Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

A three-dimensional iodo-bridged mixed-valence gold(I,III) compound, $Rb_2[Au^{I}I_2][Au^{III}I_4]$

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Received 3 August 2005
Accepted 9 August 2005
Online 17 August 2005

$Rb_2[Au^{I}I_2][Au^{III}I_4]$, dirubidium diiodoaurate(I) tetraiodoaurate(III), has a tilted and distorted perovskite-type structure which is isotypic with its bromide analogue $Rb_2[Au^{I}Br_2][Au^{III}Br_4]$. The structure contains compressed and elongated $[AuI_6]$ octahedra tilted away from each other and stacked alternately along the [001], $[1\bar{1}0]$ and [110] directions by sharing all the corner I^- ions.

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(Au–I) = 0.002 Å
R factor = 0.066
wR factor = 0.097
Data-to-parameter ratio = 35.4

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

Comment

$Rb_2Au_2I_6$, (I), is a member of the family of mixed-valence gold compounds with perovskite-type structures. A systematic investigation of the relationship between the physical properties and crystal structures of $M_2Au^{I}Au^{III}X_6$ (M is Rb or Cs, and X is Cl, Br or I), to which (I) belongs, was reported by us some time ago (Kojima, 2000). We have also reported in detail the crystal structures of $Cs_2Au_2X_6$ (X is Br or I; Matsushita *et al.*, 1997, 2005). The single-crystal X-ray analysis of $Rb_2Au_2Br_6$, which is isotypic with (I), has been reported previously by Strähle, Gelinek & Kölmel (1979). The structure analysis of (I), however, has not yet been reported, even though the atomic coordinates and the interatomic distances are indispensable for band calculations and analysis of the physical properties. One probable reason for this is the difficulty of obtaining suitable single crystals of (I).

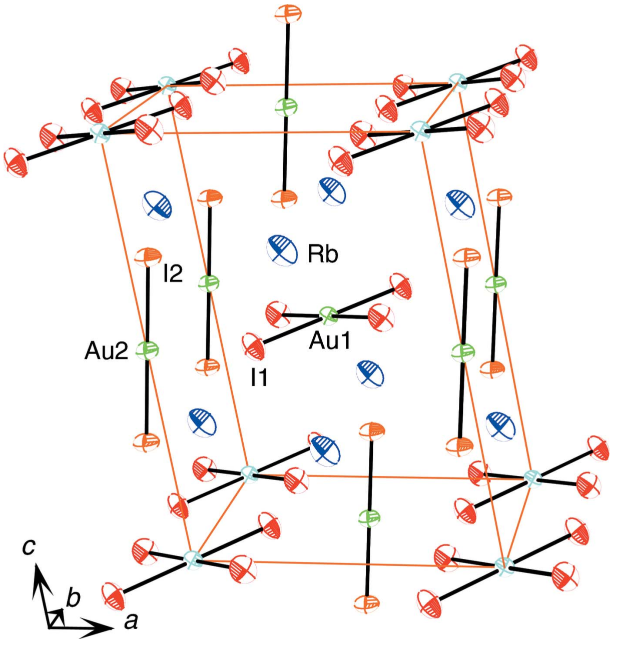

Figure 1
A view of the crystal packing of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

In the structure of (I), the Au1 cation is coordinated by four I1 anions in a square-planar arrangement, as shown in Fig. 1. The Au1—I1 distance of 2.6435 (19) Å is longer than that found in the trivalent gold compound $K[AuI_4]$ [2.592 (2)–2.604 (2) Å; Lang *et al.*, 1997], but is very similar to that for the $[AuI_4]^-$ anion in other mixed-valence gold compounds, such as $Cs_2[AuI_2][AuI_4]$ [2.646 (2) Å; Matsushita *et al.*, 1997], $K_2[AuI_2][AuI_4]$ [2.648 (3) and 2.639 (3) Å; Strähle, Gelinek, Kölmel & Nemcek, 1979], $Rb_2Ag[AuI_2]_2[AuI_4]$ [2.637 (4) and 2.633 (5) Å; Werner & Strähle, 1979], or $[NH_3(CH_2)_nNH_3]_2$-$[(Au^{I}I_2)(Au^{III}I_4)(I_3)_2]$ [2.6336 (7) Å for n = 8, and 2.6455 (11) and 2.6499 (11) Å for n = 7; Castro-Castro & Guloy, 2003]. The Au1–I1 distance of (I) is also similar to that observed in trivalent gold compounds in which elongated $[AuI_6]$ octahedra are present, such as $(NH_4)_2[(AuI_4)(MI_4)]$ [2.6366 (8) and 2.6361 (8) Å for M = Ga, and 2.6228 (8) and 2.6233 (8) Å for M = In; Lang *et al.*, 1999] and $Li[AuI_4]$ [2.629 (1) and 2.639 (1) Å; Lang *et al.*, 1997].

The Au2 cation is linearly coordinated by two I2 anions, as also shown in Fig. 1. The Au2—I2 distance of 2.568 (2) Å is in good agreement with that for the $[AuI_2]^-$ anion in other mixed-valence gold compounds, such as $K_2[AuI_2][AuI_4]$ [2.564 (3) Å; Strähle, Gelinek, Kölmel & Nemcek, 1979], $Rb_2Ag[AuI_2]_2[AuI_4]$ [2.570 (9) and 2.549 (9) Å; Werner & Strähle, 1979] and $[NH_3(CH_2)_8NH_3]_2[(Au^{I}I_2)(Au^{III}I_4)(I_3)_2]$ [2.5685 (11) Å; Castro-Castro & Guloy, 2003]. The Au2—I2 distance of (I) is, on the other hand, somewhat shorter than that found in the mixed-valence gold compounds $Cs_2[AuI_2][AuI_4]$ [2.586 (3) Å; Matsushita *et al.*, 1997] and $[NH_3(CH_2)_7NH_3]_2$-$[(Au^{I}I_2)(Au^{III}I_4)(I_3)_2]$ [2.5902 (12) Å; Castro-Castro & Guloy, 2003], but is longer than that found in the monovalent gold compound $[n\text{-}Bu_4N][AuI_2]$ [2.529 (1) Å; Braunstein *et al.*, 1986], where $[n\text{-}Bu_4N]$ is tetra(n-butyl)ammonium.

The formal oxidation state of the Au1 cation is, therefore, assigned as trivalent and that of the Au2 cation as monovalent and the structure of (I) is built up from three species, namely square-planar $[AuI_4]^-$ anions, linear $[AuI_2]^-$ anions and Rb^+ cations. Thus, $Rb_2Au_2I_6$ may be described as $Rb_2[Au^{I}I_2][Au^{III}I_4]$.

Both gold cations Au1 and Au2 are surrounded by six I^- anions when the second-nearest neighbours are included. The $[Au1(I1)_4(I2)_2]$ unit is an octahedron elongated along the c axis, whereas the $[Au2(I1)_4(I2)_2]$ unit is an octahedron compressed along the c axis. The volume of the octahedron around the Au^{III} ion [$V_{Au(III)}$ = 32.91 (5) Å^3] is smaller than that around the Au^{I} ion [$V_{Au(I)}$ = 37.74 (5) Å^3]. Therefore, a breathing-mode-type atomic distortion of $[AuI_6]$ octahedra is present in (I), as well as in the $Cs_2Au_2X_6$ compounds (X is Br or I; Matsushita *et al.*, 1997, 2005). The amplitude of the breathing-mode distortion between the elongated and compressed octahedra of (I) (0.136), estimated by the formula $[V_{Au(I)} - V_{Au(III)}]/\{0.5[V_{Au(I)} + V_{Au(III)}]\}$, is larger than that of the caesium iodide salt $Cs_2Au_2I_6$ (0.099). The elongated and compressed octahedra are three-dimensionally and alternately arranged by sharing all the corner I^- anions and, as shown in Fig. 2, tilted away from each other. The Goldschmidt tolerance factor t (Goldschmidt, 1926), expressed by the formula $t = (r_A + r_X)/[2^{\frac{1}{2}}(r_B + r_X)]$, where r_A, r_B and r_X are the ionic radii in the perovskite-type structure ABX_3, is known as a factor indicating a geometrical deviation from its perfect fit (t = 1). The tolerance factor of (I) [0.837, using the radii given by Shannon (1976)] is rather small for those compounds belonging to the perovskite family. This small tolerance factor, caused by the relatively small size of the Rb^+ ion at the A-site, induces the tilt system of $[AuI_6]$ octahedra in (I).

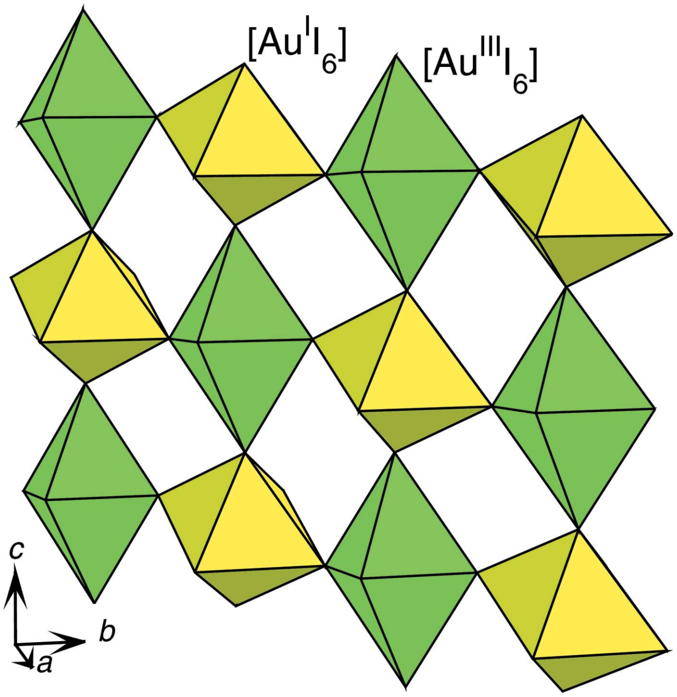

Figure 2
The arrangement of the elongated $[Au^{III}I_6]$ octahedra and compressed $[Au^{I}I_6]$ octahedra in (I).

As shown in Fig. 1, two kinds of zigzag –Au—I—Au—I– chains are formed. One is the chain ···Au1···I2—Au2—I2···Au1··· running along the c axis, with an Au1···I2 distance of 3.532 (2) Å and an Au1···I2—Au2 angle of 157.33 (10) °, and the other is the chain ···Au2···I1—Au1—I1···Au2··· running along [110] and [$1\bar{1}0$] directions (in the ab plane), with an Au2···I1 distance of 3.320 (2) Å and an Au2···I1—Au1 angle of 162.59 (7) °. Each I^- anion in the former or the latter chains is located closer to the Au^{I} or Au^{III} cation, respectively. The ratio of the shorter Au—I distance to the longer Au···I distance in the chains along the c axis, (Au2—I2)/(Au1···I2), is 0.727 (2), and that in the chains in the ab plane, (Au1—I1)/(Au2···I1), is 0.796 (2). The first value is intermediate between those of $Cs_2Au_2Cl_6$ [0.722 (1)] and $Cs_2Au_2Br_6$ [0.738 (2)], whereas the latter value is closer to that of $Cs_2Au_2Br_6$ [0.799 (1)] than to those of $Cs_2Au_2Cl_6$ [0.763 (1)] or $Cs_2Au_2I_6$ [0.824 (1)].

Experimental

The title compound was prepared by mixing concentrated aqueous solutions of $HAuCl_4$(0.0025 mol) and RbI (0.10 mol). Single crystals

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of (I) were recrystallized by a diffusion method, using an H-type glass test tube and with concentrated hydroiodic acid as the solvent. One leg of the H-tube was kept at *ca* 320 K and the other at room temperature. Single crystals suitable for X-ray analysis were obtained in a few weeks.

Crystal data

$Rb_2[AuI_2][AuI_4]$
M_r = 1326.28
Monoclinic, $I2/m$
a = 8.725 (2) Å
b = 7.932 (1) Å
c = 11.969 (4) Å
β = 99.53 (2)°
V = 816.9 (3) Å^3
Z = 2
D_x = 5.39 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.0–14.8°
μ = 34.88 mm^{-1}
T = 295 K
Plate, gold
0.20 × 0.10 × 0.06 mm

Data collection

Rigaku AFC-5*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (Coppens *et al.*, 1965)
$T_{\min}$ = 0.051, $T_{\max}$ = 0.157
1793 measured reflections
1390 independent reflections
1098 reflections with $F > 3\sigma(F)$
$R_{\rm int}$ = 0.010
$\theta_{\max}$ = 32.5°
$h = -3 \rightarrow 13$
$k = -11 \rightarrow 0$
$l = -18 \rightarrow 17$
4 standard reflections every 50 reflections intensity decay: none

Refinement

Refinement on F
$R[F > 3\sigma(F)]$ = 0.066
$wR(F)$ = 0.097
S = 1.72
1098 reflections
31 parameters
$w = 1/[\sigma^2(F_o) + 0.0012F_o^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 3.08 e Å^{-3}
$\Delta\rho_{\min}$ = −3.89 e Å^{-3}
Extinction correction: *SHELX76* (Sheldrick, 1976)
Extinction coefficient: 0.00046 (8)

Table 1
Selected geometric parameters (Å, °).

Au1—I1	2.6435 (19)	Au2—I2	2.568 (2)
Au1—I2$^{\rm i}$	3.532 (2)	Au2—I1	3.320 (2)
I1—Au1—I1$^{\rm ii}$	89.39 (6)	I2—Au2—I1$^{\rm vi}$	94.51 (6)
I1—Au1—I1$^{\rm iii}$	90.61 (6)	I1—Au2—I1$^{\rm vii}$	78.77 (5)
I1—Au1—I2$^{\rm iv}$	85.68 (5)	I1—Au2—I1$^{\rm vi}$	101.23 (5)
I1—Au1—I2$^{\rm v}$	94.32 (5)	Au1—I1—Au2	162.59 (7)
I2—Au2—I1	85.49 (6)	Au2—I2—Au1$^{\rm viii}$	157.33 (10)

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, -y, z$; (iii) $-x, y, -z$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; (v) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x+1, y, -z$; (vii) $x, -y+1, z$; (viii) $x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$.

$Rb_2Au_2I_6$, (I), is isotypic with $Rb_2Au_2Br_6$, which was described in space group $I2/m$ (Strähle, Gelinek & Kölmel, 1979). The structures of (I) and of $Rb_2Au_2Br_6$ are closely related to the structures of the $Cs_2Au_2X_6$ compounds (X is Cl: Tindemans-v. Eijndhoven & Verschoor, 1974; Br: Matsushita *et al.*, 2005; I: Matsushita *et al.*, 1997), which are isotypic with each other and crystallize in space group $I4/mmm$. In order to compare these structures, we have also chosen the setting in $I2/m$, instead of the standard setting in $C2/m$. The highest peak and deepest hole in the difference map lie within 0.85 Å of atom Au1.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1987); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *Rigaku/AFC Diffractometer Control Software*; program(s) used to solve structure: *UNICS3* (Sakurai & Kobayashi, 1979); program(s) used to refine structure: *SHELX76* (Sheldrick, 1976); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *PLATON* (Spek, 2003).

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