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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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All reagents were obtained from commercial sources and used as purchased.

Preparation of 1

58 mg Sb_2O_3 (0.2 mmol), 147 mg (0.8 mmol) of bpe and 101 mg (0.4 mmol) of I_2 were dissolved in 5 ml of concentrated HI (70°C, 1 h). After that, solution was filtered and cooled to room temperature. Within 1 day, there form dark red crystals of **1**. Yield 74%. For $C_{24}H_{28}N_4SbI_9$ calcd, %: C, 17.61; H, 1.73; N, 3.43; found, %: C, 17.77; H, 1.76; N, 3.49.

Preparation of 2

The procedure was the same as for **1**, using 93 mg (0.2mmol) of Bi_2O_3. Within 1 day, there form dark cherry-red crystals of **2**. Yield 77%. For $C_{24}H_{28}N_4BiI_9$ calcd, %: C, 16.71; H, 1.64; N, 3.25; found, %: C, 16.82; H, 1.67; N, 3.31.

Raman spectroscopy

Raman spectra were collected using a LabRAM HR Evolution (Horiba) spectrometer with the excitation by the 633 nm line of the He-Ne laser. The spectra at room temperatures were obtained in the backscattering geometry with a Raman microscope. The laser beam was focused to a diameter of 2 micrometers using a LMPlan FL 50x/0.50 Olympus objective. The spectral resolution was 0.7 cm^{-1}. The laser power on the sample surface was about 0.03 mW.

Thermogravimetric analysis (TGA)

TGA were carried out on a TG 209 F1 Iris thermobalance (NETZSCH, Germany). The measurements were made in a helium flow in the temperature range of 30–450°C using the heating rate of 10°C min^{-1} the gas flow rate of 60 mL min^{-1} and open Al crucibles.

Diffuse reflectance spectra were measured on an setup which consists of a Kolibri-2 spectrometer (VMK Optoelektronica, Russia), fiber optic cable QR-400-7 (Ocean Optics, USA), and deuterium–tungsten lamp AvaLight-DHS (Avantes, Netherlands) (see V.R. Shayapov et al., New J. Chem. 2019, 43(9), 3927). The reference of 100% reflectance was $BaSO_4$ powder. The spectra were recorded five times in the wavelength interval of 300-1000 nm and then averaged

to reduce the random error. Kubelka-Munk function *F(R)* was calculated using diffuse reflectance spectra:

$$F(R) = \frac{(1-R)^2}{2R}, \quad (1)$$

where *R* is a diffuse reflectance coefficient. The Kubelka-Munch function represents as *k*/*s* ratio where *k* is absorption coefficient and *s* is a scattering coefficient:

$$F(R) \sim \frac{k}{s} \quad (2).$$

Energy band gap E_g was determined by the Tauc method. The dependence of the $\sqrt{F(R) \cdot E}$ value (where *E*=1240/λ is photon energy) *versus* E was plotted. The energy band gap was obtained by extrapolation of the linear portion of the dependence to the intersection with the energy axis.

Powder X-ray Diffractometry

XRD analysis of polycrystals was performed on Shimadzu XRD-7000 diffractometer (CuK-alpha radiation, Ni – filter, linear One Sight detector, 5 – 50° 2θ range, 0.0143° 2θ step, 2s per step). A polycrystalline sample was slightly ground with hexane in an agate mortar, and the resulting suspension was deposited on the polished side of a standard quartz sample holder, and a smooth thin layer being formed after drying. All diffraction peaks were indexed by structure data for **1** and **2** (Figures S1 and S2), demonstrating that the samples are single phase/pure.

Table S1. Details of XRD experiments for **1** and **2**

	1	**2**
Formula	$I_6Sb{\cdot}I_3{\cdot}2(C_{12}H_{14}N_2)$	$BiI_6{\cdot}I_3{\cdot}2(C_{12}H_{14}N_2)$
M_r	1636.35	1723.58
Crystal system, space group	Monoclinic, *C*2/*m*	Monoclinic, *C*2/*m*
a, *b*, *c* (Å)	16.0250 (14), 14.5122 (13), 9.6130 (8)	16.0710 (3), 14.5366 (3), 9.6310 (2)
β (°)	122.177 (3)	122.053 (1)
V (Å^3)	1892.2 (3)	1906.98 (7)
Z	2	2
μ (mm^{-1})	8.09	11.93
T_{min}, T_{max}	0.573, 0.746	0.530, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19083, 3010, 2761	15481, 4749, 4452
R_{int}	0.039	0.023
θ values (°)	θ_{max} = 30.5, θ_{min} = 2.1	θ_{max} = 36.4, θ_{min} = 2.1
(sin θ/λ)$_{max}$ (Å^{-1})	0.715	0.835
Range of *h*, *k*, *l*	*h* = −22 →22, *k* = −20 →20, *l* = −13 →13	*h* = −26 →25, *k* = −24 →24, *l* = −15 →16
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.020, 0.037, 1.07	0.019, 0.037, 1.09
No. of reflections, parameters, restraints	3010, 95, 0	4749, 99, 1
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.75	1.09, −1.13

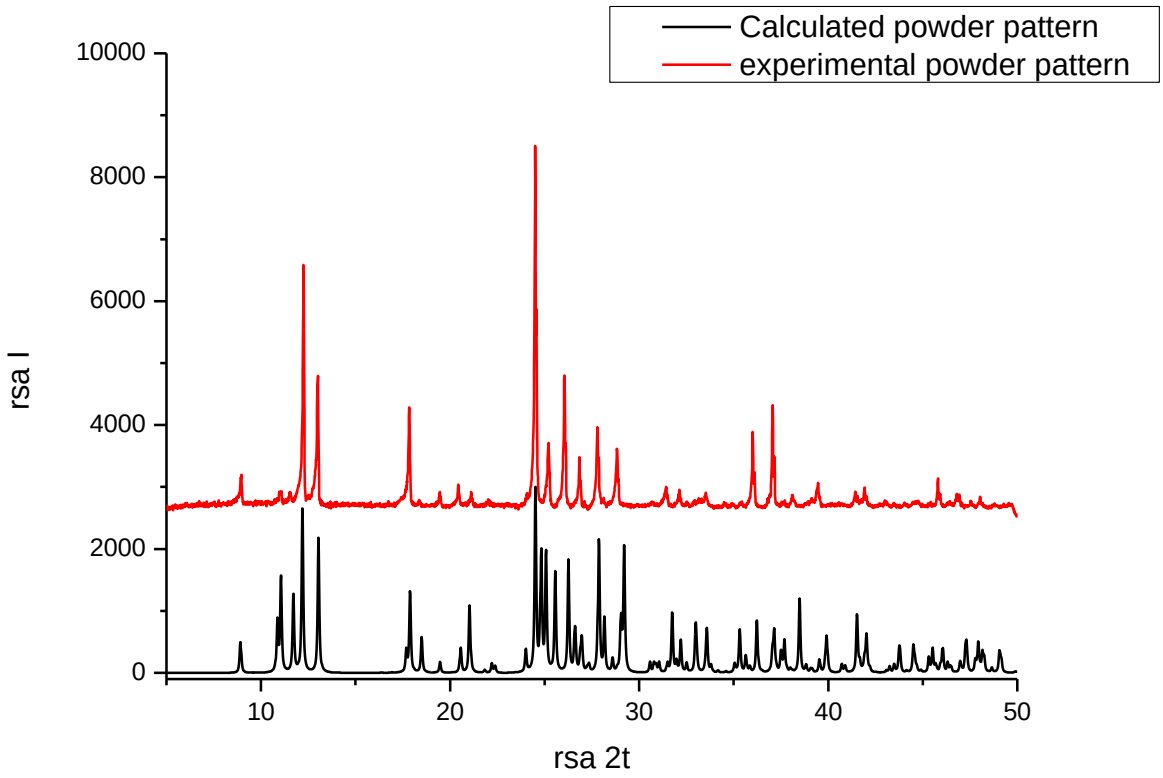

Figure S1. PXRD fata for **1**

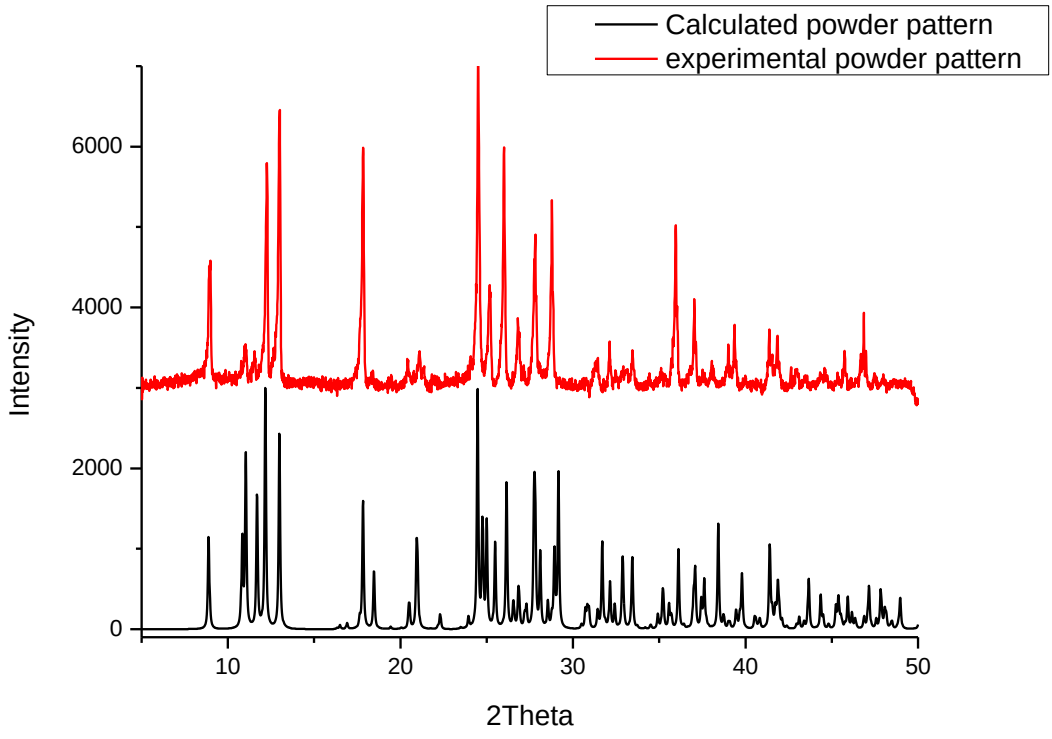

Figure S2. PXRD fata for **2**

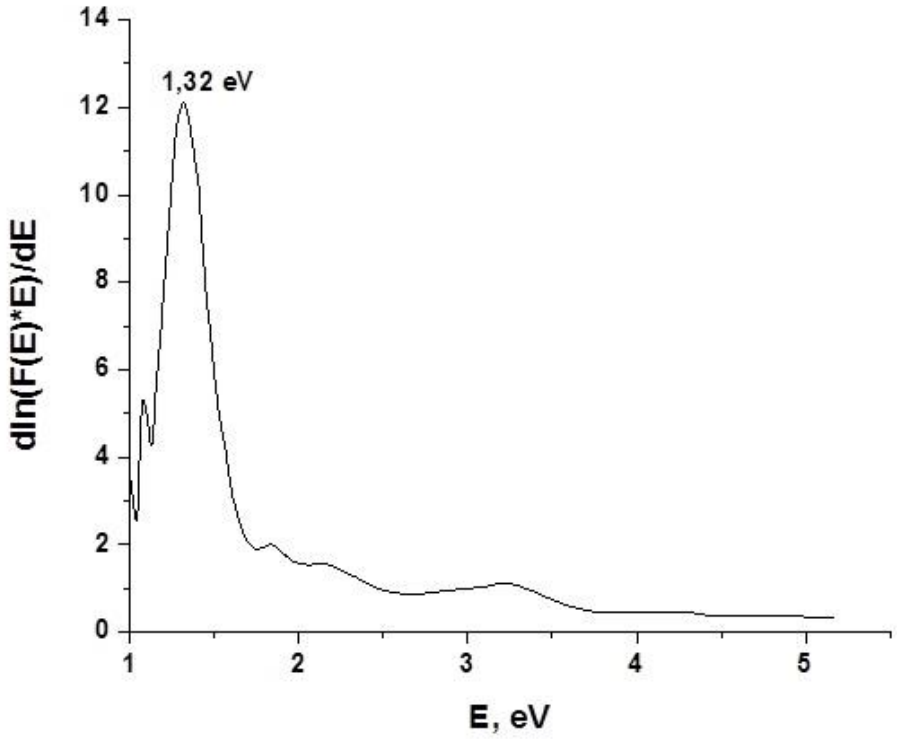

Figure S3. Optical band gap determination via Tauc coordinates for **1**

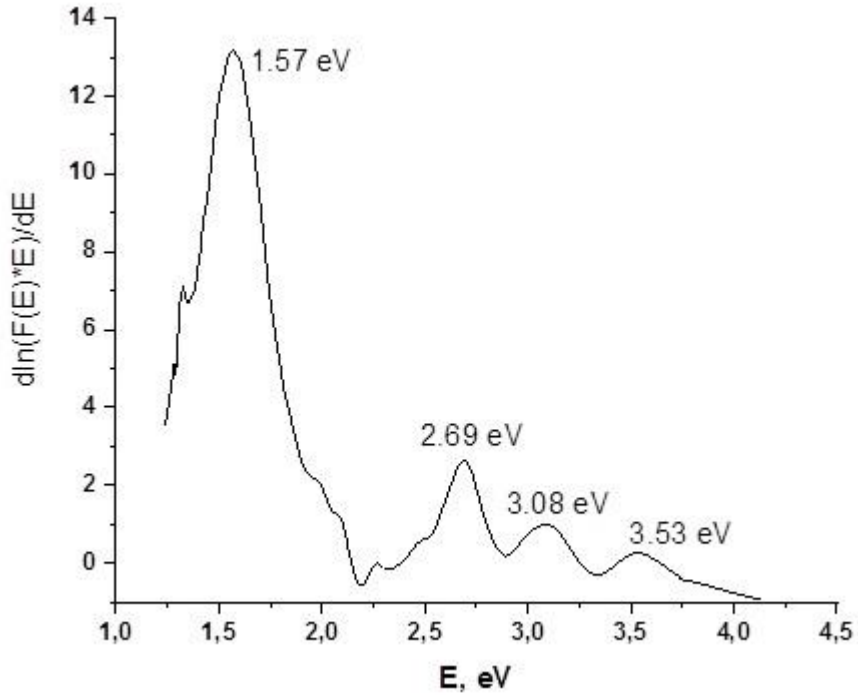

Figure S4. Optical band gap determination via Tauc coordinates for **2**