Inorg. Chem. **2008**, *47*, 11464−11466

Inorganic Chemistry
Communication

Dimensional Caging of Polyiodides

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Received September 24, 2008

Two series of iodide and polyiodide chain structures have been synthesized through the employment of secondary interactions between polycation, long-chain, hydrocarbon cations. These compounds represent examples of crystal engineering, employing a simple strategy of synthesis. The two series are related, and the capacity to incorporate polyiodide ions dependent on the length of the hydrocarbon chains is indicated.

Polyiodides display a very rich structural chemistry, and they are one of a few classes of compounds that form extensive inorganic polymeric networks.[1−5] At present, polyiodides are known in the range from I_2^- to I_{29}^{3-}, and they can be visualized in terms of both very simple units (I_3^-, I_5^-, and I_7^-) and very complicated three-dimensional arrangements containing both linear and zigzag chains as well as layers. These very different structures can with a few exceptions be described as constructed from three "building blocks": I^-, I_2, and I_3^-, where the I^- and I_3^- ions may be considered as donors and surrounding I_2 molecules as acceptors.[1] This view is particularly relevant considering the mechanism of electric conductivity in this class of compounds. One of the major reasons for the rich diversity of polyiodide structures is the linear flexibility of the triiodide ion, which makes it very sensitive to the influence from the nearest neighbors in the structure. Because of this property, the choice of cation becomes a very important factor in the synthesis of polyiodide compounds.[1−5] If a very large and bulky cation is used, then it is usually possible to stabilize formally large polyiodides. However, the cation shape and polarizability are also important factors to consider.

It was recently shown in our laboratory that it is possible to exchange fundamental "building blocks" of the $(R_3S)I_x$ (R = Me and Et and $x = 2-11$) polyiodides for new building blocks, i.e., complex metal iodides.[6−8] The modified polyiodides have structures that contain networks and one-dimensional chains. The choice of cation in these types of compounds is even more important than that in the synthesis of pure polyiodides because the interaction between I_2 and the complex metal iodides often is weaker than that in the pure polyiodides (where I_2 interacts with I^- and I_3^-).[8,9]

One of the fundamental problems in the systematic syntheses of polyiodide compounds is to exercise synthetic control, i.e., to predetermine how the polyiodides are going to aggregate in three dimensions. Such an approach is normally referred to as crystal engineering, where hierarchical interactions (in terms of interaction energies) are employed to control the aggregation and dimensionality in the solid state. The obvious strategy in this case is to use the cations, with appropriate supramolecular synthons, to force the polyiodides into a specific orientation. The attractive interaction between polyiodide fragments is strong and well understood.[9] Initial attempts were based on modification of the previously used R_3S^+ (R = Me and Et) cations, where one methyl or ethyl group was exchanged for a long-chain alkyl group.[10] In the course of experiments, it became apparent that the corresponding ammonium cations R_4N^+ (or rather Me_3RN^+) offered easier handling in terms of stability and chemical modification.

The fundamental idea of this work was based on the assumption that dispersion interactions (i.e., secondary-type interactions between the hydrocarbon tails) will make the long hydrocarbon chains, acting as the supramolecular synthon,[11] aggregate into lamellar structures, forcing the polyiodide fragments into the vicinity of the ammonium ion charges. This may seem a trivial idea; however, it should be emphasized that since our first studies on polyiodides with long-chain hydrocarbon cations, no systematic studies have been done in this field.[1,12] Studies on the crystal packing of long-chain alkyl ammonium and halide salts have been reported by Weiss et al.[13] One source of uncertainty of our strategy is the fact that excess iodine (to iodide) may also readily dissolve within the hydrocarbon bilayers instead of binding to the iodide ions to form polyiodide structural

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10.1021/ic801820s CCC: $40.75

fragments. In order to enhance the ionic electrostatic attraction and at the same time to limit the degrees of freedom for the hydrocarbon tails of the ammonium cations, these were linked into bications via an ethyl bridge.[14] Two homologous series were synthesized, only differing in the length of the hydrocarbon tails, resulting in the crystal structures of five compounds described below.

Using the bication $(C_{12}H_{25})(CH_3)_2N(C_2H_4)N(CH_3)_2(C_{12}H_{25})^{2+}$, hereafter abbreviated DA^{2+}, both the iodide, $DA[I]_2$ (**1**), and triiodide, $DA[I_3]_2$ (**2**), structures were isolated.[15] The $DA[I]_2$ bromine analogue has previously been characterized by Huc et al.[16] In **1**, the DA^{2+} bication has an out-stretched Z configuration, with the two hydrocarbon tails belonging to two neighboring lamellar bilayers (Supporting Information). The bilayers essentially are in the crystallographic *ab* plane but are tilted by approximately 25° with respect to the normal of the plane. The distance between the end carbon atoms in the Z-shaped bication is 23.8 Å. The iodide ions are confined to the cationic space around the nitrogen atoms and are running in two columns (Figure 1a). The distance between the iodide ions within the layers is in the range 6.77−9.25 Å. The bilayer thickness is approximately 15.6 Å.

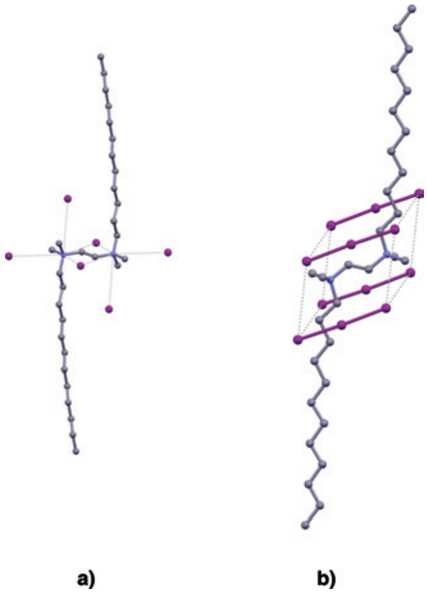

Figure 1. Visualization of the (a) iodide ion positions (**1**) and (b) triiodide positions (**2**) around the DA^{2+} bication (hydrogen atoms are omitted).

The corresponding $DA[I_3]_2$ compound **2** has a similar overall structure. The bications are out-stretched Z-shaped and are arranged in lamellar bilayers essentially in the *ab* plane. The bication end atoms are at a distance of 22.7 Å and the lamellar thickness is 18.5 Å, suggesting a slightly more expanded layer structure caused by the larger anions present. The hydrocarbon tails are tilted by 20° with respect to the normal of the plane. The triiodide ions, just like the iodides in **1**, form a layer centered around the nitrogen atoms of the bication. The triiodide ions are arranged in pairs of columns running in the crystallographic *a* direction (Figure 1b). The distance between the triiodide ions in the columns is 7.78 Å, and that between the closest triiodide ions of the two neighboring rows is 4.63 Å. The triiodide ions themselves are slightly distorted from linear centrosymmetry with I−I distances of 2.856 and 2.955 Å and an angle of 176.3°. The longer intramolecular I−I distance is found closest to the nitrogen atoms of the bication, all in accordance with the expected distortions of a triiodide ion.[17] It is noteworthy that all attempts to make higher polyiodides of the DA^{2+} bication so far have failed. The more out-stretched conformation of DA^{2+} found in **2** indicates that the reason is related to the hydrocarbon chain length and the degree of interpenetration of the lamellar layers. Compounds **3**−**5** provide further insights into this question.

Using the bication $(C_{16}H_{33})(CH_3)_2N(C_2H_4)N(CH_3)_2(C_{16}H_{33})^{2+}$, hereafter abbreviated HA^{2+}, both the iodide, $HA[I]_2$ (**3**), triiodide, $HA[I_3]_2$ (**4**), and pentaiodide, $HA[I_5]_2$ (**5**), structures were isolated.[13] In **3**, the HA^{2+} bication, in analogy to the dodecyl congener, has an out-stretched Z configuration, with the two hydrocarbon tails belonging to

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(14) The general synthesis of **1** and **2**: A total of 2.35 g of $Me_2N(CH_2)_2NMe_2$ was mixed with 12.01 g of $CH_3(CH_2)_{11}I$ (molar ratio 1:2) in acetonitrile and refluxed for 48 h. Tetrahydrofuran can also be used as the solvent. Transparent crystals of $DA[I]_2$ (**1**) were separated by filtration and washed with small aliquots of cold acetonitrile and ether. The yield was ca. 80%. The subsequent synthesis of **2** was performed by mixing **1** with excess amounts with respect to the stoichiometric ratio of I_2 in acetone. The general synthesis of **3**−**5**: A total of 1.84 g of $Me_2N(CH_2)_2NMe_2$ was mixed with 11.21 g of $CH_3(CH_2)_{15}I$ (molar ratio 1:2) in acetonitrile and refluxed for 48 h. Transparent crystals of $HA[I]_2$ (**3**) were separated by filtration and washed with small aliquots of cold acetonitrile and ether. The yield was ca. 70%. The subsequent synthesis of **4** and **5** was performed by mixing **3** with an increasing excess of I_2 in acetone. Results from bulk powder X-ray diffraction and Raman spectroscopy are collected in the Supporting Information.

(15) General crystal data for **1**−**5**: $\lambda = 71.073$ pm, Enraf-Nonius Kappa CCD diffractometer, graphite monochromator, $T = 293(2)$ K. Absorption correction was made for all compounds. Direct methods were used to determine the structure. All non-hydrogen atoms were refined anisotropically by least-squares methods. The hydrogen atoms were localized and refined using a riding model. Crystal data for **1**: space group triclinic, $P\bar{1}$ (No. 2), $a = 728.64(4)$ pm, $b = 882.16(4)$ pm, $c = 1558.63(8)$ pm, $\alpha = 80.073(1)°$, $\beta = 87.309(1)°$, $\gamma = 66.512(1)°$, $V = 904.82(8) \times 10^6$ pm^3, $\rho_{calcd} = 1.301$ g cm^{-1}, $Z = 2$, μ(Mo Kα) $= 175.6$ mm^{-1}, $F(000) = 366$, 3197 measured reflections, final R1 = 0.0368, wR2 = 0.0869 for 2631 observed reflections ($I_{obs} > 2\sigma$). Crystal data for **2**: space group triclinic, $P\bar{1}$ (No. 2), $a = 779.74(5)$ pm, $b = 856.51(5)$ pm, $c = 1851.86(11)$ pm, $\alpha = 81.644(2)°$, $\beta = 85.742(2)°$, $\gamma = 64.517(1)°$, $V = 1104.51(12) \times 10^6$ pm^3, $\rho_{calcd} = 1.829$ g cm^{-1}, $Z = 2$, μ(Mo Kα) $= 423.8$ mm^{-1}, $F(000) = 578$, 3893 measured reflections, final R1 = 0.0451, wR2 = 0.1285 for 2803 observed reflections ($I_{obs} > 2\sigma$). Crystal data for **3**: space group triclinic, $P\bar{1}$ (No. 2), $a = 724.31(6)$ pm, $b = 856.58(7)$ pm, $c = 1881.16(15)$ pm, $\alpha = 82.778(2)°$, $\beta = 81.079(2)°$, $\gamma = 65.936(2)°$, $V = 1087.06(15) \times 10^6$ pm^3, $\rho_{calcd} = 1.254$ g cm^{-1}, $Z = 2$, μ(Mo Kα) $= 147.1$ mm^{-1}, $F(000) = 430$, 3842 measured reflections, final R1 = 0.0469, wR2 = 0.1256 for 3555 observed reflections ($I_{obs} > 2\sigma$). Crystal data for **4**: space group triclinic, $P\bar{1}$ (No. 2), $a = 782.80(1)$ pm, $b = 855.60(2)$ pm, $c = 2180.30(5)$ pm, $\alpha = 91.0670(12)°$, $\beta = 96.9220(13)°$, $\gamma = 116.1371(10)°$, $V = 1297.18(5) \times 10^6$ pm^3, $\rho_{calcd} = 1.701$ g cm^{-1}, $Z = 4$, μ(Mo Kα) $= 361.6$ mm^{-1}, $F(000) = 642$, 4539 measured reflections, final R1 = 0.0391, wR2 = 0.1093 for 3529 observed reflections ($I_{obs} > 2\sigma$). Crystal data for **5**: space group monoclinic, $P21/c$ (No. 14), $a = 844.80(6)$ pm, $b = 6048.4(5)$ pm, $c = 1206.90(9)$ pm, $\beta = 108.827(1)°$, $V = 5836.9(7) \times 10^6$ pm^3, $\rho_{calcd} = 2.089$ g cm^{-1}, $Z = 2$, μ(Mo Kα) $= 533.3$ mm^{-1}, $F(000) = 3416$, 10 207 measured reflections, final R1 = 0.0800, wR2 = 0.1878 for 8531 observed reflections ($I_{obs} > 2\sigma$). Further details on the crystal structures can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk), on quoting the depository numbers CCDC 699984−699988.

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two neighboring lamellar bilayers. The bilayers essentially are in the crystallographic *ab* plane but are tilted by approximately 20° with respect to the normal of the plane. The distance between the end carbon atoms in the Z-shaped bication is 30.7 Å. The iodide ions are confined to the cationic space around the nitrogen atoms and are arranged analogously to those in **1** (see Figure 1a). The distance between the iodide ions within the layers is in the range 5.26−6.70 Å. The bilayer thickness is approximately 19.8 Å.

Again, the corresponding HA$[I_3]_2$ compound **4** has a similar overall structure. The bications are out-stretched Z-shaped and are arranged in the same types of lamellar bilayers essentially in the *ab* plane (see Figure 1b). The bication end carbon atoms are at a distance of 31.6 Å and the lamellar thickness is 23.7 Å, suggesting a slightly more expanded layered structure caused by the larger anions present. The hydrocarbon tails are tilted slightly less than 15° with respect to the normal of the plane. The triiodide ions are, just like the triiodides in the corresponding DA$[I_3]_2$ compound **2**, arranged in pairs of columns running in the crystallographic *a* direction. The distance between the triiodide ions in the columns is 7.83 Å, and that between the closest triiodide ions of the two neighboring rows is 4.59 Å. The triiodide ions themselves are slightly distorted from linear centrosymmetry with I−I distances of 2.860 and 2.955 Å and an angle of 176.3°, with the polyiodide part of the structure thus being remarkably similar to that in **2**.

In contrast to compounds **1**−**4**, the pentaiodide compound **5** offers a few surprises. Apparently, the effect of an increase in the size of the anionic polyiodide units trapped around the positively charged nitrogen atoms of the bication reduces the interpenetration of the hydrocarbon chains in the arrangement seen in compounds **1**−**4**. When the polyiodide reaches the pentaiodide size, it seems that the energetically preferred orientation of the bication instead folds into a U shape, where both hydrocarbon tails point in the same direction to form a different type of lamellar bilayer (Supporting Information). The lamellar structure is in the crystallographic *ac* plane and has a thickness of as much as 30.6 Å, where the U-shaped bications essentially overlap to half the hydrocarbon chain length and are tilted as much as 25° with respect to the normal of the plane. In analogy to the triiodide structures, the pentaiodides are arranged in pairwise columns, although the planes between the lamellar hydrophobic layers are less well defined. The I−I distance between the pentaiodide ions in the columns is 8.45 Å, and the closest distance between the rows is 4.48 Å. The V-shaped pentaiodide ions may be regarded as discrete, just like the triiodide ions, and are of the $[2I_2 \cdot I^-]$ type. The pentaiodide ions in the pairs of columns (Figure 2) are not identical; the top angles are 88.8° and 90.5°, respectively, and the angles of the I^- - I_2 legs range from 173.7 to 178.7°. The distances of the I_2 fragments are 2.754−2.827 Å, and the I^-−I_2 distances are 3.040−3.236 Å. In spite of deviations from an ideal V-shaped pentaiodide structure, the ions have typical conformations.[17]

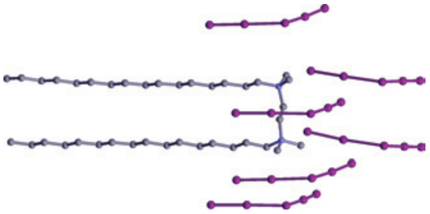

Figure 2. Visualization of the pentaiodide ion positions around the HA^{2+} bication (hydrogen atoms are omitted).

As the polyiodide ion is increased in size, from iodide to triiodide, the bilayers in both series become 3−4 Å thicker. The increase in the bilayer thickness is partly explained by a slight decrease in the angle with respect to the normal of the iodide-containing plane. However, the dominating effect is a reduced hydrocarbon tail interpenetration. This effect, in combination with the change of the bication conformation from Z- to U-shaped in the pentaiodide compound and the inability to crystallize polyiodides larger than triiodide for the smaller DA^{2+} and pentaiodides for the HA^{2+} bications, indicates that the hydrocarbon tail interaction, essentially proportional to the interexposed surfaces of the tails (interpenetration), is predominant in the stabilization of the bilayered structures.

In summary, it seems that the hypothesis of hierarchical confinement of polyiodide fragments is adequate, giving rise to caged tri- and pentaiodide ions in one-dimensional chains in two-dimensional layers. This effect can be regarded as a phase separation into a phase dominated by electrostatic interaction between the cation head groups and the polyiodide anions and another phase dominated by dispersion interaction between hydrocarbon tails. In this context, it is noteworthy that the ethyl linkage of the long-chain, monocations of the Me_3RN^+ type into bications strongly facilitates the crystallization process, probably by accumulation of positively charged groups in space. In this aspect, the polyiodide anions may be regarded as "confined" in space-through electrostatic interaction with the cation head groups. Future work will focus on the effects of the self-assembly of synthon-modified polycations. In order to gain further insights into the driving force for the observed folding from Z to U shape in the bication, a pentaiodide compound may be elucidated by the study of the analogous trication compounds. The ultimate goal is thus to gain synthetic control via the combination of polyiodiode interaction and crystal engineering of the polycations.

Acknowledgment. This work was supported by the Swedish Research Council (VR), also acknowledged for funding of the Bruker-Nonius Kappa CCD diffractometer.

Supporting Information Available: Cation molecular structures, crystallographic packing of the compounds **1**, **2**, and **5**, and powder X-ray diffraction and Raman spectroscopic data for compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801820S