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Mendeleev Commun., 2022, **32**, 517–519
Mendeleev Communications

Isostructural hybrid iodometalate(III)/triiodide salts with perovskite-like packing: comparison of physical properties for Sb^{III} and Bi^{III} complexes

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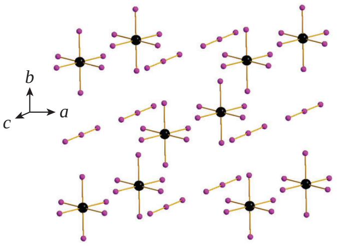
DOI: 10.1016/j.mencom.2022.07.028

Reactions of Sb_2O_3 or Bi_2O_3, 1,2-bis(4-pyridyl)ethane (bpe) and diiodine in concentrated HI resulted in isostructural salts $(H_2bpe)_2[MI_6](I_3)$ [M = Sb (1), Bi (2)] featuring perovskite-like arrangement of anions in crystal packing. Physical properties, including UV-Vis and Raman spectra, as well as thermal stability, were investigated and compared for this pair of complexes; the optical band gaps for 1 and 2 are 1.32 and 1.57 eV, respectively.



Keywords: bismuth, antimony, halide complexes, semiconductors, triiodides.

Homoleptic halide complexes (halometalates) are being investigated for decades.[1–3] This class demonstrates fascinating diversity of geometries[4–11] (alone for Bi^{III}, over 40 structural types of polynuclear anions are described yet[12]). However, the main factors promoting research in this field are the physical properties, such as catalytic activity (especially common for Cu[13–15] and Ag[16–19]), ferroelectric and ferroelastic behavior,[20–29] photochromism,[30–32] luminescence,[33–35] *etc*. Of special importance are the studies related to the use of iodometalates in photovoltaics. Those are mostly concentrated on Pb^{II} complexes,[36–42] but there also appear the works focused on the attempts to utilize iodide complexes of other p-block metals, such as Bi or Sb, in solar cells (in particular, assuming replacement of more toxic Pb^{II} by more environmentally friendly elements).[43–46] The efficiencies of such devices achieved yet are lower than for Pb^{II}-based ones,[43] but the progress in this field is evolving rapidly so, in our opinion, this topic deserves attention. Recently, it was shown[47–50] that iodometalates can form hybrid salts with di- or polyiodides. The latter are often interconnected with iodide ligands of iodometalate anions *via* halogen bonding to form 1D, 2D or even 3D supramolecular networks. Such hybrids commonly demonstrate narrow optical band gaps and relatively high thermal stability, making them favorable in terms of photovoltaic applications. There are a limited number of such examples known for Bi^{III} complexes,[47,50,51] while the Sb^{III} derivatives remain virtually unexplored. We hereby present the pair of iodometalate–triiodide hybrids – $(H_2bpe)_2[MI_6](I_3)$ [M = Sb (**1**), Bi (**2**), bpe = 1,2-bis(4-pyridyl)ethane]. These complexes are isostructural, enabling therefore the direct comparison of numerous physical properties relevant for materials science.

Synthetic procedures for **1** and **2** are given in Online Supplementary Material (SI). According to XRD,[†] the halometalate parts of both complexes consist of mononuclear $[MI_6]^{3-}$ anions. The M–I bond lengths are 2.994–3.023 and 3.041–3.077 Å. The $[MI_6]^{3-}$ are accompanied by symmetric triiodide anions (I–I = 2.921 and 2.922 Å, respectively). The most interesting feature of these structures is the mutual arrangement of anionic units (Figures 1 and 2): it can be considered as perovskite-like. Unlike in many other similar complexes,[47] the I···I non-covalent interactions between the iodide ligands and I atoms of I_3^- units are, most likely, absent (the shortest I···I distance is 4.140 Å in **1** and 4.192 Å in **2**, exceeding the sum of Bondi's van der Waals radii for two I atoms (3.98 Å[52]). At the same time, the distances between the terminal I atoms of the neighboring triiodide units (3.779 and 3.796 Å, respectively)

[†] *Crystal data for* **1**. $C_{24}H_{28}N_4SbI_9$ (M = 1636.35), monoclinic, space group $C2/m$, a = 16.0250, b = 14.5122 and c = 9.6130 Å, β = 122.177°, V = 1892.2 Å^3, Z = 2, μ(MoKα) = 8.09 mm^{-1}. Total of 19083 reflections were collected, and 3010 independent reflections (R_{int} = 0.039) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$]: R_1 = 0.020, wR_2 = 0.037.

Crystal data for **2**. $C_{24}H_{28}N_4BiI_9$ (M = 1723.58), monoclinic, space group $C2/m$, a = 16.0710, b = 14.5366 and c = 9.6310 Å, β = 122.053°, V = 1906.98 Å^3, Z = 2, μ(MoKα) = 11.93 mm^{-1}. Total of 15481 reflections were collected, and 4749 independent reflections (R_{int} = 0.023) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$]: R_1 = 0.019, wR_2 = 0.037.

The data were collected at 150 K on a Bruker D8 Venture diffractometer with a CMOS PHOTON III detector and IµS 3.0 source (MoKα radiation, λ = 0.71073 Å). Absorption correction was applied by SADABS (Bruker Apex3 software suite: Apex3, SADABS-2016/2 and SAINT, version 2018.7-2; Bruker AXS Inc., Madison, WI, 2017). The crystal structures were solved using the SHELXT[55] and were refined using SHELXL[56] programs with OLEX2 GUI.[57] Atomic displacement parameters for non-hydrogen atoms were refined anisotropically.

CCDC 2149682 and 2149683 contain 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.

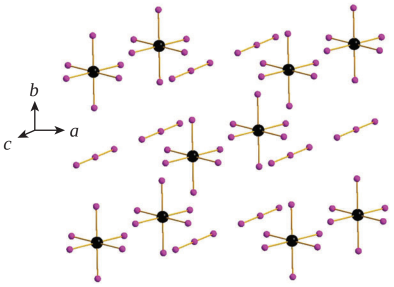


Figure 1 Mutual orientation of $[MI_6]^{3-}$ and I_3^- anions in **1** and **2**. M black, I purple.

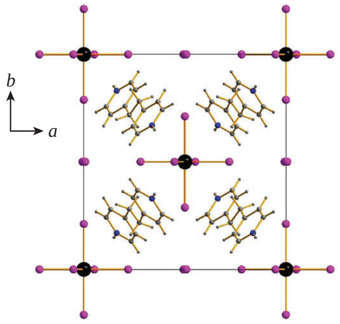


Figure 2 Crystal packing in **1** and **2**. C and H grey. N deep blue.

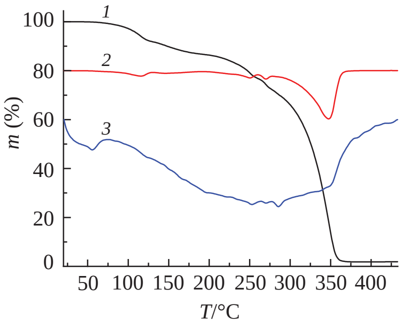


Figure 5 TG (*1*), DTG (*2*) and DTA (*3*) curves for **1**.

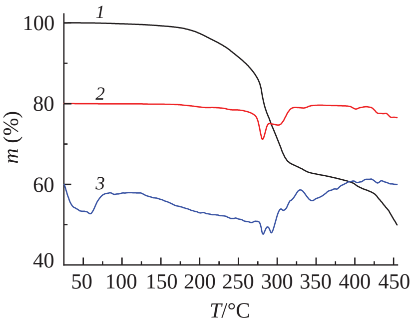


Figure 6 TG (*1*), DTG (*2*) and DTA (*3*) curves for **2**.

clearly indicate the presence of corresponding interactions so that I_3^- form infinite supramolecular chains $\{I_3\}_n$ (the I–I–I angles are 174.93° in **1** and 175.28° in **2**); similar motifs were described earlier in other triiodide-containing structures.[53]

As follows from PXRD data (see SI), both complexes can be isolated as pure phases. Considering that those are, as mentioned above, isostructural, they present an interesting opportunity to perform a straightforward comparison of diverse properties for Sb^{III} and Bi^{III} derivatives. The Raman spectra for **1** and **2** are shown in Figures 3 and 4, respectively. In both cases, the highly characteristic[53] band at 111 or 112 cm^{-1} corresponds to the vibrations of symmetric triiodide anion. The band at 103 cm^{-1} for **2** is related to ν_2 for $[BiI_6]^{3-}$; most likely, the band at 97 cm^{-1} (for **1**) is the same for $[SbI_6]^{3-}$ anion. All other modes at lower wavenumbers correspond presumably to other vibrations of iodometalate anions and translational vibrations in lattice.

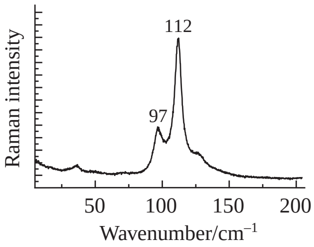


Figure 3 Raman spectrum of **1**.

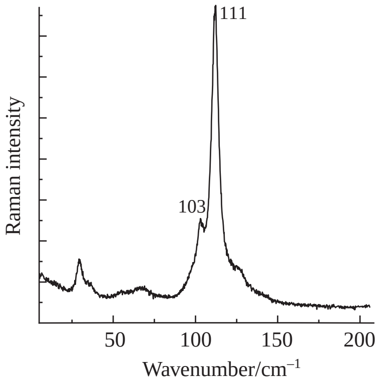


Figure 4 Raman spectrum of **2**.

The data of thermogravimetric analysis of **1** and **2** are shown in Figures 5 and 6, respectively. It can be seen that the antimony complex demonstrates lesser stability – its decomposition starts already at ~80 °C, and the first step corresponds to the loss of one iodine atom (obviously, as HI). Considering the fact that **1** and **2** are isostructural and the systems of non-covalent interactions in solid state are almost identical, it is highly unlikely that this process is related to destruction of triiodide anion – in such case, the decomposition patterns must be similar for **1** and **2**. We assume that the first stage involves simultaneous elimination of one iodide ligand of $[SbI_6]^{3-}$ and one proton of H_2bpe cations. On the one hand, this agrees with the fact that pentacoordinated halometalate species are more common and more stable for antimony than for bismuth. On the other hand, the literature data confirm[54] that halobismuthates(III) demonstrate, in general, greater thermal stability than corresponding haloantimonates(III).

The UV-Vis spectra for **1** and **2** are given in SI. The E_g values are 1.32 and 1.57, respectively. As expected, simultaneous presence of polyiodide and iodometalate species in the structure causes appearance of narrower band gaps (the same effect was described for polyiodo-iodometalates[47,48]).

To conclude, we prepared an isostructural pair of iodometalate/triiodide hybrids (combination of $[MI_6]^{3-}$ anions with $\{I_3\}_n^{n-}$ supramolecular chains) and compared their properties for M = Sb^{III} and Bi^{III}. While iodoantimonate features narrower optical band gap, it also demonstrates lesser thermal stability. Considering that these two parameters are among the most important for photovoltaics, such observations confirm that the balance between different characteristics is needed to be achieved. On the other hand, we demonstrated that polyiodide species are not necessarily connected to iodometalates *via* halogen bonding in solid state, as it appeared in other reports;[47] scenario of co-crystallization is also possible.

This work was supported by Russian Science Foundation (Grant No. 18-73-10040) and, in part, by Ministry of Science and Higher Education of the Russian Federation (structural characterization of the samples, 121031700313-8).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.028.

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Received: 28th February 2022; Com. 22/6813