Gold(I)/Gold(III) Perovskites

Organic-Based Layered Perovskites of Mixed-Valent Gold(I)/Gold(III) Iodides[**]

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One of the most appealing handles in the design and synthesis of multifunctional hybrid materials is the wide choice of available molecular building blocks, in which one can combine properties that are often difficult to achieve in extended solids. The choices are often guided by the desire to combine distinct properties attributable to each organic and inorganic component.[1–2] Critical to the design of organic–inorganic hybrid materials is the control and exploitation of relevant supramolecular and noncovalent interactions. The establishment of a clear understanding of tunable noncovalent interactions useful for the design of complex supramolecular architectures is currently a growing field of research.[3]

Organic cations combined with polarizable inorganic moieties, such as heavy-metal halides (Br and I) and polyhalides, provide interesting chemical systems where moderately strong noncovalent interactions can be investigated. Recent investigations on heavy metal iodide and polyiodide systems have revealed surprising results, including complex supramolecular structures, unprecedented physical properties, and novel chemical bonding descriptions.[4–5]

Mixed-valent gold(I/III) halides, such as $Cs_2Au_2X_6$, have received significant attention because of their similarities with $BaBiO_3$ and its superconducting derivatives.[6] The crystal structure of $Cs_2Au^{I}Au^{III}X_6$ (X = Cl, Br, I) can be derived from a tetragonal distortion of the cubic perovskite ABX_3 structure, in which the network of corner-shared ABX_6 octahedra disproportionates into distinct BX_2 (linear $Au^{I}I_2^-$) and BX_4 (square planar $Au^{III}I_4^-$) units.[7–11] The class II mixed-valent perovskites of $BaBiO_3$ and $Cs_2Au_2X_6$ have been shown to exhibit interesting optical and electronic behavior, as well as, novel transport properties by substitution (doping) or application of high pressures, respectively.[6–8]

The introduction of mixed valency in the inorganic components of hybrid materials, thus providing another handle in modulating their electronic properties, has remained relatively unexplored. Attempts to prepare organic-based analogues of Au^{III} and mixed-valent $Au^{I/III}$ halides were reported as early as 1914.[12] However, the poorly crystalline dark solids obtained from these studies were not structurally characterized and were incompletely analyzed. Surprisingly, no investigations were subsequently reported to confirm or rectify the results of the initial studies.[12] Our exploratory studies, aimed at preparing new hybrid compounds of mixed-valent gold (I/III), led to the synthesis and characterization of two new organic-based mixed-valent $Au^{I/III}$ iodides: $[NH_3(CH_2)_8NH_3]_2[(Au^{I}I_2)(Au^{III}I_4)(I_3)_2]$ (**1**) and $[NH_3(CH_2)_7NH_3]_2[(Au^{I}I_2)(Au^{III}I_4)(I_3)_2]$ (**2**).

The monoclinic crystal structure of **1** (Figure 1) features layers of corner-shared nominal AuI_6 octahedra stacked along the *a* axis, with interlayer distances of 15.5 Å.[13] Adjacent perovskite gold iodide layers are displaced by 5.8 Å along the *c* axis. Each inorganic sheet features two nonequivalent Au atoms corresponding to mixed-valent $Au^{I/III}$ iodide ions of linear $[Au^{I}I_2]^-$ and square-planar $[Au^{III}I_4]^-$ units. Tetragonally compressed nominal octahedron around each $[Au^{I}I_2]^-$ unit is completed by four coplanar iodide ions ($d_{Au^{I}\cdots I} = 3.278(1\ \text{Å})$) from neighboring $[Au^{III}I_4]^-$ units. Similarly, an elongated octahedra around each $[Au^{III}I_4]^-$ unit is completed by two apical iodine atoms ($d_{Au^{III}\cdots I} = 3.752(7\ \text{Å})$) from I_3^- ions sandwiched between the gold iodide layers. The observed structural behavior, typical for mixed-valent gold (I/III) halides, has been described as a breathing-mode distortion.[10] It is noteworthy that the I_3^- ions directed at the nearest $[Au^{III}I_4]^-$ units are strongly polarized ($d_{I\text{-}I} = 2.798(3)$, $3.093(4\ \text{Å})$). To our knowledge, this is the first report of polyiodides taking part in a network of mixed-valent $Au^{I/III}$. The organic dications, oriented nearly perpendicular to the inorganic layers, are confined between anionic sheets and tethered by parallel triiodide molecules.

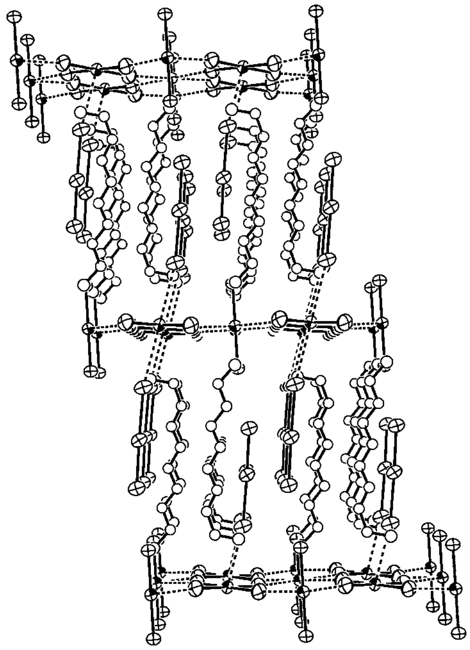

Figure 1. A [010] view of the crystal structure of (**1**). Gold and iodine atoms are represented as octant-shaded and crossed-hatched ellipsoids (75%), respectively. Light atoms are represented as small open spheres (C) and open ellipsoids (N).

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The crystal structure of **2** (Figure 2) is similar to that of **1**.[14] The significant structural differences between **1** and **2** are effected by the different conformations of the organic cations. The organic dications in **2**, $(NH_3(CH_2)_7NH_3)^{2+}$, have completely staggered *anti* conformations, but the $(NH_3(CH_2)_8NH_3)^{2+}$ dications in **1** exhibit a *gauche* conformation at the terminal amine closest to the inorganic layers. The molecular conformations result in nearly identical cation lengths of 10.13 and 10.04 Å for **1** and **2**, respectively. Compound **2** exhibits shorter noncovalent Au···I distances: $d_{\mathrm{Au^{III}\cdots I}} = 3.500(3$ Å, $d_{\mathrm{Au^{I}\cdots I}} = 3.235(3)$ and 3.248(3 Å. The polarization of I_3^- ions in **2** is also enhanced with $d_{\mathrm{I-I}} = 2.794(2)$, 3.103(2) Å. Attempts to prepare layered derivatives with other diamine homologues have been unsuccessful. The observed structural behavior of **1** and **2** affirms the crucial role of organic cation templates in the structural stability and flexibility of hybrid layered perovskites.[15] Different dication conformations also result in different cation–triiodide layered arrangements in **1** and **2**. Denser cation–triiodide arrangements in **2** result in greater buckling of the inorganic layer, as reflected by greater tilt between the nominal $Au^{III}I_6$ and $Au^{I}I_6$ octahedra. The pillaring of the mixed-valent gold-iodide perovskite layer by I_3^- units also results in nonbonding (I···I) contacts between the terminal iodide ions of the AuI_2^- and I_3^- units of 3.75 Å in **1,** and 3.56 Å in **2**.

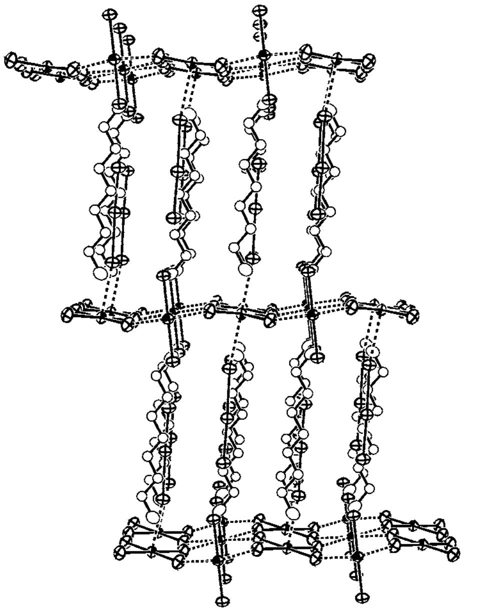

Figure 2. A [010] view of the crystal structure of (**2**). Gold and iodine atoms are represented as octant-shaded and crossed-hatched ellipsoids (75%), respectively. Carbon and nitrogen atoms are represented as small open spheres and open ellipsoids, respectively.

Compounds **1** and **2** differ from $Cs_2Au_2I_6$ in that the nominal octahedral coordination of the Au^{III} center in **1** and **2** is completed by two asymmetric I_3^- units, as illustrated in Figure 3. The perovskite structure of $Cs_2Au_2I_6$ is more 3D than that exhibited by **1** and **2**. Noncovalent Au···I distances in $Cs_2Au_2I_6$ are: $d_{\mathrm{Au^{III}\cdots I}} = 3.460(3)$ Å; $d_{\mathrm{Au^{I}\cdots I}} = 3.212(2)$ Å are slightly shorter. However, the Au–I bond lengths for the AuI_2^- and AuI_4^- units in **1**, **2** and $Cs_2Au_2I_6$ are very similar. It has been shown that I_3^- structurally and electronically substitutes for the $[AuI_2]^-$ unit in some $[AuI_4]^-/[AuI_2]^-$ derivatives to form $[AuI_4]^-/I_3^-$ analogues.[3,16] The electronic behavior of the I_3^- ion differs from $[AuI_2]^-$ ion with respect to charge-transfer interactions.

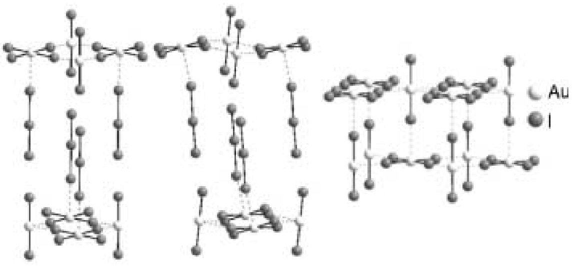

Figure 3. Representation of the inorganic substructures of **1** (left), **2** (center) and $Cs_2Au_2I_6$ (right). Gold and iodine atoms are shown as light and dark spheres, respectively. The structural parameters for $Cs_2Au_2I_6$ were obtained from reference [10].

Charge transfer in $Cs_2Au_2I_6$ and analogous $Au^{I/III}$ halides was reported to predominantly occur within $[AuI_2–AuI_4]$ perovskite layers, similar to the sheets observed in **1** and **2**.[17] Thus it is reasonable to expect that **1** and **2** would still preserve the most important electronic interactions present in the inorganic parent perovskites. Diffuse reflectance measurements indicate optical band gaps of 1.14 and 0.95 eV for **1** and **2**, respectively.[18] These values compare with the reported optical band gap of 1.31 eV for $Cs_2Au_2I_6$.[20] The unexpectedly narrower band gaps of **1** and **2** can be attributed to induced electronic interactions between I_3^- and the $AuI_2^-–AuI_4^-$ perovskite layers absent in $Cs_2Au_2I_6$. The polarization and subsequent distortion of the I_3^- ions in **1** and **2** manifests the relative strength of the interactions. DFT calculations on **2** reveal a net dipole moment of 2.18 D for I_3^-, with the more negative end of I_3^- ion directed towards the Au^{III} center. The calculated molecular electrostatic potential surface indicates an asymmetric distribution of the electron densities suggesting the possibility of I_2 removal. The DFT calculations on **2** also indicate that the $AuI_2^-–I_3^-$ interactions are significantly weaker than the $AuI_4^-–I_3^-$ interactions. Although structural similarities between the $[AuI_2]^-$ and $[I_3]^-$ units are substantial, subtle differences in their electronic behavior provides an additional handle in fine tuning the electronic properties of mixed-valent gold iodides.

Thermogravimetric analysis (TGA) was performed on **2** to assess compound stability and the possibility of I_2 removal. The first step in the TGA curve occurs above 85 °C and is consistent with the loss of an equivalent of I_2, according to the following reaction [Eq(1)]:

$$\begin{aligned}&[NH_3(CH_2)_7NH_3]_2[(Au^{I}I_2)(Au^{III}I_4)(I_3)_2]\\ &\quad\rightarrow [NH_3(CH_2)_7NH_3]_2[(Au^{I}I_2)(Au^{III}I_4)(I_3)(I)] + I_2 \end{aligned} \qquad (1)$$

Decomposition occurs above 155 °C, forming metallic gold and Au^{I} iodides.

Our findings reveal the exciting potential of organic-based mixed-valent gold(I/III) iodide polyiodides as tunable electronic materials. An intriguing possibility is the pillaring of the perovskite layers with other polyiodides and appropriate organic cations. Moreover, hybrid gold iodide polyiodides provide interesting chemical systems wherein significant noncovalent interactions and hyperpolarizabilities may be systematically investigated and exploited. The complete characterization of their electronic structures and measurement of the more relevant physical properties of these and other related compounds are currently in progress.

Experimental Section

A solution of $HAuCl_4$ (1 mL, 0.05 mol L^{-1}) was treated with stoichiometric amounts of 1,8-diaminooctane and 1,7-diaminoheptane. Six drops of iodine solution (5% w/w) in concentrated HI were added and a black precipitate was readily obtained. Shiny black crystals were recovered after the reaction mixture was left undisturbed for 4–6 weeks. The same compounds were also synthesized, in high yield, through solid-state reactions by using stoichiometric amounts of AuI, the corresponding amine, and excess I_2 (~10×) in sealed glass tubes under vacuum. The reaction tubes were heated to 160 °C for 10 days and slowly cooled to room temperature. The solution method yielded well-crystallized samples suitable for single-crystal X-ray diffraction. Chemical composition was confirmed by elemental analysis and results agree with theoretical values within the experimental error.[21] Magnetic susceptibility of **1**, measured from 5 to 300 K, corresponds to normal diamagnetic behavior.[22] All theoretical calculations on the triiodide molecule were performed by using the Gaussian 98 software package. All calculations made use of the B3LYP hybrid functional and the Stuttgart-group basis set as implemented on Gaussian 98.[23] TGA was carried out on a SIEKO TG/DTA 320 instrument. The sample was heated at a rate of 2 °C min^{-1} under a flowing nitrogen atmosphere.

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[13] Crystallographic data for $[NH_3(CH_2)_8NH_3]_2[(AuI_2)(AuI_4)(I_3)_2]$: monoclinic, space group $C2/m$ (no.12), $a = 32.1710(6)$, $b = 7.7846(2)$, $c = 8.8640(2)$ Å, $\beta = 103.17(0)°$, $V = 2161.46(2)$ Å^3, $\rho_{calc} = 3.395$ g cm^{-3}, $Z = 2$, $F(>4\sigma) = 1908$, $\lambda = 0.71073$ Å, $T = 223$ K, 6797 measured reflections, 2662 independent reflections. Single-crystal X-ray analysis was performed by using a Siemens SMART diffractometer equipped with a 1 K CCD area detector. Empirical absorption correction was applied by using ψ-scans. The structures were solved by direct methods and refined by full-matrix least-squares calculations. Thermal parameters of all non-H atoms were treated anisotropically. Hydrogen atoms were located at ideal positions using a riding model. All calculations were made by using the Siemens SHELXTL crystallographic package resulting in $R(\text{int}) = 0.0555$, $R_1 = 0.0388$, $wR_2 = 0.1006$.[24]

[14] Crystallographic data for $[NH_3(CH_2)_7NH_3]_2[(AuI_2)(AuI_4)(I_3)_2]$: triclinic, space group $P\bar{1}$ (no. 2), $a = 7.8197(1)$, $b = 8.6794(1)$, $c = 15.9093(2)$ Å, $\alpha = 80.87(0)°$, $\beta = 77.22(0)°$, $\gamma = 89.50(0)°$, $V = 1039.29(64)$ Å^3, $\rho_{calc} = 3.485$ g cm^{-3}, $Z = 1$, $F(>4\sigma) = 2844$, $\lambda = 0.71073$ Å, $T = 223$ K, 6478 measured reflections, 4490 symmetry-independent reflections. Empirical absorption correction was applied using SADABS. $R(\text{int}) = 0.0385$, $R_1 = 0.0534$, $wR_2 = 0.1423$. CCDC-197203 and CCDC 197204 (**1** and **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[18] Optical diffuse reflectance measurements were made at room temperature for pure samples of compounds **1** and **2** by using a Cary 500 double beam, double monochromator spectrometer. Several single crystals were placed on a sample holder within a Praying-Mantis apparatus. Polytetrafluoroethylene was used as a standard background reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka-Munk function:[19] $[\alpha/S = (1-R)^2/2R]$, where R is the reflectance at a given wavelength, α is the absorption coefficient and S is the scattering coefficient. The electronic excitation energy, E_g, is extracted from the $(\alpha/S)^2$ versus energy plot.

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[21] Chemical analysis was performed by SEM. Crystalline samples were placed on an adhesive carbon tape attached to a brass disk. No carbon coating was necessary for these narrow band gap semiconductors. The samples were then bombarded with a 15 eV electron beam over at least 15 1-micron diameter areas, to determine the elements present and to then average the ratio of gold and iodine. Compositional precision was found to be within 5% error. Data was collected by using a JEOL JSM 6400 scanning electron microscope equipped with a wave-dispersive spectrometer (WDS).

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