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First example of an infinite polybromide 2D-network†

M. Carla Aragoni,[a] Massimiliano Arca,*[a] Francesco A. Devillanova,*[a] Francesco Isaia,[a] Vito Lippolis,[a] Annalisa Mancini,[a] Luca Pala,[a] Alexandra M. Z. Slawin[b] and J. Derek Woollins[b]

[a] *Dipartimento di Chimica Inorganica ed Analitica, S.S. 554 bivio per Sestu, 09042 Monserrato, Cagliari, Italy. E-mail: marca@unica.it; Fax: +39 070 675 4456; Tel: +39 070 675 4483*

[b] *School of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY16 9ST*

Received (in Cambridge, UK) 17th June 2003, Accepted 8th July 2003
First published as an Advance Article on the web 28th July 2003

The reaction of the neutral dithiolene $[Pd(Et_2timdt)_2]$ (Et_2timdt = formally monoreduced diethylimidazolidine-2,4,5-trithione) with an excess of Br_2 yielded few crystals of $[\mathbf{1}^{Et}\cdot 2Br]^{2+}(Br^-)_2(Br_2)_3$ as a by-product ($\mathbf{1}^{Et}$ = 4,5,9,10-tetrathiocino-[1,2-*b*:5,6-*b′*]-1,3,6,8-tetraethyl-diimidazolyl-2,7-dithione); X-ray diffraction analysis showed that this compound represents the first example of a polybromide 2D-network templated by $[\mathbf{1}^{Et}\cdot 2Br]^{+2}$ dications, and featuring all the Br–Br distances shorter than those found in solid state bromine.

Lewis acid acceptor halogen molecules X_2 and Lewis base halides X^- (X = Cl, Br, I) are fundamental "building blocks" of polyhalides of different shape and complexity. However, the tendency of halides to catenate, very high in the case of iodine, decreases on passing to bromine and chlorine. As a consequence, a great number of discrete polyiodides, with general formula I^{n-}_{2m+n} ($n, m > 0$), such as I_4^{2-}, I_5^-, I_7^-, up to I_{29}^{3-}, have been characterized structurally.[1,2] These are generally based on I^-, I_2, and I_3^- subunits interacting through I···I contacts ranging from 2.9 to 3.6 Å. The aggregation of discrete polyiodides of this type through contacts longer than 3.6 Å up to the sum of iodine van der Waals radii (4.2 Å) can generate very intricate infinite three-dimensional networks.[3,4] Discrete large polybromides are far less numerous than polyiodides. Apart from Br_3^-, only Br_4^{2-} [isolated in $(Me_2NH^{2+})_2Br_4{}^{2-}$][5] and planar Z-shaped Br_8^{2-} [isolated in $(quinoclidinium)_2Br_8$][6] have been reported in the literature so far. Extended bromine-based networks are also known, but they are generally made up of bromides of different elements (such as Se, Sb, or Pt) linked together by bridging Br_2 molecules to form polymeric anionic networks.[7] During our studies on the reactivity of $[Pd(Et_2timdt)_2]$ neutral dithiolene (Et_2timdt = formally monoreduced diethylimidazolidine-2,4,5-trithione)[8] with Br_2, together with the neutral complex $[Pd(Et_2timdt)Br_2]$,[9] very few plate crystals of a second type of product were isolated.‡ The X-ray crystal structure§ established this product as $[\mathbf{1}^{Et}\cdot 2Br]^{2+}(Br^-)_2(Br_2)_3$ (Fig. 1).

The oxidation of the two ligands Et_2timdt generated the centrosymmetric octa-membered tetrathiocino crown $\mathbf{1}^{Et}$ (Scheme 1) in a chair conformation,¶ with the two terminal S atoms covalently bonded to Br atoms [S(1)–Br(1) = 2.249(3) Å; C(1)–S(1)–Br(1) = 99.6(1)°], so as to give the cation $[\mathbf{1}^{Et}\cdot 2Br]^{2+}$, counterbalanced by two bromides [Br(2) in Fig. 1], interacting at the same terminal S-atoms [S(1)···Br(2) = 3.256(4) Å; C(1)–S(1)–Br(2) = 72.1(1)°]. The $[\mathbf{1}^{Et}\cdot 2Br]^{2+}$ dication acts as a templating agent to construct a unique example of an infinite polybromide network. In fact, each bromide interacts with three adjacent Br_2 molecules in an approximate C_{3v} symmetry and each Br_2 molecule bridges two bromide anions (Fig. 2), generating infinite sheets of alternated Br^- and Br_2. Fig. 3 shows the sheets derived from repeating twisted-H $Br_{12}{}^{2-}$ motifs (Fig. 2), very similar to the discrete I_{12}^{2-} anions isolated in $(Me_2Ph_2N)_2I_{12}$ and $\{Ag_2([15]aneS_5)_2\}I_{12}$.[10,11] In the 2D-network, six alternated bromides and six Br_2 molecules form a "hexagonal" Br_{18} ring, which assumes a chair conformation analogous to that described for the I_{16} rings found in the case of $[Fe(phen)_3]I_{12}$.[12] The Br_{18} rings are fused together to form infinite square-waved 2D arrays stacked along *a* (Fig. 3a). Each of the eighteen atom membered rings hosts a $[\mathbf{1}^{Et}\cdot 2Br]^{2+}$ unit, through S(1)···Br(2) and Br(1)···Br(2) contacts of 3.256(3) and 3.126(3) Å, respectively, completing a pseudo-square pyramidal coordination around the Br^- anions

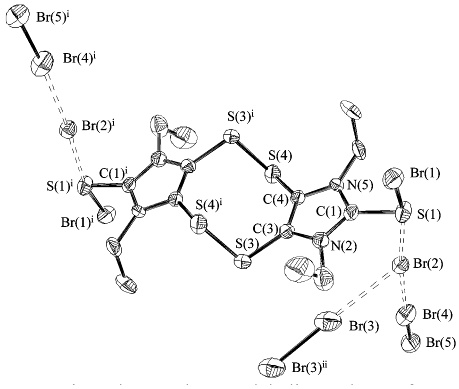
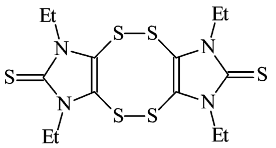


Fig. 1 Perspective view and atom labeling scheme for compound $\mathbf{1}^{Et}\cdot 5Br_2$.Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. [i] = −x + 1, −y + 1, −z + 1; [ii] = −x + 1, −y + 1, −z − 1.



$\mathbf{1}^{Et}$

Scheme 1

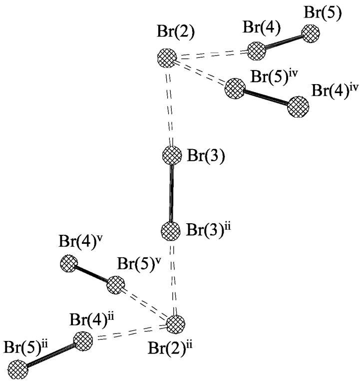


Fig. 2 Interactions between the Br(2) anion, and the Br(3)–Br(3)[ii] and Br(4)–Br(5) molecules in $\mathbf{1}^{Et}\cdot 5Br_2$. Br(3)–Br(3),[ii] 2.411(3); Br(4)–Br(5), 2.357(2); Br(2)···Br(3), 3.041(3); Br(2)···Br(4), 3.108(3); Br(2)···Br(5),[iv] 3.197(3) Å. [iv] = x, 0.5 − y, 0.5 + y; [v] = 1 − x, 0.5 + x, −2.5 − z.

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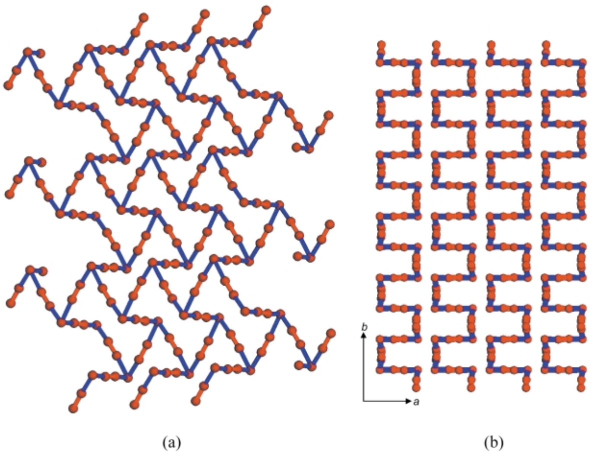
† Electronic supplementary information (ESI) available: elemental analysis and crystallographic data for $\mathbf{1}^{Et}\cdot 5Br_2$. See http://www.rsc.org/suppdata/cc/b3/b306841b/

DOI: 10.1039/b306841b



(a) (b)

Fig. 3 (a) Infinite polybromide 2D-network generated by the Br(2) anions bridged by the Br(3)–Br(3)^{ii} and Br(4)–Br(5) molecules in $\mathbf{1}^{\mathrm{Et}}\cdot5\mathrm{Br}_2$. (b) Projection of the 2D-arrays along the *c* axis.

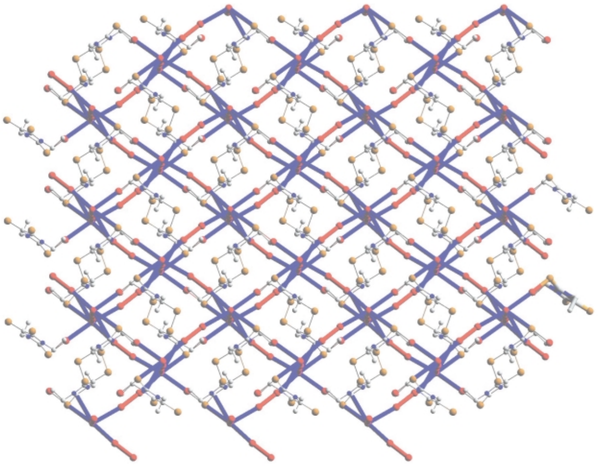


Fig. 4 Infinite boxed double-faced layer formed by the polybromide square-waved 2D-network hosting the organic $[\mathbf{1}^{\mathrm{Et}}\cdot2\mathrm{Br}]^{2+}$ dications in $\mathbf{1}^{\mathrm{Et}}\cdot5\mathrm{Br}_2$. Hydrogen atoms have been omitted for clarity.

and generating boxed double-faced infinite sheets (Fig. 4). Parallel infinite sheets are held together by very long S(1)–Br(5) interactions [3.695(4) Å].

It is worth noting that all the Br···Br contacts in this 2D-polybromide array range between 3.041(3) and 3.197(3) Å, and are of the same entity as those found in smaller discrete polybromides, such as Br_8^{2-}.[6] Moreover, all the Br···Br contacts are shorter than those found in the solid Br$_2$ (3.31 and 3.79 Å),[13] accounting for the high stability of $\mathbf{1}^{\mathrm{Et}}\cdot5\mathrm{Br}_2$ (the crystals did not show any trace of decomposition during X-ray data collection).

In summary, the crystal structure of $\mathbf{1}^{\mathrm{Et}}\cdot5\mathrm{Br}_2$ shows that cations of the type [L–S–Br]$^+$ analogous to those of the type [L–Se–I]$^+$, previously reported,[14] can act as templating agents for unprecedented infinite polybromide anionic arrays, suggesting the ability of bromine to give rise to interactions, whose nature and geometrical motifs are strictly similar to those found in the far more explored chemistry of polyiodides. Due to the difficulty in preparing large amounts of donors of type $\mathbf{1}^{\mathrm{R}}$ and to the serendipity of having obtained products such as $\mathbf{1}^{\mathrm{Et}}\cdot5\mathrm{Br}_2$, donors similar to $\mathbf{1}^{\mathrm{Et}}$, containing imidazoline-2-thione units, are being systematically reacted with Br$_2$ in our laboratories with the aim of preparing compounds with a high bromine content per molecular unit, analogous to $\mathbf{1}^{\mathrm{Et}}\cdot5\mathrm{Br}_2$, which could possibly be exploited as stoichiometric reservoirs for bromine storage or as starting materials for bromination reactions.

Notes and references

‡ $\mathbf{1}^{\mathrm{Et}}\cdot5\mathrm{Br}_2$ was isolated as a by-product of the synthesis of [Pd(Et$_2$timdt)Br$_2$].[9] After cooling of the reaction mixture, dark needle crystals of the main product [Pd(Et$_2$timdt)Br$_2$] were mixed with small orange plates of $\mathbf{1}^{\mathrm{Et}}\cdot5\mathrm{Br}_2$. The two types of crystals were separated by hand, and washed with petroleum ether 40–70 °C. Satisfactory analytical data were obtained (see ESI†). $\mathbf{1}^{\mathrm{Et}}\cdot5\mathrm{Br}_2$ is stable to air and moisture.

§ Crystal data for $\mathbf{1}^{\mathrm{Et}}\cdot5\mathrm{Br}_2$: $\mathrm{C}_{14}\mathrm{H}_{20}\mathrm{Br}_{10}\mathrm{N}_4\mathrm{S}_6$, monoclinic, space group $P2(1)/c$, a = 12.893(2), b = 13.402(2), c = 10.6610(17) Å, β = 112.671(3)°, V = 1699.6(5) Å^3, Z = 2, ρ_c = 2.415 Mg m^{-3}, T = 293(2) K, R = 0.0469, wR = 0.0909 for 2379 observed independent data. CCDC 213066. See http://www.rsc.org/suppdata/cc/b3/b306841b/ for crystallographic data in CIF or other electronic format.

¶ $\mathbf{1}^{\mathrm{i\text{-}Pr}}$ had been isolated in trace amounts from the sulfuration with Lawesson's reagent of diisopropylimidazolidine-2-thione-4,5-dione. In addition, it was also isolated from the IBr and Br$_2$ oxidation of the [Ni(i-Pr$_2$timdt)$_2$] dithiolenes.[15]

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