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Iodobismuthate(III) complex with coordinated triiodide ligand and 3D supramolecular structure

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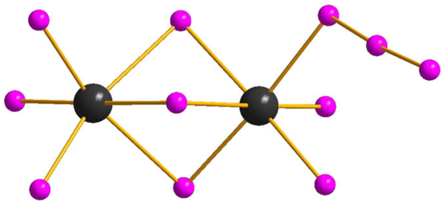
Iodobismuthate complex $(1\text{-Me-3-ClPy})_3[Bi_2I_8(I_3)]$ features the presence of coordinated triiodide ligand. The system of I···I non-covalent interactions yields in 3D supramolecular structure. This complex reveals high thermal stability (>100 °C) and relatively narrow optical band gap (1.55 eV), and it can be considered as promising candidate for testing as light absorber in photovoltaic devices.



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Recent extensive studies[1] of halide complexes, or halometalates,[2–6] in particular, iodometalates,[7–10] are largely promoted by rapid progress in so-called perovskite-type solar cells. Since it was discovered that three-dimensional iodoplumbates(II) (in particular, methylammonium and cesium salts of $\{[PbI_3]_n\}^{n-}$) can act as highly efficient light absorbers, this topic attracts a great attention[11–15] (there are literally hundreds of relevant articles), and efficiencies of such devices now exceed 20%. This fact, together with environmental issues on the use of Pb derivatives, inspired research aiming estimation whether iodide complexes of other elements, especially p-block metals next to Pb, can be used in photovoltaics.[16] The answer was found to be positive, though corresponding devices yet demonstrate less promising performance,[16] which is often explained by the fact that iodometalates used therein have, unlike $\{[PbI_3]_n\}^{n-}$, zero-, one- or, rarely, two-dimensional molecular structures, being therefore less favorable for charge-carrier mobility.

On another hand, in a series of very recent works it was shown that halometalates readily form supramolecular hybrids with di- or polyhalogens[17–22] in solid state.[23,24] In the case of polyiodides, this feature often results in compounds with: (*a*) narrower optical band gaps, often below 1.5 eV,[25–27] which are desired in light absorbers, and (*b*) pseudo-3D supramolecular structures appearing due to halogen···halogen interactions (halogen bonding) which can partially compensate the absence of isotropic 3D covalent framework. The pioneering works on this topic by Shevelkov *et al.*,[26,27] as well as our further reports,[28] demonstrated that such complexes can be prepared *via* very simple synthetic procedures but, like in chemistry of halometalates in general,[1] the nature of organic cations which halide salt is used as precursor dramatically affects the outcome of synthesis. On one hand, it determines the structure of assembling polynuclear halometalate, as well as the presence/absence of polyhalide fragments in product. On another, there yet do not exist any general laws or rules which would allow prediction of such process – in other words, screening with greater number of cationic precursors remains the only reasonable strategy while seeking new polyiodo-iodometalates. In the course of this work, we hereby present new representative of this class – $(1\text{-Me-3-ClPy})_3[Bi_2I_8(I_3)]$ **1** [see Online Supplementary Materials (SI) for preparation and XRD details].

As follows from the XRD data,† the structure of $[Bi_2I_8(I_3)]^{3-}$ anion can be considered as a derivative of widespread $[Bi_2I_9]^{3-}$ structural type which is quite common for halometalates of Sb and Bi:[29–31] there are two octahedral units connected *via* shared face. The Bi–I$_{\text{term}}$ and Bi–μ$_2$-I bond lengths are 2.909–2.985 and 3.079–3.398 Å, respectively. The main feature of 1 is the presence of coordinated (Bi–I = 3.102 Å) asymmetric triiodide ligand (Figure 1). The I–I bond lengths are 2.779 and 3.076 Å, while the average I–I distance in triiodides is 2.92 Å,[32] and in solid I_2 it is ~2.7 Å.[32] Therefore, the nature of longer I–I bond is ambiguous: judging by literature data, it can be regarded as either long covalent or very short non-covalent interaction. The I–I–I angle in I_3 unit is 174.48°.

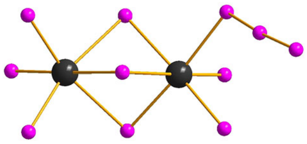

Figure 1 The structure of $[Bi_2I_8(I_3)]^{3-}$. Here and below: Bi black, I purple.

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† *Crystal data for* **1**. $C_{18}H_{21}Bi_2Cl_3I_{11}N_3$ (M = 2199.59), orthorhombic, space group $P2_12_12_1$, a = 11.0677(4), b = 15.7489(4) and c = 24.9389(7) Å, V = 4347.0(2) Å^3, Z = 4, μ(MoKα) = 16.10 mm^{-1}. Total of 14984 reflections were collected, and 8227 independent reflections (R_{int} = 0.031) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$]: R_1 = 0.033, wR_2 = 0.063.

The data were collected at 140 K on a New Xcalibur (Agilent Technologies) diffractometer with MoKα radiation (λ = 0.71073) by doing φ scans of narrow (0.5°) frames. Absorption correction was done empirically using SCALE3 ABSPACK (CrysAlisPro, Agilent Technologies, Version 1.171.37.35). The crystal structure was solved using the SHELXT[38] and refined using SHELXL[39] in ShelXle[40] programs. Atomic displacement parameters for non-hydrogen atoms were refined anisotropically.

CCDC 2167964 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

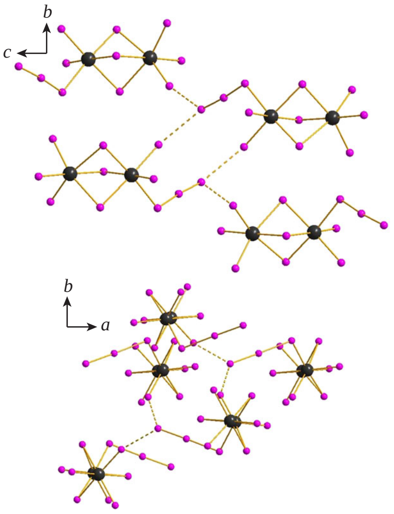

Figure 2 I···I interactions in the structure of **1**.

The system of non-covalent interactions in **1** is rather sophisticated. Considering the sums of corresponding Bondi's van der Waals radii (3.73 for I and Cl and 3.98 Å for 2 I),[33,34] the following contacts can be suggested: (*a*) between the Cl atom of 1-MePy-3-ClPy$^+$ cation and one of μ$_2$-iodide ligands (3.720 Å), (*b*) between the iodide and triiodide ligands (3.854–3.899 Å). The latter yields in 3D structure (Figure 2).

As follows from PXRD data (SI), **1** can be isolated as single phase. This complex features high thermal stability: as follows from TGA data (Figure 3), it decomposes only at >100 °C; the first step clearly corresponds to the loss of the formal diiodine unit (~11.5% of initial mass).

The Raman spectrum of **1** is presented in Figure 4. It is known that for solid I_2 the characteristic band appears at 180 cm^{-1},[32] while for diiodine-containing halometalates it is always shifted to lower wavelengths but, as follows from our previous works,[28,35] it belongs to 170–175 cm^{-1} range. At the same time, while symmetric triiodides normally demonstrate strong bands at 110–120 cm^{-1},[32,36] for asymmetric ones it can be significantly shifted as well.[37] In our opinion, the spectral features of **1** correspond rather to very strong bonding of I_2 unit than to 'true I_3' but, considering the I–I distances, it can be regarded as a borderline case.

Diffuse reflectance spectrum of **1**, as well as determination of the optical band gap, are shown in Figure 5. The E_g value is expectedly lower than for pure BiI_3 (~1.7 eV) or most of iodobismuthates(III), but not the lowest among polyiodo-iodobismuthates (1.37 eV[28]).

Therefore, the following conclusions can be made. Complex **1** expands the structural diversity of polyiodo-iodobismuthates(III) and demonstrates that it can include complexes with coordinated polyhalogen units (or, considering it in different way, such complexes can feature extraordinary strong supramolecular bonding of I_2). Relatively high thermal stability and narrow optical band gap make this compound a suitable candidate for photovoltaic tests (as component of either solar cells or photodetectors).

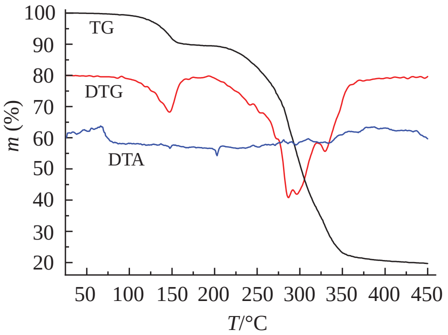

Figure 3 TG, DTG and DTA curves for **1**.

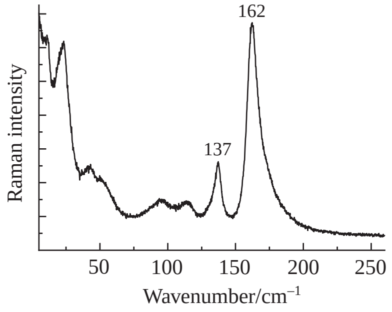

Figure 4 Raman spectrum of **1**.

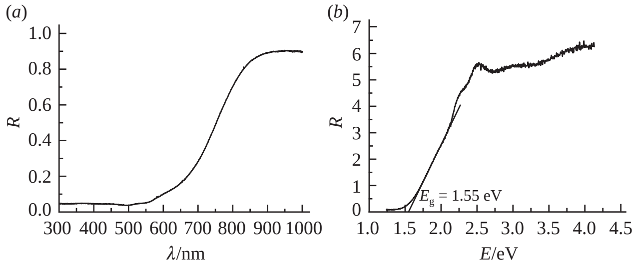

Figure 5 (*a*) Diffuse reflectance spectrum and (*b*) optical band gap determination using Tauc coordinates for **1**.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.11.026.

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