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

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Synthesis of 1

All reagents were obtained from commercial sources and used as purchased. 1-methyl-3-cloropyridinium iodide was prepared by reaction of 3-ClPy with MeI (1:1.05) with nearly quantitative yield.

46.6 mg (0.1 mmol) of Bi_2O_3, 76.6 мг (0.3 mmol) of 1-Me-3-ClPyI and 25 mg (0.1 mmol) of I_2 were dissolved in mixture of CH_3CN (3 ml) and concentrated HI (2 ml) (80°C, 1 h). After that, solution was cooled to room temperature. Partial evaporation of colvent (1 day) results in formation of dark crystals of **1**. Yield 73%. For $C_{18}H_{21}Bi_2Cl_3I_{11}N_3$ calcd, %: C, 9.83; H, 0.96; N, 1.91; found, %: C, 9.87; H, 0.99; N, 1.93.

X-ray Diffractometry. Crystallographic data and refinement details for **1** are given in Table S1. The diffraction data were collected on a New Xcalibur (Agilent Technologies) diffractometer with MoKα radiation (λ = 0.71073) by doing ϕ scans of wide (0.5°) frames at 140 K. Absorption correction was done empirically using SCALE3 ABSPACK (CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171.NET)). Structures were solved by SHELXT and refined by full-matrix least-squares treatment against |F|2 in anisotropic approximation with SHELXL 2017/1 in ShelXle program. The crystallographic data have been deposed with the Cambridge Crystallographic Data Centre under the deposition code CCDC 2167964.

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 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** (Figure S1), demonstrating that the samples are single phase/pure.

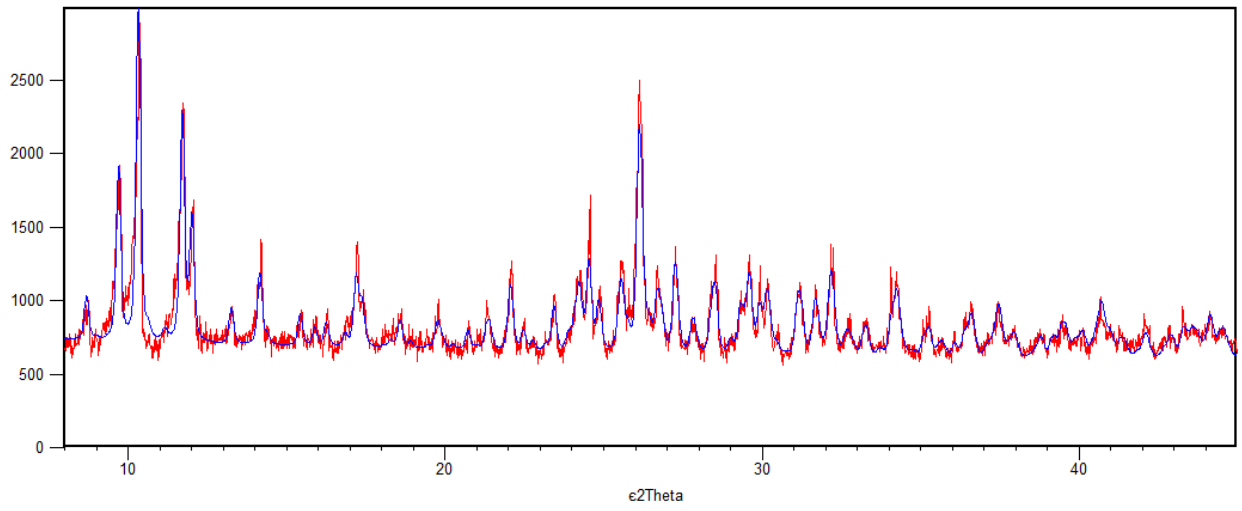

Figure S1. Experimental (red) and theoretical (blue) powder patterns of **1**

Table S1. Crystal data and structure refinement for **1**

	1
Empirical formula	$C_{18}H_{21}Bi_2Cl_3I_{11}N_3$
M, g/mol	2199.59
Crystal system, space group	Orthorhombic, $P2_12_12_1$
a,b,c, Å	11.0677 (4), 15.7489 (4), 24.9389 (7)
V, Å^3	4347.0 (2)
Z	**4**
μ (mm^{-1})	16.10
T_{min}, T_{max}	0.668, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14984, 8227, 7743
R_{int}	0.031
θ values (°)	θ_{max} = 25.7, θ_{min} = 2.0
Range of *h*, *k*, *l*	*h* = −13→11, *k* = −18→19, *l* = −28→30
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.063, 1.04
No. of reflections	8227
No. of parameters	334
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.37, −1.38