Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

A three-dimensional bromo-bridged mixed-valence gold(I,III) compound, $Cs_2Au^IAu^{III}Br_6$

Nobuyuki Matsushita,* Fumiya Fukuhara and Norimichi Kojima

Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba 3-8-1, Meguro, 153-8902 Tokyo, Japan

Correspondence e-mail:
cnmatsu@mail.ecc.u-tokyo.ac.jp

Received 11 April 2005
Accepted 24 May 2005
Online 31 May 2005

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(Au–Br) = 0.002 Å
R factor = 0.064
wR factor = 0.170
Data-to-parameter ratio = 31.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, dicaesium gold(I) gold(III) hexabromide or dicaesium dibromoaurate(I) tetrabromoaurate(III), $Cs_2[Au^IBr_2][Au^{III}Br_4]$, has a distorted perovskite-type structure which is isotypic with its chloride and iodide analogues, $Cs_2Au^IAu^{III}X_6$ (X is Cl or I). The structure contains compressed and elongated $[AuBr_6]$ octahedra stacked alternately along the [001] and [110] directions by sharing all the corner Br^- ions. The compound is also characterized by the assembly of the gold complex ions $[Au^IBr_2]^-$ and $[Au^{III}Br_4]^-$. Structural parameters indicating the mixed-valence distortion of Au^I and Au^{III} due to displacement of two crystallographically independent halide (X) ions from the mid-point between the two adjacent Au ions, expressed by $(Au-X)/(Au\cdots X)$, are 0.738 (2) along the c axis and 0.799 (1) in the ab plane. These values show that the mixed-valence distortion of the title bromide is intermediate between those of the chloride and the iodide. The distortion of the title bromide from the cubic system to the tetragonal system, expressed by $2^{1/2}a/c$ = 0.9704 (1), is also intermediate between those of the chloride and the iodide.

Comment

The title compound, $Cs_2Au_2Br_6$, (I), is a member of the family of mixed-valence compounds with perovskite-type structures. A systematic investigation of the relationship between the physical properties and the crystal structures of the group of compounds $M_2Au^IAu^{III}X_6$ (M is Rb or Cs, and X is Cl, Br or I), to which (I) belongs, has been reported (Kojima, 2000). We have already reported in detail the crystal structure of $Cs_2Au_2I_6$, which is also a member of this family and which is isotypic with (I) (Matsushita *et al.*, 1997).

$Cs_2Au_2Br_6$, in particular, has attracted much interest because it exhibits a photoinduced phase transition under high pressure (Liu *et al.*, 2000). Very recently, a structural and electronic phase transition of (I) under high pressure was reported, using powder X-ray diffraction data from synchrotron radiation and with a diamond-anvil cell as the high-pressure source (Sakata *et al.*, 2004). An X-ray single-crystal analysis of (I), however, has not yet been reported, even though the atomic coordinates and interatomic distances are indispensable for band calculations and analysis of the physical properties. One probable reason for this is the difficulty in obtaining suitable single crystals of (I).

In the structure of (I), atom Au1 is coordinated by four Br1 ions in a perfectly square-planar arrangement, as shown in Fig. 1. The Au1—Br1 distance of 2.436 (3) Å is in good agreement with that for the $[AuBr_4]^-$ anion in another mixed-valence compound, $Rb_2[AuBr_2][AuBr_4]$ [2.438 (4) Å; Strähle *et al.*, 1979] and is somewhat longer than that found in the

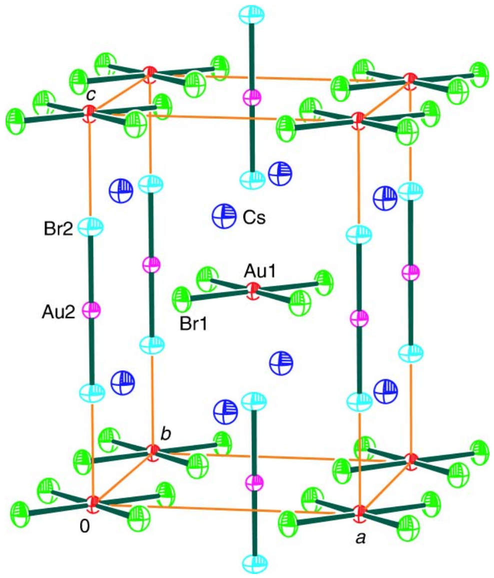

Figure 1
A view of the crystal packing of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

trivalent gold compound $Cs_3[AuBr_4]_2Br_3$ [2.422 (1) Å; Lehnis & Strähle, 1981]. On the other hand, atom Au2 is linearly coordinated by two Br2 ions, as also shown in Fig. 1. The Au2—Br2 distance of 2.400 (4) Å is in good agreement with that for the $[AuBr_2]^-$ anion in the mixed-valence compound $Rb_2[AuBr_2][AuBr_4]$ [2.402 (8) Å; Strähle *et al.*, 1979] and is longer than that found in the monovalent gold compound $[n\text{-}Bu_4N][AuBr_2]$ [2.376 (3) Å; Braunstein *et al.*, 1986], where $[n\text{-}Bu_4N]^+$ is tetra(*n*-butyl)ammonium. Therefore, the formal oxidation state of the Au1 ion is trivalent and that of the Au2 ion is monovalent in (I), as well as in the other $Cs_2Au_2X_6$ (X is Cl or I) compounds. The structure is built up from three species, namely square-planar $[AuBr_4]^-$ anions, linear $[AuBr_2]^-$ anions and Cs^+ cations. Thus $Cs_2Au_2Br_6$ may be described as $Cs_2[Au^{I}Br_2][Au^{III}Br_4]$.

Both atoms Au1 and Au2 are surrounded by six Br^- ions when the second-nearest neighbours are included. The $[Au1Br1_4Br2_2]$ unit is an octahedron elongated along the *c* axis, while the $[Au2Br1_4Br2_2]$ unit is an octahedron compressed along the *c* axis (Fig. 2). The volume of the octahedron around the higher oxidation state Au^{III} ion [25.76 (7) $Å^3$] is smaller than that around the lower oxidation state Au^{I} ion [29.78 (7) $Å^3$]. Therefore, the breathing-mode-type atomic distortion of $AuBr_6$ octahedra is present in (I), as well as in $Cs_2Au_2I_6$ (Matsushita *et al.*, 1997).

As shown in Fig. 1, two kinds of –Au—Br—Au—Br– chains are formed in the crystal structure of (I). One is the chain $\cdots$Au1$\cdots$Br2—Au2—Br2$\cdots$Au1$\cdots$ along the *c* axis and the other is the chain $\cdots$Au2$\cdots$Br1—Au1—Br1$\cdots$Au2$\cdots$ along the [110] and [$1\bar{1}0$] directions (in the *ab* plane). The Br^- ion in the former chain is located closer to the Au cation with the lower oxidation state. On the other hand, the Br^- ion in the latter chain is located closer to the Au cation with the higher oxidation state. The latter type of chain is similar to the chains observed in one-dimensional halogen-bridged mixed-valence platinum complexes (Keller, 1982). The ratio of the shorter Au—Br distance to the longer Au—Br distance in the chains along the *c* axis, (Au2—Br2)/(Au1—Br2), is 0.738 (2), and that in the chains in the *ab* plane, (Au1—Br1)/(Au2—Br1), is 0.799 (1). The ratios of (I) are intermediate between those of $Cs_2Au_2Cl_6$ [0.722 (1) along *c* and 0.763 (1) in *ab*] and $Cs_2Au_2I_6$ [0.747 (1) along *c* and 0.824 (1) in *ab*].

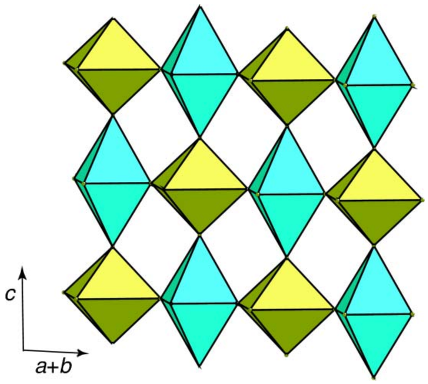

Figure 2
The arrangement of the elongated $[Au^{III}Br_6]$ octahedra and compressed $[Au^{I}Br_6]$ octahedra in (I).

The ratio of the unit-cell dimensions $2^{1/2}a/c$ denotes the level of distortion of the perovskite structure from the cubic system to the tetragonal system. When $2^{1/2}a/c = 1$, a crystal is in the cubic system. The ratio $2^{1/2}a/c$ in (I) [0.9704 (1)] is intermediate between those of $Cs_2Au_2Cl_6$ [0.9743 (3)] and $Cs_2Au_2I_6$ [0.9689 (2)], which implies that the tetragonal distortion increases in the order $Cs_2Au_2Cl_6 < Cs_2Au_2Br_6 < Cs_2Au_2I_6$.

Experimental

The title compound was prepared as described previously by Kitagawa *et al.* (1991). Single crystals of (I) were recrystallized by a diffusion method, using an H-type glass test tube and acetonitrile for the solvent. One leg of the H-tube was kept at 320 K and the other at room temperature. Single crystals suitable for X-ray analysis were obtained in a few weeks.

Crystal data

$Cs_2[AuBr_2][AuBr_4]$
$M_r = 1139.17$
Tetragonal, $I4/mmm$
$a = 7.7592$ (8) Å
$c = 11.3079$ (13) Å
$V = 680.79$ (13) $Å^3$
$Z = 2$
$D_x = 5.56$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.4$–$14.6°$
$\mu = 44.35$ mm^{-1}
$T = 296$ K
Plate, gold
0.23 × 0.18 × 0.08 mm

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (Coppens *et al.*, 1965)
$T_{min} = 0.011$, $T_{max} = 0.088$
949 measured reflections
474 independent reflections
335 reflections with $I > 2\sigma(I)$

$R_{int} = 0.003$
$\theta_{max} = 35.0°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 18$
3 standard reflections every 100 reflections
intensity decay: none

i124 Matsushita *et al.* • $Cs_2[AuBr_2][AuBr_4]$ *Acta Cryst.* (2005). E**61**, i123–i125

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.170$
$S = 1.04$
474 reflections
15 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1105P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 5.19$ e Å^{-3}
$\Delta\rho_{min} = -6.01$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0014 (4)

Table 1
Selected interatomic distances (Å).

Au1—Br1	2.436 (3)	Au2—Br2	2.400 (4)
Au1—Br2	3.254 (4)	Au2—Br1	3.050 (3)

Powder X-ray diffraction patterns have shown that $Cs_2Au_2X_6$ phases (X is Cl, Br or I) are isotypic, as reported by Brauer & Sleater (1970). Single-crystal X-ray analysis of $Cs_2Au_2Cl_6$ (Tindemans-v. Eijndhoven & Verschoor, 1974) and $Cs_2Au_2I_6$ (Matsushita *et al.*, 1997) showed that they have space group *I*4/*mmm*. Therefore, we have also chosen the space group *I*4/*mmm* for $Cs_2Au_2Br_6$. The highest peak in the difference map is located 1.01 Å from Au2 and the deepest hole is located 0.74 Å from Au1.

Data collection: *MSC*/*AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC*/*AFC Diffractometer Control Software*; data reduction: local program *F2-AFC* (Matsushita, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

References

Brandenburg, K. (2005). *DIAMOND*. Version 3.0. Crystal Impact, Bonn, Germany.
Brauer, G. & Sleater, G. (1970). *J. Less Common Met.* **21**, 283–291.
Braunstein, P., Müller, A. & Bögge, H. (1986). *Inorg. Chem.* **25**, 2104–2106.
Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Keller, H. J. (1982). *Linear-Chain Platinum Haloamines*. *Extended Linear-Chain Compounds*, Vol. 1, edited by J. S. Miller, pp. 357-407. New York: Plenum Press.
Kitagawa, H., Kojima, N. & Nakajima, T. (1991). *J. Chem. Soc. Dalton Trans.* pp. 3121–3125.
Kojima, N. (2000). *Bull. Chem. Soc. Jpn*, **73**, 1445–1460.
Lehnis, B. & Strähle, J. (1981). *Z. Naturforsch. Teil B*, **36**, 1504–1508.
Liu, X.-J., Moritomo, Y., Ichida, M., Nakamura, A. & Kojima, N. (2000). *Phys. Rev. B*, **61**, 20–23.
Matsushita, N. (1998). *F2-AFC*. University of Tokyo, Japan.
Matsushita, N., Kitagawa, H. & Kojima, N. (1997). *Acta Cryst.* C**53**, 663–666.
Molecular Structure Corporation (1988). *MSC*/*AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sakata, M., Itsubo, T., Nishibori, E., Moritomo, Y., Kojima, N., Ohishi, Y. & Takata, M. (2004). *J. Phys. Chem. Solids*, **65**, 1973–1976.
Strähle, J., Gelinek, J. & Kölmel, M. (1979). *Z. Anorg. Allg. Chem.* **456**, 241–260.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Tindemans-v. Eijndhoven, J. C. M. & Verschoor, G. C. (1974). *Mater. Res. Bull.* **9**, 1667–1670.

Acta Cryst. (2005). E**61**, i123–i125 Matsushita *et al.* • $Cs_2[AuBr_2][AuBr_4]$ **i125**