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Layered Organic-Based Metal Iodide–Polyiodide with Unique Mixed-Valent Gold(I/III) Iodide Chains

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We report the synthesis, optical spectrum, and crystal and electronic structures of a new organic–inorganic hybrid compound, $[(p\text{-}NH_3C_6H_4)_2CH_2]_4[(AuI_2)(AuI_4)(I_2)_2(I_5)_2Cl_4]$, with unique mixed-valent gold(I/III) chains. The chains feature face-shared octahedral $[Au^IAu^{III}I_6]^{2-}$ units and are embedded within polyiodide layers. The new mixed-valent gold iodide crystallizes in the orthorhombic space group *Pnnm*, with $a = 27.0703(2)$, $b = 8.9363(5)$, $c = 18.4280(1)$ Å, $Z = 2$, and exhibits an optical band gap of 0.53 eV.

The desire to create and effectively control the synthesis of new molecular architectures has yielded remarkable examples of organic–inorganic supramolecular arrays that exhibit novel structures in the solid state.[1] These efforts are motivated by the need for multifunctional materials with enhanced physical properties that address the needs of new optical and electronic devices.[2]

Polyiodides are well-known for their ability to form extended networks and exhibit unique transport and optical properties.[3] The ability to predict solid-state structures of metal iodide–polyiodides is largely empirical.[4,5] This is particularly the case for transition metal iodide–polyiodides because of the scarcity of known compounds.[6] Moreover, modern bonding theories on the nature of weak chemical interactions have not been extensively applied to polyiodides.

Organic molecules have been widely employed to template unusual polyiodide networks.[7] Recently, organic-based gold(III) iodides were reported to form supramolecular networks with polyiodides.[8] The systematic incorporation of gold iodide units within polyiodide networks allows for the modulation of their structural and electronic properties.[9] Organic-based metal iodide–polyiodides are expected to exhibit unusual structures and optical properties resulting from the synergism between hyperpolarizable molecular components.[10] Organic-based metal iodide–polyiodides also provide unique chemical systems wherein important noncovalent interactions can be investigated and exploited.[7] In addition, mixed valency in gold iodides further adds a handle in tuning their electronic properties.[9] The pseudo-one-dimensional mixed-valent Au(I/III) chains in $[AuX_2(DBS)]$ (DBS = dibenzylsulfide, X=Cl, Br) are based on halogen-bridged square-planar complexes of gold and were reported to exhibit novel electronic and structural transitions.[11]

Most of the mixed-valent gold(I/III) halides have structures that are related to the perovskite structure. These distorted 3D perovskites, $CsAuX_3$ (X=Cl, Br, I), are formulated as disproportionations into $Cs_2Au^IAu^{III}X_6$.[12] Recently, the use of alkyldiamine cations as templates for a class of tunable mixed-valent gold(I/III) iodide–triiodide layered perovskites was reported.[9] Efforts aimed at preparing organic-based mixed-valent gold(I/III) iodide–polyiodides culminated in the synthesis of an unprecedented hybrid compound, bismethylenedianilinium diiodoaurate tetraiodoaurate bis-iodine bis-pentaiodide tetrachloride, $[(p\text{-}NH_3C_6H_4)_2CH_2]_4[(AuI_2)(AuI_4)(I_2)_2(I_5)_2Cl_4]$ **(1)**. It features unique chains of face-shared octahedra of mixed-valent $Au^{I/III)}I_{6/2}$ that form layers with polyiodide I_5^- and I_2 molecules.

The title compound was prepared from a solution of $HAuCl_4$ (1 mL, 0.05 mol L^{-1}) that was reacted with a stoichiometric amount of *p*-methylenedianiline. A homogeneous black precipitate was readily obtained upon addition of 10 drops of 2.8 M HI solution, saturated with I_2, and 6 drops of 12 M HCl. Lustrous black crystals were recovered after the reaction mixture had been allowed to sit undisturbed for

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(1) (a) Gier, T. E.; Stucky, G. D. *Nature* **1991**, *349*, 508. (b) Mitzi, D. B.; Wang, S.; Feild, C. A.; Chess, C. A.; Guloy, A. M. *Science* **1995**, *267*, 1473. (c) Tang, Z.; Guloy, A. M. *J. Am. Chem. Soc.* **1999**, *121*, 452.

(2) (a) Lacroix, P. G.; Clement, R.; Nakatani, K.; Zyss, J.; Ledoux, I. *Science* **1994**, *263*, 658. (b) Takada, J.; Awaji, H.; Koshioka, M.; Nakajima, A.; Nevin, W. A. *Appl. Phys. Lett.* **1992**, *61*, 2184.

(3) Marks, T. J.; Kalina, D. W. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; vol. 1, 197.

(4) Soehnel, T.; Brown, R.; Kloo, L.; Schwerdtfeger, P. *Chem. Eur. J.* **2001**, *7*, 3167.

(5) Soehnel, T.; Hermann, H.; Schwerdtfeger, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 4382.

(6) Schulz, E.; Straehle, J. *Z. Anorg. Allg. Chem.* **1996**, *622*, 981.

(7) Mitzi, D. B. *Prog. Inorg. Chem.* **1999**, *48*, 1.

(8) Svensson, P. H.; Rosdahl, J.; Kloo, L. *Chem. Eur. J.* **1999**, *5*, 305.

(9) Castro, L. M. C.-; Guloy, A. M. *Angew.* Chem., Int. Ed. **2003**, *42*, 2771.

(10) Guloy, A. M.; Tang, Z.; Miranda, P. B.; Srdanov, V. I. *Adv. Mater.* **2001**, *13*, 833.

(11) (a) Takahashi, K.; Tanino, H. *Chem. Lett.* **1988**, 641. (b) Tanino, H.; Holtz, M.; Hanfland, M. Syassen, K. *Phys. Rev.* **1989**, *B39*, 9992.

(12) Kojima, N.; Hasegawa, M.; Kitagawa, H.; Kikegawa, T.; Shimomura, O. *J. Am. Chem. Soc.* **1994**, *116*, 11368.

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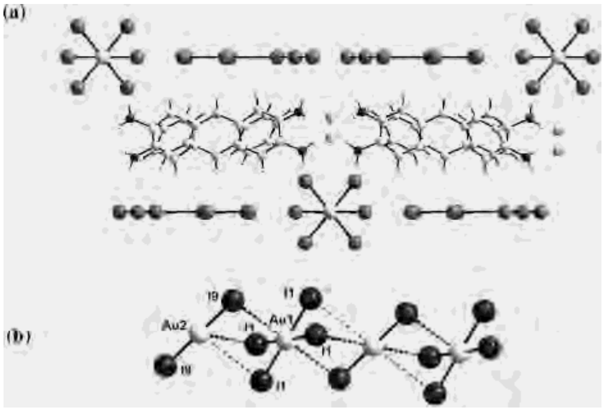

Figure 1. (a) Crystal structure of **1** viewed along the *b* axis. (b) Section of the gold(I/III) iodide chain of face-shared octahedra. I, Au, and Cl are shown as large gray, large white, and medium gray spheres, respectively. N, C, and H are shown as medium black, medium white, and small white spheres, respectively.

6 weeks. This method yielded well-crystallized samples suitable for single-crystal X-ray diffraction analysis. Semiquantitative SEM elemental analysis indicated that Au (7%), Cl (15%), and I (78%) were the only heavy elements present.[13] Typical reaction yields, based on gold content, is >85%.

The crystal structure of **1** features two unique layers alternately stacked along the *c* axis, as shown in Figure 1.[14] The cationic layers, $[(p\text{-NH}_3C_6H_4)_2CH_2]^{2+}Cl^-$, contain organic dications with chlorides partially counteracting the charge. The Cl^- ions, located within channels parallel with the *b* axis, form nominal zigzag chains with Cl···Cl distances of 4.62 Å. Each Cl^- ion is tetrahedrally coordinated by four dications, with N···Cl distances ranging from 3.13 to 3.20 Å (see Figure 2a). The organic dications effectively isolate the Cl^- ions (interchain distance = 13.56 Å). Furthermore, the cationic layers are less polarizable than the inorganic anionic layers.

The anionic layers contain mixed-valent ($[Au^IAu^{III}I_6]^{2-}$) chains and I_2 and I_5^- units, as shown in Figure 2b. The gold(I/III) iodide chains can be described as a distortion of an ideal chain of face-shared $AuI_{6/2}$ octahedra. The unique distortion of the ideal chain of $AuI_{6/2}$ octahedra results in two inequivalent Au atoms corresponding to linear $[Au^II_2]^-$ and square planar $[Au^{III}I_4]^-$ units, with Au−I (short/long) distances of $d(Au^I-I) = 2.54/4.02$ Å and $d(Au^{III}-I) = 2.64/3.65$ Å. Primary and secondary bond distances within the nominal $[Au^{III}I_6]^{3-}$ octahedra of **1** are comparable to those found in the corresponding octahedra of the gold(I/III) iodide perovskites.[9,12] However, the nominal $[Au^II_6]^{3-}$ octahedra in **1** have shorter primary bonds and longer secondary bond distances than those of the corresponding perovskite gold(I/III) iodides.[9,12]

In addition, the anionic layers exhibit unusual noncovalent interactions of the type $I_2\cdots[AuI_2]^-\cdots I_2$ with $I\cdots I_2$ distances of 3.25 Å and I···I−I angles of 170.6(3)°. The I_2 units have bond distances (2.74 Å) that are shorter than those in I_2 molecules within polyiodide networks (2.75−2.78 Å)[15] but longer than those in solid I_2 (2.715 Å).[16] Typical V-shaped I_5^- anions form dimers with $I_5^-\cdots I_5^-$ distances of 3.66 Å.[17] The I_5^- units also exhibit intermolecular I···I distances of 3.92 and 3.96 Å with I_2 molecules in $Au^II_2^-\cdots I_2\cdots I_5^-$ and in $Au^{III}I_4^-\cdots I_5^-$, respectively. The interlayer distance between repeating anionic layers is 9.48 Å. The shortest I···Cl distance between adjacent ionic layers is 4.22 Å.

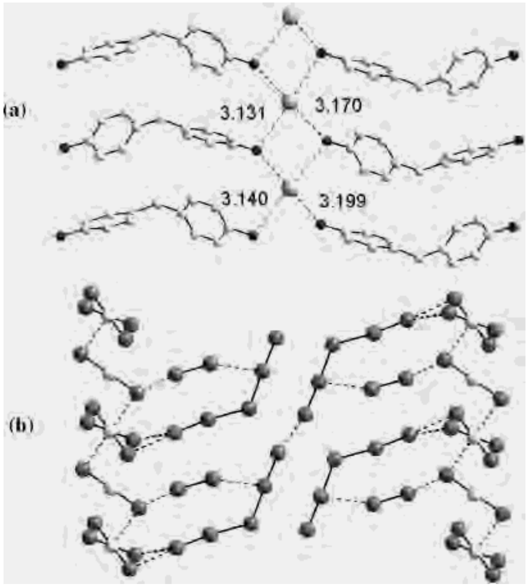

Figure 2. [001] views of the (a) cationic layer and (b) anionic layer in **1**. Au, I, and Cl atoms are represented as large white, large gray, and small gray spheres, respectively. Small white (C) and black (N) spheres represent the light atoms. Hydrogen atoms have been omitted for clarity.

It is interesting to compare the ($[Au^IAu^{III}I_6]^{2-}$) chains in **1** with the typical close-packed structures of complex metal halides, AMX_3, with octahedrally coordinated divalent metals (M).[18] Filling the octahedral interstices of cubic close-packed (ccp) AX_3 layers with M yields the perovskite structure, a 3-D network of corner-shared MX_6 octahedra. Filling the analogous interstices in a hexagonal close-packed (hcp) AX_3 layers leads to the $CsNiCl_3$ type, with infinite chains of face-shared MX_6 ($NiCl_6$) octahedra.[19] The gold(I/III) iodide chains in **1** are directly related to the $[NiCl_3]^-$ chains of $CsNiCl_3$.[20] In general, face-shared octahedral chains $[MX_3]^-$ with electronic instabilities undergo structural and electronic transitions (e.g., Peierls distortion, M−M bond formation, magnetic ordering).[21] Magnetic ordering transitions have been observed for $CsVCl_3$, $CsFeCl_3$, $CsCoCl_3$, and $CsNiCl_3$,[16,22−24] whereas Jahn−Teller distortions are exhibited by Cu^{2+} and

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[13] Chemical analysis was performed via SEM. See ref 9 for details. Exp/Calc Au% 7.4/7.7, Cl% 15.0/15.4, I% 77.6/76.9.

[14] Crystallographic data for **1**: orthorhombic, *Pnnm* (no. 58), $a = 27.0703(2)$ Å, $b = 8.9363(5)$ Å, $c = 18.4280(1)$ Å, $V = 4457.9(5)$ Å^3, $\rho_{calc} = 2.887$ g/cm^3, $Z = 2$, F_{obs} ($F > 4\sigma$) = 3560, 5381 unique reflections, $\lambda = 0.71073$ Å, $T = 223$ K, $\mu = 10.368$ (6 psi scans), $R_{int} = 0.0704$, $R = 0.0466$, wR = 0.1171. SHELXTL (Sheldrick, G. M.; Gould, O. R. *Acta Crystallogr.* **1995**, *B51*, 423).

(15) Blake, A. J.; Gould, R. O.; Li, W. S.; Lippolis, V.; Parsons, C. R.; Schroeder, M. *Inorg. Chem.* **1998**, *37*, 5070.

(16) Bolhius, F.; Koster, P. B. *Acta Crystallogr. B* **1967**, *B23*, 90.

(17) Tebbe, K. F.; Loukili, R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 820.

(18) Longo, J. M.; Kafales, J. A. *J. Solid State Chem.* **1969**, *1*, 103.

(19) Sassmannshausen, M.; Lutz, H. D. *Acta* Crystallogr. C **1998**, *C54*, 704.

(20) Li, T.; Stucky, G. D.; McPherson, G. L. *Acta* Crystallogr. B **1973**, *B29*, 1330.

(21) Whangbo, M. H. *Acc. Chem. Res.* **1983**, *16*, 95.

(22) Hause, A.; Falk, U.; Fischer, P.; Güdel, H. *J.* Solid *State Chem.* **1985**, *56*, 343.

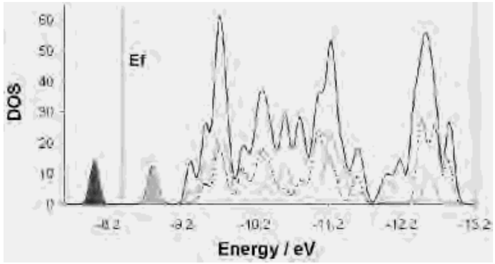

Figure 3. (a) Total (solid line) and projected DOS for the I_5^- (light gray) and AuI_4^- (dotted and gray) fragments on the inorganic layers of **1**.

Cr^{2+} (in $[CrCl_3]^-$ chains).[25,26] It is interesting to note that a ternary $AAuX_3$ with a $CsNiCl_3$-type structure is still unknown.

The electronic instability of a divalent gold $[Au^{II}I_3]^-$ chain is manifested as charge density waves (disproportionation), resulting in alternating Au^I and Au^{III} states, as in the $AuI_{6/2}$ chains in **1**. Thus, **1** contains uniquely distorted face-shared octahedral chains, derived from the $CsNiCl_3$ type—unprecedented among transition metal halides. The face-shared linkage in **1** also results in shorter direct Au^I−Au^{III} distances than in any of the mixed-valent gold(I/III) halide perovskites and related compounds.[9]

The absorption spectrum of **1** shows a broad peak composed of an intense band (maximum at 1.82 eV), with an absorption edge at 1.18 eV, and a sharp shoulder at lower energies, indicating a band gap of $E_g = 0.53$ eV.[27] The observed band gap is significantly smaller than those reported for $Cs_2Au^{III}Au^{I}I_6$ ($E_g = 1.35$ eV) and the recent organic-based mixed-valent gold(I/III) iodide layered perovskites ($E_g = 1.14$ and 0.95 eV).[9,28]

To understand the optical spectrum, extended-Hückel tight-binding (EHTB) calculations were performed on the inorganic layers using relativistic parameters for Au and I.[29] Although EHTB calculations are inherently semiempirical and qualitative, they have been successfully employed on several gold-containing systems and found to agree well with results from higher-level calculations and XPS measurements.[30] Results of the preliminary EHTB calculations indicate a completely filled band at the Fermi level with a band gap of 0.85 eV (see Figure 3). The band immediately below the Fermi level is mainly formed from the p states (HOMO) of I_5^-. The empty conduction band is mainly derived from AuI_4^--based MOs. The most significant intermolecular interactions occur along the mixed-valent gold(I/III) chain. Our calculations indicate an intrachain band gap of 1.63 eV for the $[Au^IAu^{III}I_6]^{2-}$ chain. This could correspond to the most intense absorption peak observed in the optical spectrum at 1.82 eV. The optical absorption spectrum can then be interpreted as the sum of these two electronic transitions within the metal iodide−polyiodide layers.

The summed overlap population between Au^I and $Au^{III}I_4^-$ ($Au^I\cdots I-Au^{III}$) is 0.0362 (6.29% of the Au−I overlap in AuI_2^-). The summed overlap population between Au(III) and $[AuI_2]^-$ ($Au^{III}\cdots I-Au^I$) is 0.0742 (16.78% of the Au−I overlap in AuI_4^-). These values indicate significant interactions along the mixed-valent gold iodide chains. However, crystal orbital overlap population analyses show the interactions between the mixed-valent Au chains with the I_5^- and I_2 units are essentially weak and nonbonding.

The d atomic orbital population (aop) for Au reveals values of 9.27 and 9.92 for Au(III) and Au(I), respectively. The significant difference between the corresponding aop's indicates two distinct oxidation states for Au atoms in **1**. This compares well with previously reported molecular electronic structure calculations on gold compounds.[31,32] It has also been proposed that mixed-valent gold(I/III) iodide perovskites can be described as Au(I) (d^{10}) compounds with mixed-valent iodine (0.5−/1−).[33] This does not seem to be the case in **1** given that the aop values (s and p) of all iodine atoms within the mixed-valent chains are essentially identical. The differences are significantly smaller than for the Au atoms: 7.403 for I in AuI_4^- and 7.477 for I in AuI_2^-. Results from subsequent molecular ab initio (CISD level) calculations on the gold and iodine complexes support the bonding description obtained from the EHTB calculations.

Our findings confirm a remarkable layered structure with electronically active 1-D mixed-valent gold(I/III) iodide chains that are embedded within a hyperpolarizable layer of polyiodides and iodine molecules. Combining low-dimensional mixed-valent and hyperpolarizable components is crucial to the assembly of prospective excitonic superconductors, as envisioned by Little.[34]

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Supporting Information Available: Crystallographic information file (CIF), experimental details, and diffuse reflectance spectrum for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] Kohne, A.; Kemnitz, E. *Z. Kristallogr.* **1993**, *203*, 316.

[24] Soling, H. *Acta Chem. Scand.* **1968**, *22*, 2793.

[25] Crama, W. J. *Acta* Crystallogr. B **1981**, *B37*, 2133.

[26] Crama, W.; Maaskant, J.; Verschoor, G. *Acta* Crystallogr. B **1978**, *B34*, 1973.

[27] Diffuse reflectance measurements were made at T_{298} for pure samples of **1** using a Cary 500 double-beam spectrometer. See ref 9 for additional details. E_g was found to be 0.53 eV.

[28] Liu, X. L.; Matsuda, K.; Moritomo, Y.; Nakamura, A.; Kojima, N. *Phys. Rev. B* **1999**, *59*, 7925.

[29] EHTB calculations were performed using CAESAR (PrimeColor Software, Cary, NC), using a 121 *k*-point set. Relativistic EH parameters for I and Au were obtained from refs 30 and 31.

[30] (a) Munzarova, M. L.; Hoffmann, R. *J. Am. Chem. Soc.* **2002**, *124*, 5542. (b) Lee, W. R.; Jung, D. *Bull. Korean Chem. Soc.* **1999**, *20*, 147.

[31] (a) Pyykko, P.; Lohr, L. L. *Inorg. Chem.* **1981**, *20*, 1950. (b) Assefa, Z.; DeStefano, F.; Garepapaghi, M. A.; LaCasce, J. H.; Ouellete, S.; Corson, M. R.; Nagle, J.; Patterson, H. H. *Inorg. Chem.* **1991**, *30*, 2868.

[32] Schwerdtfeger, P.; Boyd, P. D. W.; Brienne, S.; Burrell, A. K. *Inorg. Chem.* **1992**, *31*, 3411.

[33] Paradis, J. A.; Whangbo, M. H.; Kasowski, R. V. *New J. Chem.* **1993**, *17*, 525.

[34] Davis, D.; Gutfreund, H.; Little, W. A. *Phys. Rev.* **1976**, *B13*, 4766.