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A Three-Dimensional Iodo-Bridged Mixed-Valence Gold(I,III) Compound, $Cs_2Au^{I}Au^{III}I_6$

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Abstract

The title compound, dicaesium gold(I) gold(III) hexaiodide, has a distorted perovskite structure. The crystal contains compressed and elongated [AuI_6] octahedra stacked alternately along the [001] and [110] directions by sharing all the corner I atoms. The compound is also characterized by the assembly of the gold complex ions [$Au^{I}I_2$]$^-$ and [$Au^{III}I_4$]$^-$. The position of the two halogen atoms in $Cs_2Au^{I}Au^{III}I_6$ is closer to the midpoint between the two Au atoms than in $Cs_2Au^{I}Au^{III}Cl_6$. On the other hand, the distortion from the cubic system to the tetragonal system in the iodide is slightly larger than that in the chloride.

Comment

Mixed-valence systems with perovskite-type structures have attracted much attention in view of high-temperature superconductors such as $La_{2-x}Ba_xCuO_4$ (Bednorz & Müller, 1986) and $Ba_{1-x}K_xBiO_3$ (Cava *et al.*, 1988). In these systems, interesting physical properties such as superconductivity depend remarkably on the valence states present and the crystal structure. From these viewpoints, we have systematically investigated the relationship between the physical properties and the crystal structures of $Cs_2Au^{I}Au^{III}X_6$ (X = Cl, Br, I), which are well known as three-dimensional halogen-bridged mixed-valence gold compounds (Kojima, Kitagawa, Ban, Amita & Nakahara, 1990, 1991; Kitagawa, Kojima, Matsushita, Ban & Tsujikawa, 1991; Kitagawa, Kojima & Nakajima, 1991; Kitagawa, Kojima & Sakai, 1991; Kitagawa, Sato, Kojima, Kikegawa & Shimomura, 1991*a*,*b*; Kitagawa, Kojima, Takahashi & Mori, 1993). The crystal structure of $Cs_2Au_2X_6$ determined by powder X-ray diffraction (Brauer & Sleater, 1970) and the crystal structure analysis of $Cs_2Au_2Cl_6$ using a single crystal (Tindemans-v. Eijndhoven & Verschoor, 1974) have been reported. The characteristic properties of the crystal structure and mixed valence of $Cs_2Au_2X_6$ are analogous to those of $BaBiO_3$, which is the parent compound of the superconductors Ba_{1-x}(K or Rb)$_x$$BiO_3$ and $BaPb_{1-x}Bi_xO_3$. Therefore, these gold compounds are interesting materials for research on Cu-free high-T_c superconductors.

An X-ray single-crystal analysis of $Cs_2Au_2I_6$ has not been reported, even though the atomic coordinates and interatomic distances in $Cs_2Au_2I_6$ are indispensable for band calculations and analysis of the physical properties. One probable reason is the difficulty in obtaining a suitable single crystal of $Cs_2Au_2I_6$. Very recently, we have succeeded in carrying out an X-ray single-crystal analysis of $Cs_2Au_2I_6$.

Fig. 1 shows the crystal structure of $Cs_2Au_2I_6$. The Au(1) atom is surrounded by four I(1) atoms in a perfectly square-planar arrangement. The Au(1)—I(1) distance [2.646 (2) Å] is in good agreement with that for the [AuI_4]$^-$ anion in other mixed-valence compounds: $K_2[AuI_2][AuI_4]$ [2.648 (3) and 2.639 (3) Å] (Strähle, Gelinek, Kolmel & Nemcek, 1979), $Rb_2[AuI_2][AuI_4]$ [2.643 (2) Å] (N. Matsushita, unpublished results) and $Rb_2Ag[AuI_2]_2[AuI_4]$ [2.637 (4) and 2.633 (5) Å] (Werner & Strähle, 1979). Crystal structures of mononuclear complexes of Au^{III} surrounded by four I atoms in a square-planar arrangement have not been reported to the best of our knowledge. On the other hand, the Au(2) atom is linearly coordinated by two I(2) atoms, as shown in Fig. 1. The Au(2)—I(2) distance [2.586 (3) Å] is close to that for the [AuI_2]$^-$ anion in the mixed-valence compounds $K_2[AuI_2][AuI_4]$ [2.564 (3) Å] (Strähle *et al.*, 1979), $Rb_2[AuI_2][AuI_4]$ [2.570 (3) Å] (N. Matsushita, unpublished results) and $Rb_2Ag[AuI_2]_2[AuI_4]$ [2.570 (9) and 2.549 (9) Å] (Werner & Strähle, 1979), and it is longer than that found in [n-Bu_4N][AuI_2] [2.529 (1) Å] (Braunstein, Müller & Bogge, 1986) where [n-Bu_4N]$^+$ is the tetra(n-butyl)ammonium ion. Therefore, Au(1) is formally trivalent and Au(2) is formally monovalent. The crystal is built up from square-planar [AuI_4]$^-$ anions, linear [AuI_2]$^-$ anions and Cs^+ cations, and the compound may be described as $Cs_2[Au^{I}I_2][Au^{III}I_4]$.

The Au^{I}—I distances in [AuI_2]$^-$ in the mixed-valence compounds are longer than that in the compound containing discrete [AuI_2]$^-$ ions. The I atom in

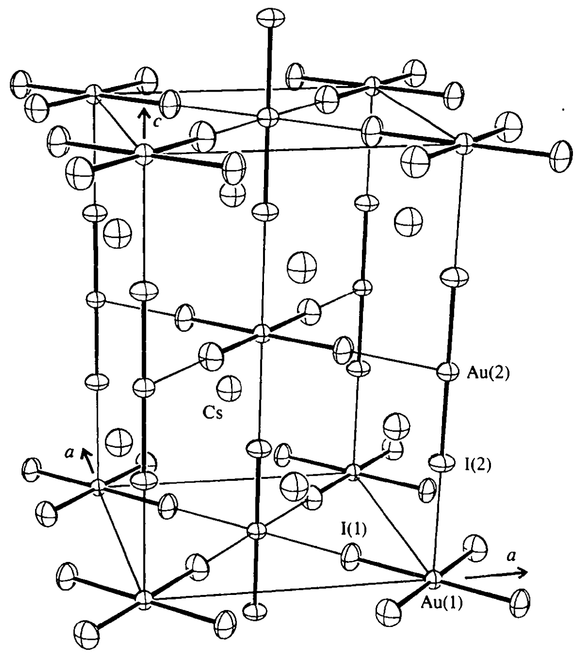

Fig. 1. A view of the crystal structure of $Cs_2Au_2I_6$ showing the atomic labelling scheme and displacement ellipsoids at the 50% probability level. Thick solid lines connect the nearest neighbour I atoms with the Au atoms and thin solid lines connect the second nearest neighbour I atoms with the Au atoms.

the $[AuI_2]^-$ anion between Au^I and Au^{III} is shifted towards Au^{III} from Au^I due to an intervalence charge-transfer interaction between Au^I and Au^{III} through the bridging I atom in the mixed-valence compounds. The Au^I—I distances [2.586 (3) Å ($Cs_2Au_2I_6$) > 2.570 (3) Å ($Rb_2Au_2I_6$) > 2.564 (3) Å ($K_2Au_2I_6$)] in the mixed-valence compounds show that the molecular character of the crystal increases in the order of $K_2Au_2I_6$ > $Rb_2Au_2I_6$ > $Cs_2Au_2I_6$. This result supports a result of ^{197}Au Mössbauer spectroscopy regarding the ratios of the recoil-free fractions for Au^I and Au^{III} in the mixed-valence compounds (Kitagawa, Kojima & Sakai, 1991; Kojima, Tanaka, Sakai & Maeda, 1993). Considering only the nearest neighbour I atoms, Au^I is coordinated by two I atoms and Au^{III} is coordinated by four I atoms. Therefore, the environment of the Au^{III} site is more rigid than that of the Au^I site. This is responsible for the difference in the absorption intensities of Au^I and Au^{III} in ^{197}Au Mössbauer spectra, because the absorption intensity is generally proportional to the recoil-free fraction. The intensity ratios $I(Au^I)/I(Au^{III})$ are 0.88, 0.47 and 0.28 for $Cs_2Au_2I_6$, $Rb_2Au_2I_6$ and $K_2Au_2I_6$, respectively, which implies that the environment of the Au^I site becomes softer and the molecular character of the crystal increases in the order of $K_2Au_2I_6$ > $Rb_2Au_2I_6$ > $Cs_2Au_2I_6$.

Both Au(1) and Au(2) are surrounded by six I atoms when the second nearest neighbours are included. The $[Au(1)I(1)_4I(2)_2]$ unit is an octahedron elongated along the *c* axis while the $[Au(2)I(1)_4I(2)_2]$ unit is an octahedron compressed along the *c* axis. The volume of the octahedron around the higher oxidation state Au^{III} ion [32.28 (6) Å^3] is smaller than that around the lower oxidation state Au^I ion [35.63 (6) Å^3]. Therefore, the breathing-mode-type atomic distortion of AuI_6 octahedra is present in this system. The elongated and compressed octahedra are three-dimensionally and alternately arranged by sharing each corner of the octahedral units, as shown in Fig. 2.

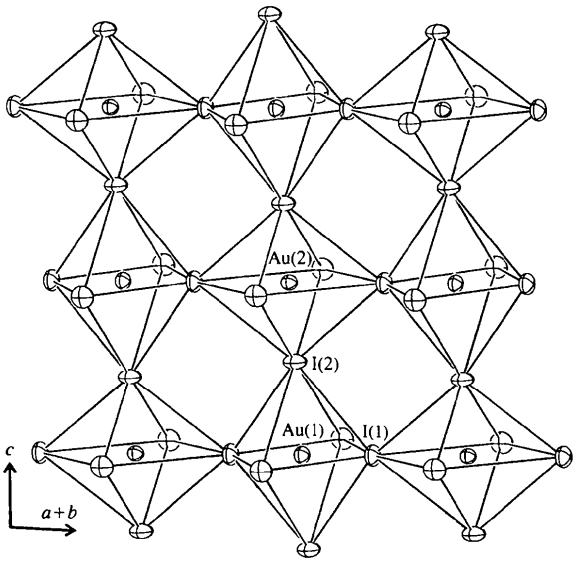

Fig. 2. The arrangement of the elongated and compressed octahedra in $Cs_2Au_2I_6$.

As shown in Fig. 1, two kinds of —Au—I—Au—I— chains are formed in the crystal. One is the chain ···Au(1)···I(2)—Au(2)—I(2)···Au(1)··· along the *c* axis and the other is the chain ···Au(2)···I(1)—Au(1)—I(1)···Au(2)··· along the [110] and [1$\bar{1}$0] directions (in the *ab* plane). The I atom in the former chain is located closer to the Au atom with the lower oxidation state. On the other hand, the I atom in the latter chain is located closer to the Au atom with the higher oxidation state. The latter type of chain is similar to the chain observed in one-dimensional halogen-bridged mixed-valence platinum complexes (Keller, 1982). The ratio of the shorter Au—I distance to the longer Au—I distance in the chains along the *c* axis, {Au(2)—I(2)}/{Au(1)—I(2)}, is 0.747 (1) and that in the chains in the *ab* plane, {Au(1)—I(1)}/{Au(2)—I(1)}, is 0.824 (1). Therefore, the I(1) atom in the *ab* plane is located closer to the midpoint between the Au(1) and Au(2) atoms than the I(2) atom on the *c* axis. Considering the ratios {Au(2)—I(2)}/{Au(1)—I(2)} and {Au(1)—I(1)}/{Au(2)—I(1)}, and the Au···Au distances [5.858 (1) Å in the *ab* plane and 6.046 (1) Å along the *c* axis], the intervalence charge-transfer interaction in the *ab* plane should be stronger than that along the *c* axis. In fact, from XPS measurements (Kitagawa, Kojima & Nakajima, 1991), ^{197}Au Mössbauer spectra (Kitagawa, Kojima & Sakai, 1991) and polarized reflection spectra (Kojima & Kitagawa, 1994), it is strongly suggested that a two-dimensional correlation between the Au ions is present in the intervalence charge-transfer interaction in spite of the three-dimensional perovskite structure. This is explained by the intervalence charge-transfer interaction between the donor $d_{x^2-y^2}$ orbital of Au$^{\rm I}$ and the acceptor $d_{x^2-y^2}$ orbital of Au$^{\rm III}$ in the *ab* plane being most effective (Kitagawa, Kojima, Matsushita, Ban & Tsujikawa, 1991).

Turning to the case of $Cs_2Au_2Cl_6$, {Au(2)—Cl(2)}/{Au(1)—Cl(2)} along the *c* axis is 0.722 (1) and {Au(1)—Cl(1)}/{Au(2)—Cl(1)} in the *ab* plane is 0.763 (1) (Tindemans-v. Eijndhoven & Verschoor, 1974). Therefore, it is obvious that the positions of the halogen atoms in $Cs_2Au_2I_6$ are closer to the midpoints between the Au atoms than those of the halogen atoms in $Cs_2Au_2Cl_6$. Consequently, it is considered that the intervalence charge-transfer interaction in $Cs_2Au_2I_6$ is stronger than that in $Cs_2Au_2Cl_6$, and the valence states of Au$^{\rm I}$ and Au$^{\rm III}$ in $Cs_2Au_2I_6$ are closer to Au$^{\rm II}$ than those of Au$^{\rm I}$ and Au$^{\rm III}$ in $Cs_2Au_2Cl_6$. This fact is in good agreement with the results of XPS (Kitagawa, Kojima & Nakajima, 1991), ^{197}Au Mössbauer spectra (Kitagawa, Kojima & Sakai, 1991), and the absorption and reflection spectra (Kojima & Kitagawa, 1994).

The ratio of the unit-cell constants $2^{1/2}a/c$ denotes the level of distortion from the cubic system. For the unit-cell setting shown in Fig. 1, a ratio $2^{1/2}a/c = 1$ suggests that the crystal is in the cubic system. In $Cs_2Au_2I_6$, the ratio $2^{1/2}a/c$ is 0.9689 (2), which is smaller than that in $Cs_2Au_2Cl_6$ [0.9743 (3)] (Tindemans-v. Eijndhoven & Verschoor, 1974); nevertheless, the ratio of the shorter Au—*X* distance to the longer Au—*X* distance in $Cs_2Au_2I_6$ is closer to 1 than that in $Cs_2Au_2Cl_6$. However, this fact is not so surprising. It has been reported for $Cs_2Au_2Cl_6$ that $2^{1/2}a/c$ decreases slightly (Kojima, Tanaka, Sato, Kitagawa, Kikegawa & Shimomura, 1993) and the Au—Cl ratios approach unity (Denner, Schulz & D'Amour, 1979) with increasing pressure up to 6.5 GPa. This phenomenon suggests that the intervalence charge-transfer interaction in $Cs_2Au_2Cl_6$ in the *ab* plane increases more than that along the *c* axis with increasing pressure. It may also be concluded that the intervalence charge-transfer interaction in the *ab* plane increases more than that along the *c* axis when the bridging halogen atom changes from Cl to I.

Experimental

The title compound was prepared as described previously (Kitagawa, Kojima & Nakajima, 1991). Single crystals were recrystallized by a diffusion method using an H-type glass test tube and 55% hydroiodic acid as the solvent. One bottom of the H-tube was kept at 318 K and the other at 293 K. Single crystals suitable for X-ray analysis were obtained in two or three weeks.

Crystal data

$Cs_2Au_2I_6$
$M_r = 1421.17$
Tetragonal
*I*4/*mmm*
$a = 8.284\,(1)$ Å
$c = 12.092\,(2)$ Å
$V = 829.8\,(2)$ Å^3
$Z = 2$
$D_x = 5.69$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.1–14.9°$
$\mu = 32.94$ mm^{-1}
$T = 297$ K
Plate
0.25 × 0.20 × 0.09 mm
Dark bronze

Data collection

Rigaku AFC-5*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian by integration method (Busing & Levy, 1957)
$T_{\rm min} = 0.013$, $T_{\rm max} = 0.115$
1063 measured reflections
573 independent reflections

497 reflections with $F > 3\sigma(F)$
$R_{\rm int} = 0.0441$
$\theta_{\rm max} = 35°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 19$
3 standard reflections every 50 reflections intensity decay: none

Refinement

Refinement on *F*
$R = 0.070$
$wR = 0.085$
$S = 2.66$
483 reflections
14 parameters
$w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 1.93$ e Å^{-3}
$\Delta\rho_{\rm min} = -2.04$ e Å^{-3}

Extinction correction: Zachariasen (1967) type I, isotropic Gaussian
Extinction coefficient: $g = 0.26\,(1) \times 10^{-4}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Au(1)	0	0	0	0.0279 (6)
Au(2)	1/2	1/2	0	0.0322 (7)
I(1)	0.2258 (2)	*x*	0	0.0488 (9)
I(2)	1/2	1/2	0.2139 (2)	0.0446 (10)
Cs	0	1/2	1/4	0.0625 (16)

Table 2. *Selected geometric parameters (Å)*

Au(1)—I(1)	2.646 (2)	Au(2)—I(1)	3.212 (2)
Au(1)—I(2$^{\rm i}$)	3.460 (3)	Au(1)···Au(2$^{\rm i}$)	6.046 (1)
Au(2)—I(2)	2.586 (3)	Au(1)···Au(2)	5.858 (1)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$.

Powder X-ray diffraction patterns have shown that the compounds $Cs_2Au_2X_6$ (X = Cl, Br, I) are isomorphous, as reported by Brauer & Sleater (1970). Single-crystal X-ray analysis of $Cs_2Au_2Cl_6$ (Tindemans-v. Eijndhoven & Verschoor, 1974) showed that it has space group *I*4/*mmm*. Therefore, we chose the space group *I*4/*mmm* for $Cs_2Au_2I_6$. Fourteen reflections influenced by extinction (extinction factor < 0.90) were not included in the final refinement. In the final difference map, the largest positive and negative peaks are near the Au atoms.

Programs used were *UNICS*III (Sakurai & Kobayashi, 1979) and *SHELX*76 (Sheldrick, 1976) for the structure analysis, *RADIEL* (Coppens *et al.*, 1979) of *CHARGE SYSTEM* (Ito, Ooba, Tanaka, Sasaki & Haga, 1986) for the extinction correction, and *DABEX* (Toriumi & Ooba, 1985) of *CHARGE SYSTEM* for the absorption correction, on a HITAC M-880/310 at the Computer Centre of the University of Tokyo and a HITAC M-680H at the Computer Center, Institute for Molecular Science, Okazaki. *ORTEP*II (Johnson, 1976) was used for drawing the structure on a TOSHIBA SS-R590 personal computer.

One of the authors (NM) wishes to thank Professor T. Iwamoto of The University of Tokyo for his kind advice and valuable discussions.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: OA1010). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Acid Selenite: $Mg(HSeO_3)_2$

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Abstract

Magnesium bis[hydrogentrioxoselenate(IV)] crystallizes in a new structure type with Mg^{2+} and hydrogen-bonded dimers of trigonal pyramidal SeO_2OH^- ions in an NaCl-like arrangement forming MgO_6 octahedra linked *via* O—Se—O bonds to create a three-dimensional network structure. The Mg—O and Se—O distances reflect the bonding schemes of the corresponding atoms. The hydrogen bonds in the $(SeO_2OH^-)_2$ dimers are strong, with $d(OH\cdots O) = 2.616(2)$ Å. They are joined through Se and Mg atoms to form layered hydrogen-bond systems parallel to (100).

Comment

As a part of our investigations of strong hydrogen bonds in acid selenites (Unterderweide, Engelen & Boldt, 1994; Engelen, Boldt, Unterderweide & Bäumer, 1995), single crystals of the hitherto unknown compound $Mg(HSeO_3)_2$ were prepared and the crystal structure was determined by means of X-ray diffraction measurements (Unterderweide, Boldt & Engelen, 1993; Boldt, 1994).

The Mg^{2+} ions, occupying the 2*a* positions of space group $P2_1/n$, are coordinated octahedrally by six O