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Copper- and silver-containing heterometallic iodobismuthates(III) with 4-(dimethylamino)-1-methylpyridinium cation: structures, thermal stability and optical properties

Irina A. Shentseva, Andrey N. Usoltsev, Pavel A. Abramov, Vladimir R. Shayapov, Nikita A. Korobeynikov, Maxim N. Sokolov and Sergey A. Adonin

Experimental section

4-(dimethylamino)pyridine, BiI_3, acetonitrile, acetone and ethanol were obtained from commercial sources and used without additional purification. 1-methyl-4-(dimethylamino)pyridinium iodide was prepared by the reaction of 4-(dimethylamino)pyridine with methyl iodide, the product was identified by ^{1}H NMR spectra and elemental analysis data.

(1) $(MeDMAP)_2Bi_2Cu_2I_{10}$

30 мг BiI_3 (0.05 mmol), 9.5 mg CuI (0.05 mmol) and 12 mg (0.05 mmol) 1-methyl-4-(dimethylamino)pyridinium iodide were dissolved in 5 ml of a mixture of solvents CH_3CN/acetone (1:1) by heating to 70°C for 1 h. After dissolution, 5 ml of EtOH was added to the mixture. Then the solution was slowly cooled to room temperature and kept for 1 day. Dark red crystals were obtained. Product yield: 63 %. Elem anal. Calcd for $C_{16}H_{26}N_4Bi_2Cu_2I_{10}$, %: C 9.20; H 1.26; N 2.68; Found: C 9.25; H 1.31; N 2.72.

(2) $(MeDMAP)_2Bi_2Ag_2I_{10}$

15 mg BiI_3 (0.025 mmol), 6 mg AgI (0.025 mmol) and 6,5 mg (0.025 mmol) 1-methyl-4-(dimethylamino)pyridinium iodide were dissolved in 24 ml of a mixture of solvents CH_3CN/acetone (1:1) by heating to 70°C for 1 h. after dissolution, the mixture was slowly cooled to room temperature and kept for 1 day. After partial evaporation, red crystals were obtained. Product yield: 69%. Elem anal. Calcd for $C_{16}H_{26}N_2Bi_2Ag_2I_{10}$ C 8.82; H 1.20; N 2.57; Found: C 8.85; H 1.27; N 2.63.

Powder X-ray diffractometry

XRD analysis of polycrystalline samples 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). Samples were slightly ground with hexane in an agate mortar, and the resulting suspensions were deposited on the polished side of a standard quartz sample holder, and a smooth thin layer being formed after drying. Plotting of PXRD patterns (Figures 1S and 2S) and data treatment was performed using X'Pert Plus software.

Thermogravimetric analyses (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[72]. The dependence of the $\sqrt{F(R) \times E}$ value (where E=1240/λ is photon energy) *versus* **E** for **1** and $d[\ln(F(R) \times E)]/dE$ *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.

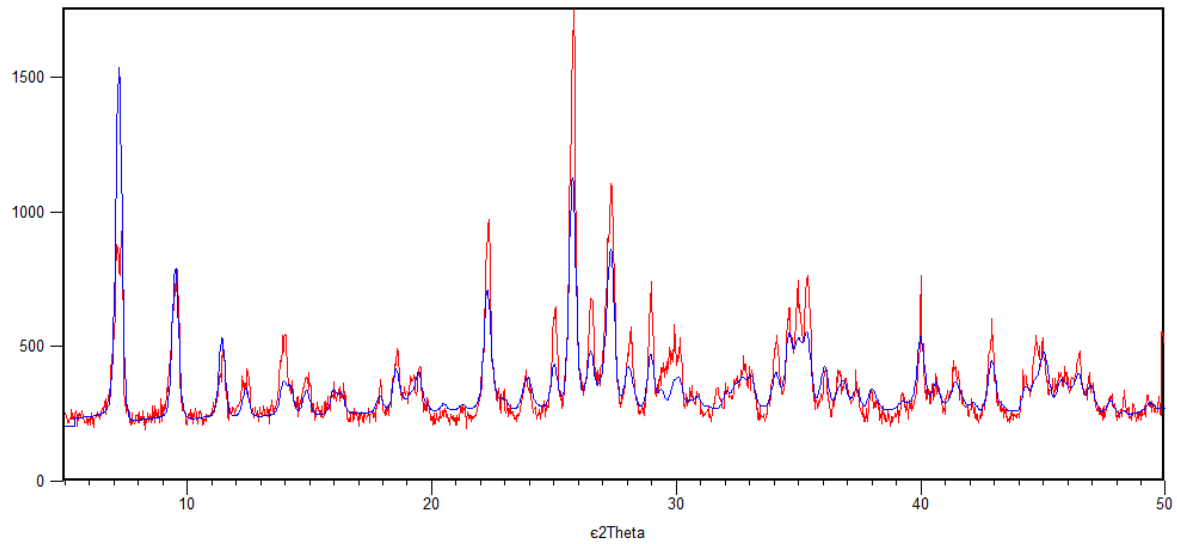

Figure S1. Calculated (blue) and experimental (red) PXRD patterns of **1.**

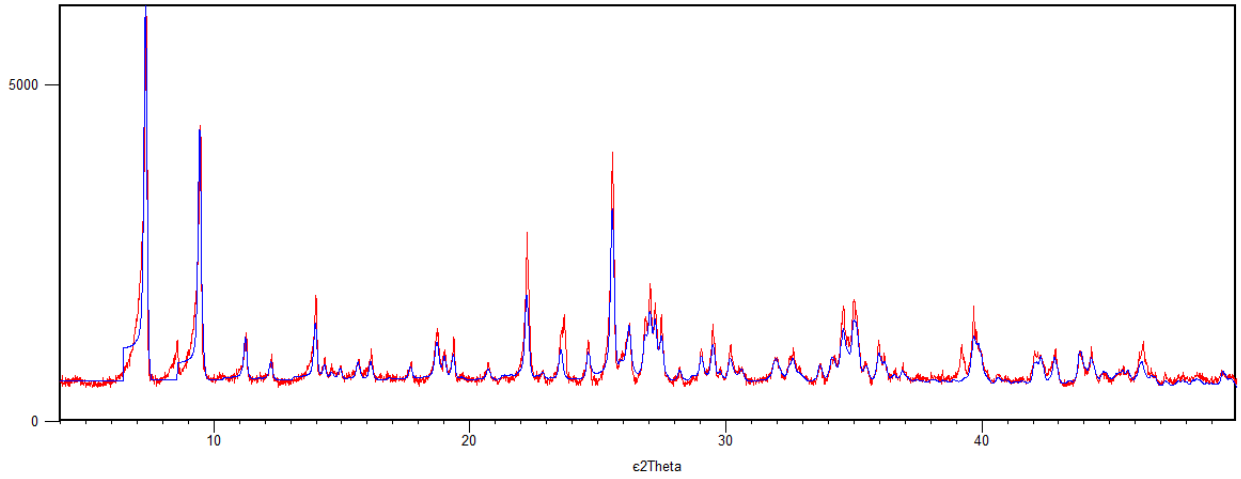

Figure S2. Calculated (blue) and experimental (red) PXRD patterns of **2.**