Halogen-bonded assembly of hybrid inorganic/organic 3D-networks from dibromocuprate salts and tetrabromomethane†

Sergiy V. Rosokha, Jianjiang Lu, Tetyana Y. Rosokha and Jay K. Kochi*

Received (in Austin, TX, USA) 17th April 2007, Accepted 18th May 2007
First published as an Advance Article on the web 18th June 2007
DOI: 10.1039/b705882a

The critical halogen-bonding motif (CBr···BrCu) is responsible for the successful synthesis of three-dimensional networks of unusual 4,5-connected dodecahedron cells (each containing the encapsulated cation) *via* the self-assembly of tetra-*n*-propylammonium dibromocuprate(I) and tetrabromomethane as prototypical donor/acceptor dyads.

The intermolecular interactions of halogen acceptors with various electron donors (commonly referred to as halogen bonding[1,2]) have recently appeared as a powerful method for the supramolecular design of nonlinear optical materials, pharmaceutical drugs, chiral resolution, control of solid-state reactivity, *etc.*[2–5] Previous studies on halogen bonding have for the most part concentrated on organic systems.[2–5] On the other hand, the use of such non-covalent interactions for crystal engineering of hybrid networks consisting of organic molecules and transition-metal complexes[6,7] has also attracted attention for a variety of solid-state applications. However, such studies have focused heretofore on short halogen···halide contacts between oppositely charged ions[8] or intermolecular contacts between halides and halogen-substituted ligands coordinated to the same metal ion.[9] As a result, their crystalline compositions are largely determined by traditional coordination chemistry as well as by the charge balance within a single transition-metal complex—and halogen-bonding merely contributed to the details of the crystal structure.

In our search for *bona fide* hybrid networks based on the halogen bonding of independent organic and inorganic units (*i.e.*, those without other covalent/coordination links or coulombic attractions between halogen-bonded components), we now turn to the interaction of tetrabromomethane with various transition-metal halide complexes. Such a choice is based on: (i) earlier data on the long-distance bonding of bromocarbon acceptors with halide donors (Cl^-, Br^-, I^-) leading to the formation of 1 : 1 complexes in solution and diamondoid or honeycomb networks in the solid state,[3,8] and (ii) previous observations of short halide···halogen contacts in crystals of tetrahalometallates.[9,10] In this study, the crystallization of equimolar amounts of CBr_4 and $n\text{-}Pr_4N^+CuBr_2^-$ from dichloromethane solution resulted in the formation of colourless crystals **I** containing both components in 1 : 1 stoichiometry. Contrastingly, a similar solution but containing a large excess of tetrabromomethane resulted in the formation of pale yellow crystals **II** with 2 : 1 stoichiometry(see ESI†).

X-Ray crystallography of **I** shows the unit cell in space group $P\bar{1}$,‡ with the asymmetric unit containing tetrabromomethane, two crystallographically independent halves of the linear dibromocuprate anion, and the tetrapropylammonium cation (see ORTEP diagram in Fig. S1 in ESI†). Further consideration of this structure reveals multiple halogen-bonding CBr···BrCu contacts of 3.3–3.5 Å (as compared to the sum of the van der Waals radii of 3.7 Å[11]), with each tetrahedral CBr_4 being coordinated to four linear $CuBr_2^-$ anions, and, in turn, each dibromocuprate showing shortened $Br\cdots Br^-$ contacts (two per bromide) with four tetrabromomethane moieties. While the geometries of the bromine···bromide contacts are somewhat different for the two crystallographically independent copper(I) complexes (see Table S1 in ESI†), these separations, as well as the corresponding C–Br···Br angles of 158–178°, lie in the range characteristic of halogen bonding.[9,10,12] Most importantly, such multiple (4 × 4) halogen bondings between tetrabromomethane and dibromocuprate lead to the formation of the three-dimensional network shown in Fig. 1 with the channels occupied by tetra-*n*-propylammonium counterions.

By way of contrast, the unit cell of crystal **II** (space group $P2_1/c$) contains one linear dibromocuprate complex (with its Pr_4N^+ counterion) together with two molecules of tetrabromomethane. Each bromine of CBr_4 shows the same close CBr···BrCu separations of 3.40 ± 0.05 Å as those found in **I**, and the corresponding C–Br···Br angles are 174 ± 5° (Table S1 in ESI†). In turn, each dibromocuprate anion coordinates eight CBr_4 *via* four short $Br\cdots Br^-$ contacts at each bromide site, in accord with

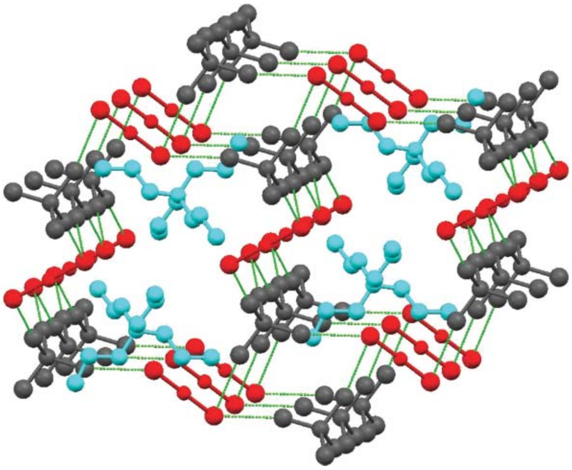

Fig. 1 Hybrid network of **I** formed by halogen bonding (green lines) between CBr_4 (grey) and $CuBr_2^-$ (red) and containing Pr_4N^+ counter-ions (light blue) in the channels. Hydrogen atoms omitted for clarity.

Department of Chemistry, University of Houston, Houston, TX, 77204, USA. E-mail: jkochi@uh.edu; Fax: 713-743-2709; Tel: 713-743-3293

† Electronic supplementary information (ESI) available: ORTEP diagrams for **I**, **II** and $NMe_4^+Cu_2Br_3^-$, geometry of halogen bonding in **I** and **II**. See DOI: 10.1039/b705882a

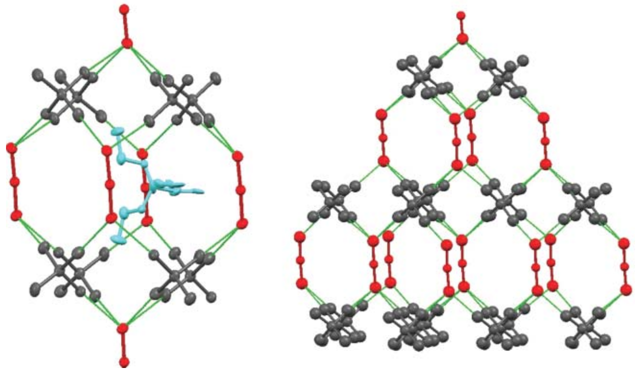

Fig. 2 Left: ORTEP diagram of the elongated dodecahedron cell of **II** resulting from halogen bonding (green lines) between CBr_4 (grey) and $CuBr_2^-$ (red) shown with a tetra-*n*-propylammonium cation (light blue) encapsulated within each cavity. Right: 3D-network of the $CuBr_2^-/CBr_4$ assembly shown without the counter-cation for clarity.

the 2 : 1 stoichiometry. Such bromine···bromide interactions (green lines in Fig. 2) result in the formation of the unusual 3D-network in which each of the elongated (rhombic) dodecahedron cells is occupied by a single tetra-*n*-propylammonium counterion (light blue in left figure).

The elongated dodecahedron in Fig. 2(left) contains both 4- and 5-connected nodes (with close to tetrahedral and square-pyramidal arrangements in 1 : 1 ratios) to form eight rhombic polygons and four equilateral hexagons; and it represents one of five unique convex space-filling primary parallelohedra.[13] Similar **tcs** nets (this acronym is made with reference to $ThCr_2Si_2$)[14] with every 4-node (circuit symbol 4^46^2) connected to four 5-nodes, and every 5-node (circuit symbol 4^46^6) connected to four 4-nodes and one 5-node, are well-known in inorganic alloys,[15] and have been documented mathematically.[13] However, such nets are unknown (to our knowledge) with molecular building units[16] since the latter is related to difficulties inherent to generating 5-connected nodes in a square pyramidal geometric arrangement. Compound **II** satisfies such a requirement because each tetrabromomethane represents the 4-connected node and each bromide of the linear ($CuBr_2^-$) spacer serves as the 5-connected node. While the highest symmetry of the **tcs** net shown in Fig. 3 (with equivalent edges and all polygonal atoms in the same plane) is tetragonal, the symmetry of **II** is lower because this dodecahedron has somewhat different edges (C–Br···Br of 5.2 Å and Br–Cu–Br of 4.4 Å), and the hexagons are tilted slightly from the plane and exhibit minor chair conformations.

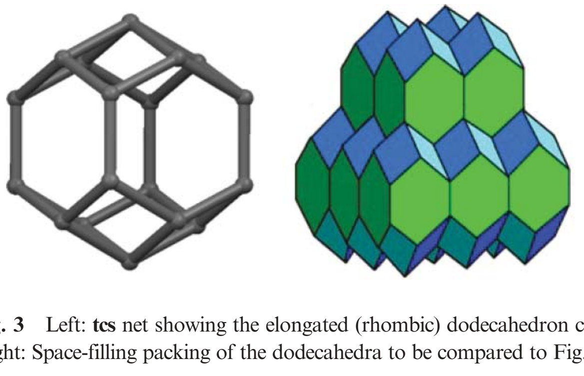

Fig. 3 Left: **tcs** net showing the elongated (rhombic) dodecahedron cell. Right: Space-filling packing of the dodecahedra to be compared to Fig. 2.

The CBr···BrCu separations of 3.3–3.5 Å that are characteristic of the halogen bond in crystals **I** and **II** are somewhat greater than the values of 3.15–3.35 Å measured in various three- and two-dimensional networks formed by the tetrabromomethane acceptor with a simple bromide-anion donor.[3] In addition, the electronic absorption at $\lambda > 250$ nm of ($CBr_4/CuBr_2^-$) solutions represents the superposition of the spectra of the components—in contrast to the distinct charge-transfer band at 290 nm found in similar systems containing only a single Br^- donor.[3] Such differences are readily attributed to the weakening of the donor properties of the latter upon coordination to the positive Cu(I) ion that leads to the blue shift of the corresponding charge-transfer band to $\lambda < 250$ nm (where it is overshadowed by the absorption of the components) and lengthening of the $Br \cdots Br^-$ distance. [The same effects were observed earlier in bromocarbon/bromide systems upon replacement of CBr_4 with the weaker $CHBr_3$ acceptor[8]]. The coordination to M = Cu^{II}, Co^{II}, Ni^{II} or Fe^{II} ions further decreases the donor abilities of bromide, so that the halogen bondings in the combinations of these MBr_4^{2-} with CBr_4 become even weaker. Thus, the earlier observation of halogen bonding with these complexes was facilitated by crystallization induced by charge balance and electrostatic attraction;[9,10] but without such an additional electrostatic support we isolated only the separate reactants from mixtures of $(Alk_4N^+)_2MBr_4^{2-}$ and CBr_4. In the case of $(Pr_4N^+)_2Cu^{II}Br_4^{2-}$ and CBr_4, the partial reduction of Cu^{II} and the co-crystallizations of the reduced **I** and **II** were observed.

It is particularly important to note the unique templating role of the tetra-*n*-propylammonium counter-cation in the formation of tetrabromomethane/dibromocuprate networks. Indeed, the oblate cell cavity comprising the elongated dodecahedron of **II** is just sufficient (~ 850 Å^3) to accommodate the quasi-spherical tetra-*n*-propylammonium counterion (diameter $d \sim 12$ Å). Thus, crystallization with other alkylammonium counterions merely resulted in the separation of either the pure components or the CBr_4/Br^- network.[3] For example, crystallization from solutions of CBr_4 with the smaller $Me_4N^+Cu^IBr_2^-$ afforded single crystals showing $[Cu_2Br_3]^-$ ion as an infinite double chain of edge-sharing Cu(I)–Br tetrahedra with tetramethylammonium cations filling the void between these rods (see Fig. S3 in ESI†). Likewise, crystallization from CBr_4–$Et_4N^+CuBr_2^-$ solutions afforded the previously reported (halide-bonded) $Et_4N^+Br^-/CBr_4$ network.[3] Moreover, the larger $Bu_4N^+CuBr_2^-$ and CBr_4 led to separation of only $Bu_4N^+CuBr_2^-$ crystals,[17] but neither **I** nor **II** was evident.

We conclude that the acceptor ability of tetrabromomethane combined with the moderate weakening of the donor ability of the bromide anion upon coordination to copper(I) ion is the special combination that allows halogen bonding to be sufficiently strong to support the hybrid network between these (otherwise independent) organic and inorganic components. While the nature and principal components (electrostatics, charge-transfer, *etc.*) that determine the geometry and strength of halogen bonding[8–10,12] requires further refinement, the combination of strong donor/acceptor interactions in halogen-containing pairs, as shown in this study, provides a viable opportunity to design other hybrid organic/inorganic frameworks, and these are under current study in our laboratory. Furthermore, this work provides insight into the synthetic strategy (involving the use of a linear spacer and a tetrahedral node that can interact in a 1 : 2 ratio with an appropriate template) for the preparation of other unusual (4,5)-connected networks composed of elongated rhombic dodecahedra.

We thank the R. A. Welch Foundation and National Science Foundation for financial support.

Notes and references

‡ *Crystallization* of **I** and **II**. The colorless crystalline $Pr_4N^+CuBr_2^-$ salt was prepared by dissolving equimolar quantities of CuBr and $Pr_4N^+Br^-$ in dichloromethane, followed by solvent evaporation and recrystallization of the residue from ethyl acetate.[17] To prepare pure **I**, a mixture of 40 mg of CBr_4 and 40 mg of $Pr_4N^+CuBr_2^-$ in a 1.2 : 1 molar ratio was dissolved in 3 ml of dichloromethane, and 0.3 ml of hexane was added. The slow evaporation of the clear solution (during several days) resulted in the separation of colourless crystals **I** with 1 : 1 CBr_4 : $Pr_4N^+CuBr_2^-$ stoichiometry. Similar crystallization with a large excess of tetrabromomethane (160 mg CBr_4 and 40 mg of $Pr_4N^+CuBr_2^-$ in 5 : 1 molar ratio) resulted in the separation of pale yellow crystals **II** with the 2 : 1 CBr_4 : $Pr_4N^+CuBr_2^-$ stoichiometry (together with amorphous CBr_4). Intensity data were collected with aid of a Bruker SMART Apex diffractometer equipped with a CCD detector, and the structures were solved by direct methods and refined by full matrix least-squares procedure as described earlier.[8]

Crystal data: $Pr_4N^+CuBr_2^-\cdot CBr_4$ **I**: $C_{13}H_{28}Br_6CuN$, $M = 741.36$, triclinic, space group $P\bar{1}$, $a = 8.298(14)$, $b = 10.536(16)$, $c = 13.75(3)$ Å, $\alpha = 92.04(6)$, $\beta = 103.73(7)$, $\gamma = 97.26(5)°$, $V = 1156(3)$ Å^3, $Z = 2$, $D_c = 2.130$ g cm^{-3}, $T = 173$ K, reflections collected/unique: 18040/6814, $R1 = 0.0429$, $wR2 = 0.1070$ for 4806 reflections ($I > 2\sigma$).

$Pr_4N^+CuBr_2^-\cdot 2CBr_4$ **II**: $C_7H_{14}Br_5Cu_{0.5}N_{0.5}$, $M = 536.51$, monoclinic, space group $P2_1/c$, $a = 12.022(4)$, $b = 12.703(4)$, $c = 19.990(7)$ Å, $\beta = 102.994(8)°$, $V = 2974.7(17)$ Å^3, $Z = 8$, $D_c = 2.396$ g cm^{-3}, $T = 173$ K, reflections collected/unique: 22201/4465, $R1 = 0.0425$, $wR2 = 0.0872$ for 2416 reflections ($I > 2\sigma$).

CCDC 644447–644449. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b705882a

1 A. C. Legon, *Angew. Chem., Int. Ed.*, 1999, **38**, 2687.

2 P. Metrangolo and G. Resnati, *Chem.–Eur. J.*, 2001, **7**, 2511; P. Metrangolo, H. Neukirch, T. Pilati and G. Resnati, *Acc. Chem. Res.*, 2005, **38**, 386.

3 S. V. Lindeman, J. Hecht and J. K. Kochi, *J. Am. Chem. Soc.*, 2003, **125**, 11597.

4 A. Farina, S. V. Meille, M. T. Messina, P. Metrangolo, G. Resnati and G. Vecchio, *Angew. Chem., Int. Ed.*, 1999, **38**, 2433; T. Caronna, R. Liantonio, T. Logothetis, P. Metrangolo, T. Pilati and G. Resnati, *J. Am. Chem. Soc.*, 2004, **126**, 4500; E. Cariati, A. Forni, S. Biella, P. Metrangolo, F. Meyer, G. Resnati, S. Righetto, E. Torbin and R. Ugo, *Chem. Commun.*, 2007, DOI: 10.1039/b702724a.

5 A. Crihfield, J. Hartwell, D. Phelps, R. B. Walsh, J. L. Harris, J. F. Payne, W. T. Pennington and T. W. Hanks, *Cryst. Growth Des.*, 2003, **3**, 313; H. L. Nguyen, P. N. Horton, M. B. Hursthouse, A. C. Legon and D. W. Bruce, *J. Am. Chem. Soc.*, 2004, **126**, 16.

6 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; A. P. Wight and M. E. Davis, *Chem. Rev.*, 2002, **102**, 13589.

7 J. Jia, X. Lin, C. Wilson, A. J. Blake, N. R. Champness, P. Hubberstey, G. Walker, E. J. Cussen and M. Schroeder, *Chem. Commun.*, 2007, 840; M. Du, Z. H. Zhang, L. F. Tang, X. G. Wang, X. J. Zhao and S. R. Batten, *Chem.–Eur. J.*, 2007, **13**, 2578; S. M. Hawxwell, G. M. Espallargas, D. Bradshaw, M. J. Rosseinsky, T. J. Prior, A. J. Florence, J. van de Streek and L. Brammer, *Chem. Commun.*, 2007, 1532.

8 S. V. Rosokha, I. S. Neretin, T. Y. Rosokha, J. Hecht and J. K. Kochi, *Heteroat. Chem.*, 2006, **17**, 449.

9 R. D. Willett, F. F. Awwadi, R. Butcher, S. Haddad and B. Twamley, *Cryst. Growth Des.*, 2003, **3**, 301; G. M. Espallargas, L. Brammer and P. Sherwood, *Angew. Chem., Int. Ed.*, 2006, **45**, 435.

10 F. Zordan, L. Brammer and P. Sherwood, *J. Am. Chem. Soc.*, 2005, **127**, 5979; B. J. Prince, M. M. Turnbull and R. D. Willett, *J. Coord. Chem.*, 2003, **56**, 441.

11 A. J. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

12 F. F. Awwadi, R. D. Willett, K. A. Peterson and B. Twamley, *J. Phys. Chem. A*, 2007, **111**, 2319.

13 H. Steinhaus, *Mathematical Snapshots*, Dover, New York, 3rd edn, 1999, pp. 185–207. Compare also: H. S. M. Coxeter, *Regular Polytopes*, Dover, New York, 1973; E. W. Weisstein, Space-Filling Polyhedron, from *MathWorld–A Wolfram Web Resource* (http://mathworld.wolfram.com/Space-FillingPolyhedron.html).

14 For **tcs** net, see: http://rcsr.anu.edu.au/.

15 H. Nyman and S. Andersson, *Acta Crystallogr., Sect. A*, 1979, **35**, 305; W. B. Pearson, *J. Solid State Chem.*, 1985, **56**, 278; A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, London, 1962.

16 But for examples of some other convex space-filling polyhedra, see: O. Delgado-Friedrichs and M. O'Keeffe, *Acta Crystallogr., Sect. A*, 2006, **61**, 358–362; M. O'Keeffe, *Acta Crystallogr., Sect. A*, 1998, **54**, 320–329; S. Lidin, T. Popp, M. Somer and H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 924–927; J. Lu, A. Mondal, B. Moulton and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2001, **40**, 2113.

17 M. Asplund, S. Jagner and M. Nilsson, *Acta Chem. Scand., Ser. A*, 1983, **37**, 57.