crystal structures of these species. In addition Table 2 lists the networks present in structures they form. In this analysis the graph set nomenclature of Etter and Bernstein is used[13] to define the networks formed. In order to exploit this established method of analysis we have denoted the X groups "acceptors" and the E atoms "donors" by analogy with jargon of the hydrogen bonding literature in which the Lewis acid (H) is the "donor" of the hydrogen bond and the Lewis base ($Cl^-$ or similar) the "acceptor". The frequency with which secondary bonds are formed by these various moieties is given in Table 2. It is striking that the strong Lewis acid sites (*trans* to the electronegative substit-



**Scheme 3** Molecular species for which secondary bonding has been studied [E = Sb(III) or Bi(III)] (see Table 1).

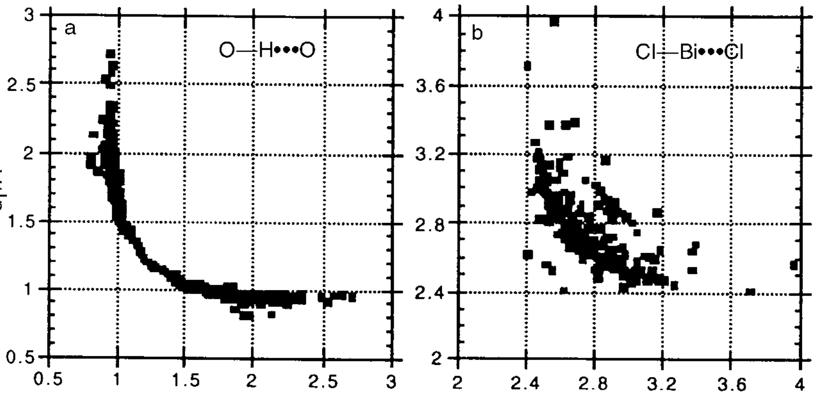


**Fig. 2** Scattergrams of bond lengths (Å) in (*a*) O–H···O and (*b*) Cl–Bi···Cl 3c-4e systems in the CSD.‡

**Table 2** Secondary bonding interactions in bismuth(III) and antimony(III) structures‡

| Moiety | $n$(CSD)[a] | $n$(frag)[b] | $N_s$ | $F_s$[c] | $N_w$ | $F_w$[c] | Network family[d] |
|---|---|---|---|---|---|---|---|
| $ER_2X$ | 18 | 24 | 1 | 71 | 2 | 8 | 44% C(2); 11% $R_3^3(6)$ |
| $ERX_2$ | 20 | 21 | 2 | 81 | 1 | 19 | 50% C(2) |
| $EX_3L_2$ | 67 | 75 | 1 | 85 | 0 | — | 39% C(2); 39% $R_2^2(4)$ |
| $EX_3L$ | 60 | 90 | 2 | 85 | 0 | — | 40% C(2); 18% $R_2^2(4)$ |
| $ER_2XL$ | 27 | 28 | 0 | — | 2 | 18 | — |

[a] Number of unique crystal structures located from the CSD. [b] Number of unique moieties located from the CSD. [c] Percentage of possible secondary bonds actually formed. [d] Family to which graph set[13] of secondary bond network belongs.

uents, X) are consistently involved in secondary interactions at a frequency of between 70 and 90%. This contrasts with frequencies of <20% for the weaker secondary bonding sites. The marked difference is therefore in accord with the postulate that the electronegativity of the *trans* substituent is a major determinant in the likelihood and strength of secondary bond formation. This parallels the familiar[9] influence of the electronegativity of the element to which a hydrogen atom is bonded on the strength of the hydrogen bonds it forms. The high frequency of secondary bond formation in the "strong" Lewis acid sites implies that such sites have considerable potential as components of robust supramolecular synthons; that is, they can be relied upon to form secondary bonds. The predominant mode of association in these species is that in which chains of molecules are formed (see Table 2), albeit by a variety of specific networks in which considerable complexity may be present. Rings are also formed in a substantial number of cases. For example, in the structures of $[BiCl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$[14] and $[BiCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$[15] (*i.e.*, structures of type $ER_2X$) polymeric [C(2)] and ring [$R_n^n(2n)$ ($n = 3$)] structures are observed in which secondary bonds with near linear Cl–Bi···Cl moieties form the links between the molecular units (see Scheme 4). It is noteworthy that in an analogous class of organic crystals of molecules with exactly one hydrogen bond donor and one hydrogen bond acceptor (the monoalcohols) Brock and Duncan have shown[16] that unusual space groups are often encountered and that in many cases $R_n^n(2n)$ ($n = 4$, 6) ring and C(2) chain networks are formed. The same classes of network occur in the category of Bi(III) species with exactly one Lewis acid site and one available secondary bond acceptor (the $ER_2X$ set).

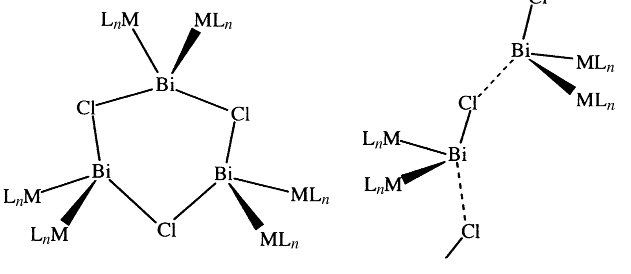
Previously we have shown that the networks formed by these species in the solid state may be disrupted by dissolution in Lewis basic solvents such as THF.[12] In this respect again there is an analogy with the behaviour of H-bonded solids in which the intermolecular H-bonds are frequently lost on dissolving in strongly hydrogen bonding solvents such as water.

In summary hydrogen bonds and secondary bonds have the following similarities

(*a*) The preference for linearity at the central atom in 3c-4e interactions

(*b*) The softness of the bond lengths in the 3c-4e interactions

(*c*) The formation of solid state networks of these interactions, describable by graph set nomenclature.



**Scheme 4** Typical (*a*) $R_3^3(6)$ ring and (*b*) C(2) chain networks formed by $ER_2X$ species.

(*d*) The disruption of these networks in solution.

(*e*) The percentages of intermolecular interactions formed are high for the stronger Lewis acid sites.

In other respects the two classes of intermolecular bond do differ, as listed below.

(*a*) The metric. E···X bonds are typically about twice as long as comparable X···H contacts

(*b*) The variability of E···X bond lengths. In particular, there is less strong coupling between the two lengths.

In hydrogen bonding, bifurcated bonds in which the hydrogen interacts with two acceptors, are relatively common if often difficult to predict or control. Similar interactions are possible in secondary bonding systems [*e.g.*, for cases in which the E centre is >6 coordinate, as in $BiCl_3(THF)_2$[17]]. However, more significant "bifurcation" or branching of the intermolecular bond network is possible in this class of supramolecular synthon because of the ability of the Lewis acidic E centre to be simultaneously involved in two or even three 3c-4e interactions in approximately perpendicular directions. This and the other properties noted above may offer new opportunities for the preparation of novel solids based on secondary bonding with characteristics that complement those currently available. It is noteworthy that the work of Mitzi and others[18] has already demonstrated the potentially important properties that such solids might possess.

## Acknowledgements

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## Notes and references

† Data for relevant structures (neutron diffraction studies only for O–H···O hydrogen bonds) were retrieved from the CSD[19] and bond lengths and angles calculated. The data sets for Figs. 1 and 2 were permuted[10] to reflect the symmetry of the potential energy hypersurface for the reaction path in question.

‡ Data for relevant structures were retrieved from the CSD[19] and bond lengths and angles calculated. Intermolecular contacts involving E shorter than the sum of the van der Waals radii[20] were recorded as being secondary bonds and the networks and frequencies computed accordingly.

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