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Photochromic Crystals

Photochromism of a Methyl Viologen Bismuth(III) Chloride: Structural Variation Before and After UV Irradiation**

Gang Xu, Guo-Cong Guo, Ming-Sheng Wang, Zhang-Jing Zhang, Wen-Tong Chen, and Jin-Shun Huang*

Since the discovery of its reduction by Michaelis in 1932, viologen has been widely researched in biology, electrochemistry, photochemistry, and conductivity because of its electron-accepting nature.[1] One of the most interesting properties of viologen is its photoinduced color change, which derives from the photocatalyzed electron transfer to the viologen dication from the counter anion. Up to now, this property of viologen has mainly been found in liquid crystals, as well as solution and film systems, but rarely in crystalline solids.[1h,2] Although crystalline viologen complexes have been widely synthesized, few of are photochromic. The only known examples include the viologen polycyano–polycadmate complexes studied by Nishikiori and the viologen halides studied by Kamogawa, in which the crystal structures before irradiation by light were determined; however, no crystal structure after irradiation was studied.[3,4] It is important to obtain the structures of the same crystal before and after light irradiation for a better understanding of the mechanism of the photoinduced color change of a compound. In the course of our research on inorganic–organic hybrid materials,[5] we have synthesized a new kind of reversibly photochromic viologen hybrid, $(MV)Bi_2Cl_8$ (MV^{2+}: *N,N′*-dimethyl-4,4′-bipyridinium; methyl viologen), with metal halides as electron donors to MV^{2+} dications generated in situ. Herein, we report the synthesis, photochromism, and structures before (yellow, **1**) and after (black, **2**) UV irradiation of the same $(MV)Bi_2Cl_8$ single crystal.[6]

Compound **1** was obtained by the solvothermal reaction of $BiCl_3$ (200 mg, 0.64 mmol), 4,4′-bipyridine (60 mg, 0.38 mmol), methanol (10 mL), and concentrated HCl (1.0 mL, 36–38 %) at 120 °C. Unlike the syntheses of other viologen-based hybrids, in which the viologen cation was derived from the starting reagent, the preparation of **1** resulted in unprecedented in situ generation of the MV^{2+} dication. This opens a new route for the synthesis of viologen-based hybrid materials, and makes the synthesis of viologen comparatively less toxic and more efficient. The in situ formation of the MV^{2+} dication was confirmed by liquid chromatography–electrospray ionization mass spectrometry (LC-ESI-MS^n) and IR spectroscopy, and the purity of **1** was checked by a powder XRD study (see the Supporting Information).

Compounds **1** and **2** have the same crystal structure with only minor differences in molecular geometry. The crystal structure of **1** consists of infinite anionic $([Bi_2Cl_8]^{2-})_\infty$ double chains and MV^{2+} dications. There is only one crystallographically independent bismuth atom, which is coordinated by six Cl^- ions in a slightly distorted octahedral coordination environment. The Bi–Cl bond lengths can be divided into three kinds involving terminal, corner-sharing, and edge-sharing Cl^- ions with values of 2.5530(8), 2.7682(5), and 2.8682(7) Å, respectively, consistent with those found in other halogenobismuthates(III).[7] Two $BiCl_6$ octahedra share edges to form the fundamental building block, and such blocks further share corners to form a planar double chain extending along the *c* direction (Figure 1). Notably, although the chain-like structures of metal halides are well documented,[1e,3d,7c,8] the planar $([Bi_2Cl_8]^{2-})_\infty$ double chain described above represents, to the best of our knowledge, a new type of metal halide structure. The double-octahedral chains are cross-linked through interchain Cl···Cl interactions along the *a* and *b* directions to form a three-dimensional framework with channels, which accommodate the MV^{2+} dications (Figure 2). The shortest N···Cl distance of 3.441(1) Å is longer than the sum of the van der Waals radii, which indicates that there is no significant hydrogen-bonding between the inorganic and organic moieties.

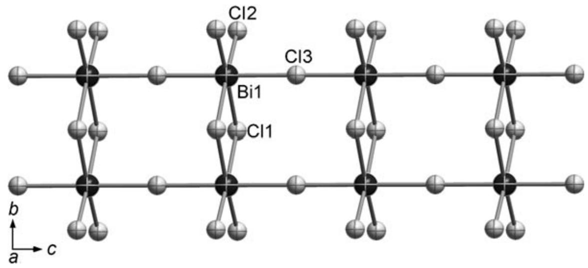

Figure 1. Planar double-octahedral chains of bismuth chloride for the title complex.

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[*] G. Xu, Prof. Dr. G.-C. Guo, Dr. M.-S. Wang, Z.-J. Zhang, Dr. W.-T. Chen, Prof. J.-S. Huang
State Key Laboratory of Structural Chemistry
Fujian Institute of Research on the Structure of Matter
Chinese Academy of Sciences
Fuzhou, Fujian 350002 (P.R. China)
Fax: (+86) 591-8371-4946
E-mail: gcguo@ms.fjirsm.ac.cn

G. Xu
Graduate School, Chinese Academy of Sciences
Beijing 100039 (P.R. China)

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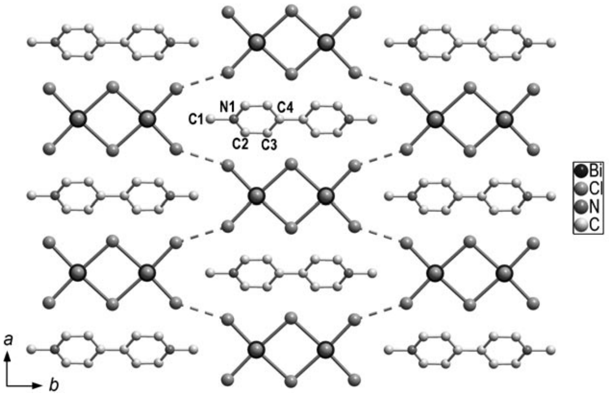

Figure 2. Crystal structure of the title complex, viewed along the *c* axis.

In comparison with the structure of **1**, in which the C−C and C−N bond lengths of MV^{2+} are consistent with those found in $(MV)Cl_2$, $(MV)Cu_2Cl_6$, and $(MV)Ni(CN)_4$,[3h,9] the C4−C4A (symmetry code A: $-x+1, -y, -z+1$) and C1−N1 bond lengths in the crystal structure of **2** are elongated by 0.040 and 0.018 Å, respectively, whereas the other distances tend to shrink slightly (see the Supporting Information). The largest change in bond angles of viologen between **1** and **2** is observed for C3-C4-C3B (B: $-x+1, y, -z+1$) with a value of 1.4°; however, the twist angle of the two aromatic rings remains invariant.

Compound **1** shows an interesting photochromic transformation from yellow to black upon UV irradiation, and color reversion is accomplished by heating (Figure 3). The yellow complex **1** is rather sensitive to light and even turns slightly black upon irradiation by sunlight for several hours. The threshold wavelength for the photoinduced transformation of **1** is 480 nm, and shorter wavelengths more readily develop the color change. The black complex **2** is stable and can be kept for over two months in air in a dark box. It undergoes complete reverse transformation to yellow crystals of **1** by heating at 130 °C in air; however, color reversion does not occur when heating is carried out in an argon atmosphere, which indicates that reverse transformation of **2** to **1** is significantly affected by temperature and the O_2 atmosphere.

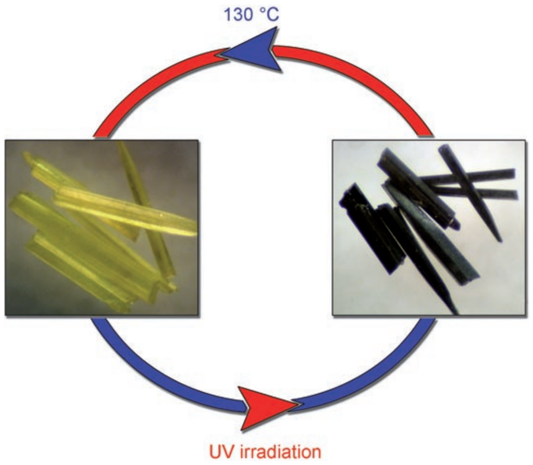

Figure 3. Photochromic properties of the title complex.

The production of $MV^{\bullet+}$ can be confirmed by UV/Vis spectroscopy and electron paramagnetic resonance (EPR) measurements. Two absorption bands appear at approximately 484 and 640 nm for **2**, which can be ascribed to the charge-transfer absorptions of monocation radical $MV^{\bullet+}$.[4a,b] EPR studies show that 1) before UV irradiation, no EPR signal is detected; 2) after UV irradiation, a symmetric EPR signal with a *g* value of 20000 is observed; and 3) after color conversion by heating, this EPR signal has disappeared again (see the Supporting Information), which indicates that the formation of monocation radical $MV^{\bullet+}$ is induced by UV irradiation and that $MV^{\bullet+}$ can be oxidized to MV^{2+} by O_2 at elevated temperatures.[1i,4b] The photochromism of the title complex arises from reversible interconversion between monocation radical $MV^{\bullet+}$ and dication MV^{2+}, which is similar to the cases found in some viologen compounds.[1i,4b]

Simple Hückel molecular orbital calculations indicate that for the lowest-energy vacant orbital (LUMO) in MV^{2+}, the largest changes in π charge density in the transformation from MV^{2+} to $MV^{\bullet+}$ occur at the N1 and C4 atoms,[3a] which implies that the metric parameters involving these two atoms may be expected to exhibit differences upon comparing **1** with **2**. This is first confirmed by single-crystal X-ray diffraction (XRD) experiments, which show that the bond lengths and angles around the C4 and N1 atoms, especially C4−C4A, change significantly when MV^{2+} is converted to $MV^{\bullet+}$. The shortest Cl···N contact of 3.441(1) Å in **1** is almost perpendicular to the methyl viologen rings at the N atom. This contact is significantly shorter than the Cl···N distance of 3.82 Å, which is the longest distance for charge transfer observed in viologen metal halides,[10] and suggests interactions between MV^{2+} and bismuth halide anions through the chlorine atoms. The shortest plane-to-plane separation of 5.536(1) Å excludes electron transfer between the methyl viologen units. Accordingly, the observed color change may originate from the electron transfer from the bismuth atoms in the $([Bi_2Cl_8]^{2-})_\infty$ chain to the MV^{2+} dication to form $MV^{\bullet+}$ by σ–π interaction, as is the case in other charge-transfer complexes of viologen.[3a,e,11]

In summary, we have prepared a new kind of viologen-based reversibly photochromic compound with metal halide as the charge donor, and the crystal structures before and after UV irradiation have been determined for the first time. The in situ formation of MV^{2+} in the title complex may serve as a more efficient approach for the synthesis of viologen-based hybrid materials.

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[6] a) Crystal data for **1**: $C_{12}H_{14}Bi_2Cl_8N_2$, $M = 887.81$, monoclinic, space group $C_{2/m}$ (no. 12), $a = 9.583(2)$, $b = 21.889(4)$, $c = 5.536(1)$ Å, $\beta = 100.78(3)°$, $V = 1140.8(4)$ Å^3, $T = 293(2)$ K, $Z = 2$, $\mu(\mathrm{Mo}_{K\alpha}) = 16.341$ mm^{-1}, 3864 reflections measured, 1079 unique, $R(F) = 0.0206$ and $R_W(F^2) = 0.0468$. b) Crystal data for **2**: $C_{12}H_{14}N_2Bi_2Cl_8$, $M = 887.81$, monoclinic, space group $C_{2/m}$ (no. 12), $a = 9.550(2)$, $b = 21.850(3)$, $\mathrm{c} = 5.525(1)$ Å, $\beta = 100.718(6)°$, $V = 1132.7(3)$ Å^3, $T = 293(2)$ K, $Z = 2$, $\mu(\mathrm{Mo}_{K\alpha}) = 16.341$ mm^{-1}, 3737 reflections measured, 1069 unique, $R(F) = 0.0288$ and $R_W(F^2) = 0.0681$. CCDC-632699 and -632700 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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