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

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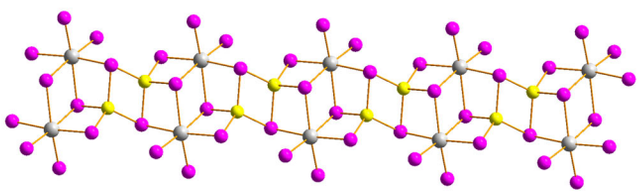
Reactions of BiI_3, copper or silver iodide and 4-(dimethylamino)-1-methylpyridinium iodide [(Me-DMAP)I] result in formation of heterometallic complexes $(MeDMAP)_2\{[Bi_2Cu_2I_{10}]\}$ and $(MeDMAP)_2\{[Bi_2Ag_2I_{10}]\}$. Their crystal structures, thermal stability and optical properties have been studied. Optical band gaps calculated from diffuse reflectance spectroscopy data are 1.81 and 2.06 eV for copper- and silver-containing complexes, respectively.



Keywords: bismuth, copper, silver, halide complexes, semiconductors.

During the last years, halide complexes of p-block metals receive much attention[1] due to their remarkable structural diversity[2–10] and applicability in materials science.[11–13] There are many exceptional physical properties useful for a wide range of applications, such as thermo-[14] and photochromism,[15,16] ferroelectricity and ferroelasticity,[17–20] luminescence,[21–25] *etc.*, but of special interest is the fact that iodometalates can be used as components of photovoltaic devices. The solar cells based on three-dimensional perovskite-like iodoplumbates[26–30] now demonstrate efficiencies exceeding 20%. However, toxicity of lead(II) and stability issues inspire research aiming at investigation of photovoltaic properties of other halometalates, in particular those of 15 group (Sb and Bi).[31] A promising way to create new materials of this type is combining of different p- and d-metals in the same anionic structure. An argument in favor of this approach is that homometallic iodoargentates[32–34] and iodocuprates[35–39] demonstrate photovoltaic and luminescent properties. The examples of Bi/Cu and Bi/Ag iodide[40–48] anionic complexes are known; in last years, large amount of work in this field has been done by the Heine's group.[49–54] However, the number of such studies is yet incomparable with one for homometallic iodometalates. Therefore, preparation and investigation of new heterometallic (Bi/Cu and Bi/Ag) complexes are well justified.

In this work, we describe a preparation of $(MeDMAP)_2Bi_2Cu_2I_{10}$ **1** and $(MeDMAP)_2Bi_2Ag_2I_{10}$ **2**. Synthetic procedures for **1** and **2** are given in Online Supplementary Materials (SI); the complexes were prepared with good (>60%) yields by reaction of BiI_3, CuI or AgI and MeDMAP iodide in acetonitrile/acetone/ethanol or acetonitrile/acetone mixtures, respectively. As follows from both element analysis and PXRD data (see SI), both compounds were isolated as pure single phases.

According to XRD,† **1** and **2** are isostructural. The anionic parts of both complexes are 1D polymeric. There are two dimeric $\{Bi_2I_{10}\}$ units connected *via* terminal and μ_2-iodide ligands with copper or silver atoms (Figure 1).

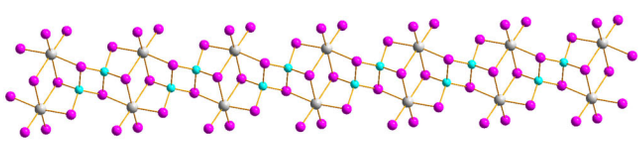


Figure 1 Anionic part in **1** and **2**. Bi white, I purple, heterometal cyan.

† *Crystal data for* **1**. $C_8H_{13}BiCuI_5N_2$ (M = 1044.22), triclinic, space group $P\bar{1}$, a = 8.1043(4), b = 10.1446(6) and c = 13.1303(7) Å, α = 108.118(5)°, β = 97.669(4)°, γ = 105.060(4)°, V = 963.37(10) Å^3, Z = 2, μ(MoKα) = 18.22 mm^{-1}. Total of 7006 reflections were collected, and 4119 independent reflections (R_{int} = 0.040) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$], R_1 = 0.044, wR_2 = 0.092.

Crystal data for **2**. $C_8H_{13}BiAgI_5N_2$ (M = 1088.55), triclinic, space group $P\bar{1}$, a = 8.2888(4), b = 10.2404(6) and c = 13.0507(7) Å, α = 108.116(2)°, β = 99.187(2)°, γ = 104.645(2)°, V = 983.84(9) Å^3, Z = 2, μ(MoKα) = 17.76 mm^{-1}. Total of 21719 reflections were collected, and 5963 independent reflections (R_{int} = 0.044) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$], R_1 = 0.026, wR_2 = 0.058.

The data were collected at 15 K. (**1**) New Xcalibur (Agilent Technologies) diffractometer with MoKα radiation (λ = 0.71073) by doing φ scans of narrow (0.5°) frames at 150 K. Absorption correction was done empirically using SCALE3 ABSPACK (CrysAlisPro, Agilent Technologies, Version 1.171.37.35). (**2**) 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 refined using SHELXL[56] in ShelXle[57] programs. Atomic displacement parameters for non-hydrogen atoms were refined anisotropically.

CCDC 2168549 and 2168550 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.

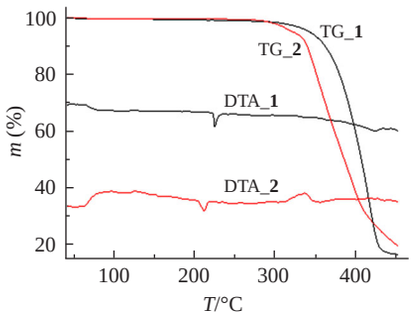


Figure 2 TG and DTA curves for **1** and **2**.

The lengths of Bi–I_{term} bonds in **1** are 2.892 and 2.913 Å. Cu–μ_2-I and Cu–μ_3-I distances are 2.638 and 2.640–2.651 Å, so the {CuI_4} tetrahedra are undistorted. The Bi–μ_2-I and Bi–μ_3-I are 3.046 and 3.161–3.304 Å, respectively. In **2**, lengths of corresponding bonds are very similar: Bi–I_{term} = 2.890 and 2.908 Å, Bi–μ_2-I = 3.070 Å, Bi–μ_3-I = 3.070 and 3.324–3.325 Å, respectively. Corresponding {AgI_4} tetrahedra are slightly distorted: Ag–μ_2-I and Ag–μ_3-I distances are 2.798 and 2.848–2.879 Å, respectively.

According to TGA data (Figure 2), both compounds are stable up to 270 °C, and there is only one prominent decomposition step (the processes at >200 °C detectable by DSC are, most likely, related to melting or other phase transition). High stability is favorable in terms of the potential applicability of **1** or **2** as photovoltaic materials.

Diffuse reflectance spectra are shown in Figure 3. The absorption edge is sharper in **2** spectrum. To determine the band gap, diffuse reflectance spectra were recalculated utilizing the Kubelka–Munk formula (Figures 4 and 5). The band gap for silver-containing compound is slightly higher than in cuprous derivative (2.06 *vs.* 1.81 eV in **1** and **2**, respectively), which is a common feature in a series Bi/Ag and Bi/Cu-based heterometallic iodides characterized so far.[9,43,46,47]

To conclude, we prepared two isostructural heterometallic complexes of bismuth with methylated dimethyammonium cation. Great thermal stability and promising optical properties make these compounds of interest for further research in terms of photovoltaic devices and/or, possibly, in photocatalysis.

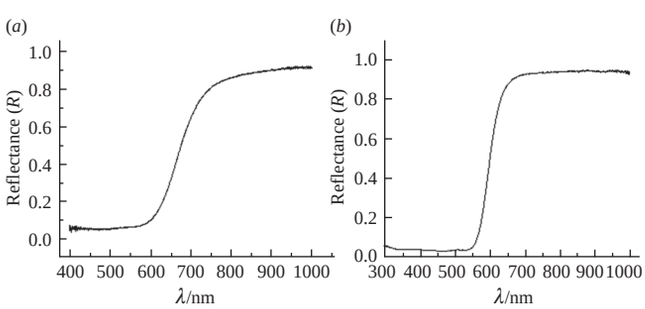


Figure 3 Diffuse reflectance spectra of complexes (*a*) **1** and (*b*) **2**.

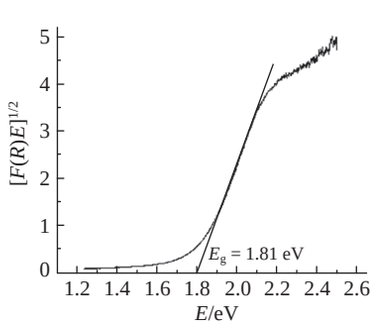


Figure 4 Band gap determination for **1** using Tauc coordinates.

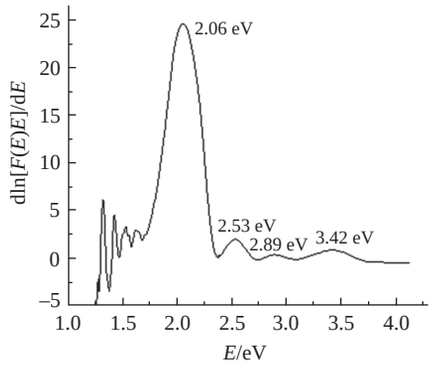


Figure 5 Band gap determination for **2** using Tauc coordinates.

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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.2022.11.015.

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