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Linear Pentaiodide in the Radical Cation Salt of a Tetrathiafulvalene Bisannulated Macrocycle

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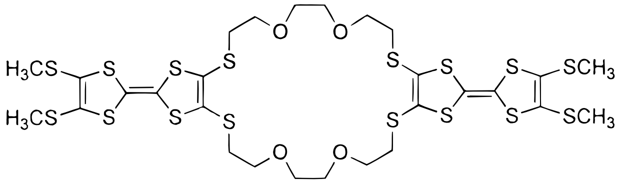
Iodine has a tendency to aggregate in various anionic forms such as I^-, linear I_3^-, V-shaped I_5^-, linear I_5^-, I_7^-, and nonplanar I_9^-.[1] The classic iodostarch reaction has been used for the detection of minute amounts of starch through the drastic color change to intense blue-black. The major component of starch is amylose with a helix structure, and the iodine atoms are present in a one-dimensional chain within the amylose helix.[2] The exact structure of the polyiodide chromophore was determined as having a linear pentaiodide form from the measurements of the resonance Raman and ^{129}I Mössbauer spectra.[3]

Three crystal structures of the linear pentaiodide have been reported. (i) Herbstein and Kapon reported the formation of a linear I_5^- ion in (trimesic acid·H_2O)$_{10}$(H^+)(I_5^-), the crystal structure of which was interpreted from the intensity distribution in the one-dimensional diffuse lines of the X-ray powder pattern.[4] (ii) Luss and Smith showed the crystal structure of cation radical salt (tetraphenyldithiapyranylidene)$(I_3^-)_{0.36}(I_5^-)_{0.4}$ with the coexistence of linear I_5^- and I_3^- in an infinite linear chain. From the several models of disordered iodine atoms, they concluded that the I_3^- and I_5^- model was the most reasonable.[5] (iii) A linear I_5^- was also found in (1,1′-(propane-1,3-diyl)ferrocenium)$_3(I_3^-)_2(I_5^-)$ as a linear polyiodide chain of $(I_3^-{-}I_5^-{-}I_3^-)_\infty$.[6] In the latter cases, the linear I_5^- species have been found as part of polymeric chains.

We report here a new network of linear I_5^- and I_3^- within the cation radical salt of bis(dimethylthio)tetrathiafulvalene (DMT-TTF) bisannulated tetraoxatetrathiatetracosane (**1**), in which the isolated I_5^- species exist as a part of a cage-like network structure of I_3^- and I_5^- rather than as a part of an alternate polyiodide chain, determined from the crystal structural analysis and optical measurements.



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Compound **1** has been synthesized using the cyanoethyl protection/deprotection protocols.[7] Possible applications for ion-active organic devices using macrocycles such as **1** are pointed out.[8] The electrocrystallization of **1** with tetrabutylammonium triiodide (n-$Bu_4N^+I_3^-$) in 1,2-dichloroethane gave metallic greenish-colored single crystals. The composition of $(\mathbf{1}^{2+})(I_3^-)(I_5^-)$ was determined from the structural analysis.[9] The salt was insulating due to the fully charge transfer (CT) state of $\mathbf{1}^{2+}$.

Figure 1 shows the molecular structure of I_5^- and I_3^- anions together with $\mathbf{1}^{2+}$. Half units of $\mathbf{1}^{2+}$, I_3^-, and linear I_5^- molecules are crystallographically independent, and I_3^- and I_5^- are located on the center of inversion. Disorder of molecular arrangements of iodide anions was not observed.

The I−I distance of triiodide (I(3)−I(5) = 2.929(1) Å) is much smaller than the sum of the van der Waals (vdw) radius of an iodine atom (3.96 Å) and slightly longer than the covalent single-bond length of an I_2 molecule (2.67 Å).[10] The I_3^- in $Cs^+I_3^-$ showed asymmetric I−I distances of 2.83 and 3.04 Å, whereas the bond lengths in n-$Bu_4N^+I_3^-$ were 2.89 and 2.95 Å.[11] The I−I distance (2.929(1) Å) in $(\mathbf{1}^{2+})(I_3^-)(I_5^-)$ falls in a range similar to that of the above reference compounds. The intramolecular I(2)−I(4) (inner bond) and I(4)−I(1) (outer bond) distances are 3.191(1) and 2.785(1) Å, respectively. The angles 174.54(3)° and 180° for I(1)−I(4)−I(2) and I(4)−I(2)−I(4), respectively, strongly indicate the linear arrangement of I_5^-. The I(1)−I(4) distance is close to that of the covalent bond of I_2, while the I(2)−I(4) distance is about 0.52 Å longer. However, the large contraction of 0.769 Å from the sum of the vdw radius of iodine suggests the formation of a chemical bond. A V-shaped I_5^- structure was previously reported in the crystal of (benzophenone)$_4$(Li^+)(I_5^-), where I−I distances of outer bonds (2.78 and 2.78 Å) were smaller compared with inner ones (3.09 and 3.17 Å).[12] The order of bond lengths of inner and outer bonds of the V-shaped I_5^- is similar to that of the linear I_5^- in the present crystal. The intramolecular iodine arrangement in (1,1′-(propane-1,3-diyl)ferrocenium)$_3(I_3^-)_2(I_5^-)$ was estimated as having I−I distances of 3.2207(5) (inner) and 2.8003(4) Å (outer), which is consistent with our results. The isolated linear I_5^- in $(\mathbf{1}^{2+})(I_3^-)(I_5^-)$ is completely identified by the single-crystal X-ray structural analysis.

Molecule $\mathbf{1}^{2+}$ is folded over, and therefore two DMT-TTF moieties are overlapped at the inner five-membered rings of 4,5-

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(9) $C_{14}H_{18}O_2S_8I_4$, M = 1109.23, triclinic, space group $P\bar{1}$ (No. 2), a = 12.221(2) Å, b = 12.758(3) Å, c = 9.946(2) Å, α = 93.22(2)°, β = 91.68(2)°, γ = 66.17(1)°, V = 1416.4(5) Å^3, T = 298 K, Z = 2, 6800 reflections measured, 6494 independent reflections, 4103 reflections with $I > 4\sigma(I)$, R = 0.0757, R_w = 0.0753, refinement on F.

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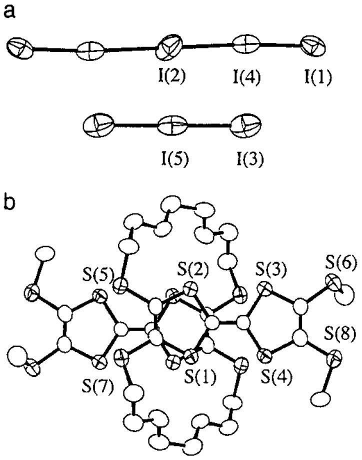

Figure 1. Molecular structure of $(\mathbf{1}^{2+})(I_5^-)(I_3^-)$: (a) linear pentaiodide (I_5^-) and triiodide (I_3^-) anions with numbering scheme; (b) $\mathbf{1}^{2+}$ viewed along the perpendicular direction to the plane of DMT-TTF moieties.

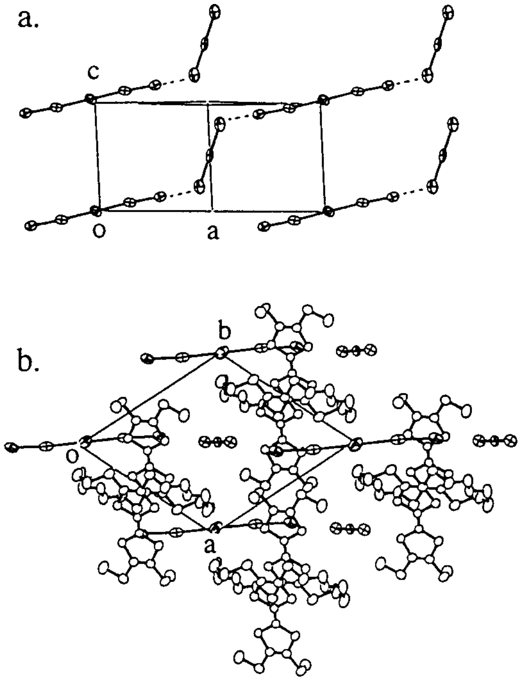

Figure 2. Crystal structure of $(\mathbf{1}^{2+})(I_5^-)(I_3^-)$: (a) $I_5^- - I_3^-$ zigzag chain viewed along the $b-a$ direction. Dashed lines show the close I···I contacts shorter than the sum of the vdw radii. (b) Molecular packing of $\mathbf{1}^{2+}$ and the $I_5^- - I_3^-$ chain within the *ab* plane viewed along the *c*-axis.

dimethylthio-1,3-dithiolium relative to each other. Between the DMT-TTF moieties within the same molecule, short S···S contacts, shorter than the sum of the vdw radii of sulfur atoms,[10] are observed at S(1)···S(2) (3.216(3) Å) and S(4)···S(5) (3.613(3) Å). The mean interplanar distance between two DMT-TTF moieties is 3.404 Å, and the intramolecular overlap integral ($s = 40.3 \times 10^{-3}$) determined by the extended Hückel molecular orbital calculation is much larger than inter- or intrastack s values ($2-6 \times 10^{-3}$) of typical BEDT-TTF organic metals.[13] Therefore, a strong intramolecular $\pi-\pi$ overlap exists between the DMT-TTF moieties within the molecule.

Figure 2 shows the molecular packing of $\mathbf{1}^{2+}$ and the $I_3^- - I_5^-$ network. The intermolecular I(1)···I(3) contacts are indicated by dashed lines in Figure 2a, the distance (3.628(1) Å) of which is 0.33 Å shorter than the sum of the vdw radii of iodine atoms, indicating the existence of intermolecular interaction between I_3^- and I_5^-. The zigzag chains formed by the weak interaction between I_3^- and I_5^- are located on the $a + b + c$ plane. The linear I_5^- molecules are elongated along the direction which makes an angle of 15° with the $a + b$ plane, and I_3^- molecules are inclined about 15° to the c-axis. There are no strong interactions between $I_3^- - I_5^-$ chains. The $\mathbf{1}^{2+}$ molecules are arranged within the *ab* plane (Figure 2b). The $\mathbf{1}^{2+}$ molecules are surrounded by $I_3^- - I_5^-$ zigzag chains, and there are no intermolecular contacts between the $\mathbf{1}^{2+}$ molecules. Weak intermolecular contacts between the terminal sulfur atoms of $\mathbf{1}^{2+}$ and I_5^- (I(1)···S(5) = 3.796(2) Å) are observed within the sum of vdw radii. In short, a cage-like structure made of I_5^- and I_3^-, in which the isolated donor molecules are located, was observed within the $a + b + c$ plane as shown in Figure 2b.

The UV−vis−near-IR spectrum of salt $(\mathbf{1}^{2+})(I_3^-)(I_5^-)$ shows an absorption (A-band) at 9.1×10^3 cm^{-1} accompanied by a small band at around 12.5×10^3 cm^{-1} (B-band). In addition, two broad bands of C (24.1×10^3 cm^{-1}) and D (33.9×10^3 cm^{-1}) are observed in the energy region of intramolecular excitation.

Since the molecule $\mathbf{1}^{2+}$ is isolated from the neighboring $\mathbf{1}^{2+}$, the A-band is attributable to the intramolecular CT transition between two DMT-TTF moieties. The isolated TTF$^+$ dimer in (TTF$^+$)Br$^-$ showed a CT transition at $\sim 12 \times 10^3$cm^{-1}, while the partial CT salt of (TTF$^{+0.79}$)Br$^-_{0.79}$ had a CT transition at the lower energy of $\sim 4 \times 10^3$ cm^{-1}.[14] The red shift of the A-band in $\mathbf{1}^{2+}$ compared to TTF$^+$ dimer suggests the reduction of effective on-site Coulomb repulsion energy of **1**.

The C- and D-bands correspond to the intramolecular transitions within each DMT-TTF moiety. It should be noted that the B-band is attributed to the linear I_5^- species. The linear relationship between the intramolecular excitation energy and the length of polyiodide has been reported, and the (trimesic acid $H_2O)_{10}(H^+)(I_5^-)$ exhibited an absorption at around 13×10^3 cm^{-1}, which is close to that of the B-band.[11]

The resonance Raman spectra of $(\mathbf{1}^{2+})(I_3^-)(I_5^-)$ further confirmed the linear structure of I_5^-. Bands at 324, 304, 163, 130, and 110 cm^{-1} appeared in the energy range from 50 to 400 cm^{-1}. We assign the peak at 163 cm^{-1} as the outer I−I symmetrical stretching mode of the linear I_5^- molecule.[15] Since both 163 and 304 cm^{-1} peaks showed the same angular-dependent intensity distribution, the band at 304 cm^{-1} can be assigned to the second harmonic (band (2ν)) of the outer I−I stretching mode. The 110 and 324 cm^{-1} bands of $(\mathbf{1}^{2+})(I_3^-)(I_5^-)$ are due to the I_3^- species, whereas the peak at 130 cm^{-1} may be related to the $\mathbf{1}^{2+}$ or lattice mode.[15]

In summary, we have prepared the cation radical salt of dimethylthiotetrathiafulvalene bisannulated tetraoxatetrathiatetracosane with linear pentaiodide and triiodide counterions. In the crystal, linear I_5^- and I_3^- form a cage-like network, in which isolated cation radicals are located. Multi-TTF macrocycles will also give rise to unique solid state structures and interesting electrical and optical properties through careful molecular design. Studies along these lines are in progress.

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Supporting Information Available: Text giving a detailed account of the synthesis, optical measurements, and crystallographic data and tables listing atomic positional parameters and bond lengths and angles (19 pages). Ordering information is given on any current masthead page.

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