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$Na_2Au_6In_5$, the first compound in the system sodium–gold–indium

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Abstract

Silver coloured brittle single crystals of a hitherto unknown $Na_2Au_6In_5$ were synthesized by the reaction of sodium azide, gold sponge and indium at 550 °C. The structure was determined from X-ray single-crystal diffractometry data: space group $Pm\bar{3}$, $Z = 3$, $a = 9.245(4)$ Å, R/R_w $(w = 1) = 0.038/0.054$ for 363 structure factors with $F_o^2 \geqslant 3\sigma(F_o^2)$ and 23 variables.

$Na_2Au_6In_5$ crystallizes with the $Mg_2Cu_6Al_5$ structure type. The gold and indium atoms form a framework structure with a caesium chloride-like arrangement of indium centred Au_{12} icosahedra and empty Au_6 octahedra. The indium environment and the interconnecting pattern of these building units can be described by the formula $\{InAu_{12}In^{i-i}_{8/2}In^{a-a}_{12/4}\}\{Au_6In^{i-i}_{8/2}(In_2)^{a-a}_{6/4}\}_{8/8}$, according to Schäfer and von Schnering's notation for transition metal clusters.

Keywords· Sodium auride indide; Gold; Indium

1. Introduction

Recently we reported on the synthesis of alkali metal auride single crystals with gold sponge and alkalimetal azides MN_3 with M = Na, K, Rb, Cs as starting materials [1–5]. The brittleness, small molar volumes and short M–Au distances of these compounds (e.g. $NaAu_2$ [1], CsAu [2], Rb_2Au_3 [3], Rb_3Au_7 (4), $RbAu_4$ [5]) led to a simplified "salt-like" formulation $(M^+)_n[Au_m]^{n-}$. This simplified picture of chemical bonding is supported by the ionic conduction behaviour of CsAu melts [6,7] and the existence of the transparent caesium auride oxide Cs_3AuO [8] and the mixed crystals of CsBr/CsAu [9,10]. The Au^- anion in CsAu melts and in the compound Cs_3AuO can easily be understood by the assumption of a closed shell inert s-pair configuration, isoelectronic with Hg^0, Tl^+, Pb^{2+} and Bi^{3+}. Whereas the more gold rich compounds, e.g. Rb_2Au_3 [3], are difficult to understand, because they must contain extremely electron deficient gold polyanions. For example, there are only 5/3 s-electrons for each four-fold bonded gold atom in the $[Au_3]^{2-}$ layers of the compound Rb_2Au_3.

The polyanions in binary alkali metal main group element compounds like K_4Si_4 [11] or Na_8In_4 [12] are well described by application of the Zintl–Klemm concept [13,14] with tetrahedral Si_4^{4-} and In_4^{8-} anions, similar to P_4 in white phosphorus. The polyanions in the more electron poor compounds like $Na_{15}In_{27.4}$ [12] are generally interpreted as Wade clusters which are connected via exo-bonds. So, we are interested in the structural chemistry of gold in ternary alkali metal gold compounds with a main group element as the third component. Here we report the synthesis and structure of the first sodium gold indium compound $Na_2Au_6In_5$.

2. Synthesis

Gold sponge was prepared by the reaction of $HAuCl_4$ solution with oxalic acid according to Ref. [15]. NaN_3 (Fluka, 99.9%) was recrystallized from water. Gold sponge and NaN_3 were dried under vacuum at 150 °C. The surface of indium (Ventron, 99.999%) was cleaned with a knife before use. The starting materials (molar ratio $n(NaN_3)$:$n(Au)$:$n(In)$ = 2.4:6:5) were placed in a corundum crucible. This was placed in an incompletely closed steel container and heated in an evacuated silica tube at 550 °C for three days and then cooled to room temperature within one day. This leads to single-phased samples of $Na_2Au_6In_5$. The compound was obtained in the form of brittle, silver coloured, air-stable crystal aggregates. The surplus sodium was found in the colder part of the silica tube.

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Table 1
Data collection and refinement parameters for $Na_2Au_6In_5$

Crystal size (mm^3)	$0.025 \times 0.050 \times 0.025$
Unit cell parameter (Å)	$a = 9.245(4)$
Volume (Å^3)	790.2
D_x ($g\,cm^{-3}$)	11.360
Formula units	3
Space group	$Pm\bar{3}$ (No. 200)
$1/\mu$(Ag Kα) (mm)	0.020
Absorption correction	empirical method ("psi-scan") 29.1% min. rel. transmission
Radiation	Ag Kα (graphite-monochromator)
Scan mode	$\Omega/2\Theta$
Θ_{max} (°)	30
h,k,l	±16, 0–16, 0–16
R_{merge} (%)	5.0
Independent reflections	898
Reflections with $F_o^2 \geq 3\sigma F_o^2$	363
Variables	23
$R/R_w(w = 1)$	0.038/0.054
Largest peak in the final difference map (eÅ^{-3})	5.1

3. Structure determination

Precession photographs (Mo Kα) of single crystals and Guinier data (vacuum Guinier camera FR552, Enraf-Nonius, Delft, NL, Cu Kα_1 radiation and silicon as standard) of polycrystalline samples are consistent with a cubic primitive unit cell: $a = 9.234(1)$ Å. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with monochromated Ag Kα radiation. Experimental details are summarized in Table 1. The program SHELXTL PLUS [16] was used for structure solution by direct methods. Data reduction, absorption correction and final refinements were performed using the SDP system of programs [17]. Final values of positional and thermal parameters are given in Tables 2 and 3.

4. Structure description and discussion

Distances and angles are given in Table 4. $Na_2Au_6In_5$ crystallizes with the $Mg_2Cu_6Al_5$ structure type [18], a ternary variant of the Mg_2Zn_{11} type [19] that is also found for the compound Na_2Cd_{11} [20]. Interestingly, these compounds have a comparable number of valence (s- and p-) electrons per formula unit, with 23 for $Na_2Au_6In_5$, 24 for Na_2Cd_{11}, 25 for $Mg_2Cu_6Al_5$ and 26 for Mg_2Zn_{11} respectively.

Table 4
Interatomic distances (not above 4 Å) in the structure of $Na_2Au_6In_5$

Au(1)–4Au(1) 2.978(2), 1Au(1) 3.193(2)
–2In(1) 2.821(2), 1In(2) 2.715(2), 1In(3) 2.871(2)
–1Na 3.130(2), 2Na 3.17(1)

Au(2)–4Au(2) 3.056(2)
–4In(1) 2.837(2), 2In(2) 2.875(4)
–2Na 3.91(2)

In(1)–3In(2) 3.338(2)
–3Au(1) 2.821(2), 3Au(2) 2.837(2)
–3Na 3.46(1)

In(2)–1In(2) 2.971(5), 4In(1) 3.338(1)
–2Au(1) 2.715(2), 2Au(2) 2.875(2)
–2Na 3.38(1), 2Na 3.52(2)

In(3)–12Au(1) 2.871(2)

Na–2Au(1) 3.130(7), 4Au(1) 3.17(1), 2Au(2) 3.91(2)
–4In(1) 3.455(8), 2In(2) 3.38(2), 2In(2) 3.52(1)
–1Na 3.18(4)

Table 2
Positional and isotropic displacement parameters (Å^2) for $Na_2Au_6In_5$

Site	Occupancy	x	y	z	B
12j	Au(1)	0	0.1727(2)	0.2582(2)	1.04(2)
6h	Au(2)	0.2663(3)	1/2	1/2	1.26(3)
8i	In(1)	0.2833(2)	x	x	1.30(1)
6g	In(2)	0.3393(4)	1/2	0	0.68(5)
1a	In(3)	0	0	0	0.74(3)
6f	Na	0.172(3)	0	1/2	2.1(5)

Table 3
Anisotropic displacement parameters U_{ij}($\times 10^3$ Å^2) for $Na_2Au_6In_5$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Au(1)	10.5(4)	16.2(5)	12.8(5)	0	0	−3.6(5)
Au(2)	19.9(9)	12.8(7)	15.2(2)	0	0	0
In(1)	16.4(6)	U_{11}	U_{11}	−3.6(6)	U_{12}	U_{12}
In(2)	8(1)	6(1)	12(1)	0	0	0
In(3)	9(1)	U_{11}	U_{11}	0	0	0
Na	10(10)	40(10)	30(10)	0	0	0

Two crystallographically independent gold and three indium atoms form a framework structure. The gold atoms form empty Au(2)$_6$ octahedra and Au(1)$_{12}$ icosahedra which are centred by In(3). The Au(2)$_6$ and In(3)Au(1)$_{12}$ units, which are connected by In(1) and In(2), form a caesium chloride analogous {In(3)Au(1)$_{12}$} {Au(2)$_6$}$_{8/8}$ arrangement. Fig. 1 provides a perspective view of the structure.

The In(1) and In(2) environment of the empty Au(2)$_6$ octahedra (Fig. 2) reminds of the topology of M$_6$X$_8$-type transition metal clusters like {[Mo$_6$Cl$^i_8$]Cl$^a_6$}$^{2-}$ (e.g. in PbMo$_6$Cl$_{14}$ [21]). The X atoms are designated X^i (i = inner) if they are located above octahedral faces and X^a (a = outer) if they are bonded to the apices [22]. The environment of the Au(2)$_6$ unit is therefore designated [Au(2)$_6$In(1)$^i_8$](In(2)$_2$)$^a_6$, with the triangular faces capped by In(1) and "chelating" apical In(2) pairs. The distance d(In(2)–In(2)) = 2.97 Å matches well with the single bond distances between indium Wade clusters in many indium network structures of alkali metal indides [12]. Each In(2) pair connects two Au(2)$_6$ clusters. This leads to a cubic primitive network of these building units (Fig. 1). The Au(2) atoms are coordinated by four In(1) and two In(2) atoms. The distance d(Au(2)–Au(2)) = 3.06 Å (octahedral edges) is significantly longer than the distance d(Au–Au) = 2.88 Å in metallic gold. The distance between the centre of the Au$_6$ octahedron and the Au(2) atoms is $3.06/\sqrt{2}$ = 2.16 Å. This value is comparable with the mean distance d(C–Au) = 2.13 Å in the octahedral, carbon centred molecular gold cluster cation [C(AuPPh$_3$)$_6$]$^{2+}$ [23]. So, we intend to study the reaction behaviour of Na$_2$Au$_6$In$_5$ with non-metals like carbon or hydrogen.

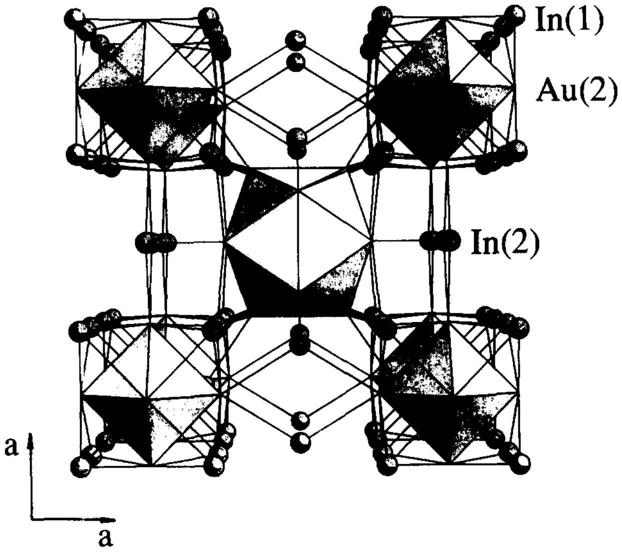

Fig. 1. Caesium chloride-like arrangement of icosahedral [In(3)Au(1)$_{12}$In(1)$^i_8$]In(2)$^a_{12}$ and octahedral [Au(2)$_6$In(1)$^i_8$](In(2)$_2$)$^a_6$ building units in Na$_2$Au$_6$In$_6$ (with In(3) in 0,0,0).

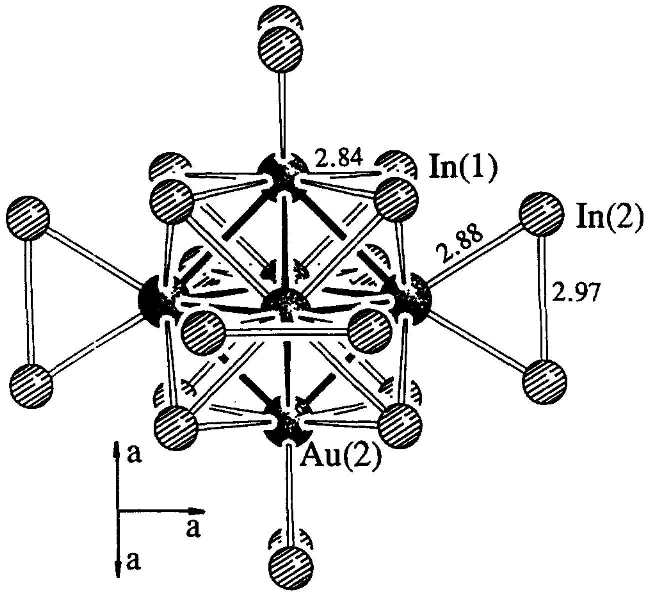

Fig. 2. [Au(2)$_6$In(1)$^i_8$](In(2)$_2$)$^a_6$ building unit with d(Au(2)–Au(2)) = 3.06 Å in Na$_2$Au$_6$In$_5$. The distance between the centre of the Au(2)$_6$ octahedron and the Au(2) atoms is $3.06/\sqrt{2}$ = 2.16 Å.

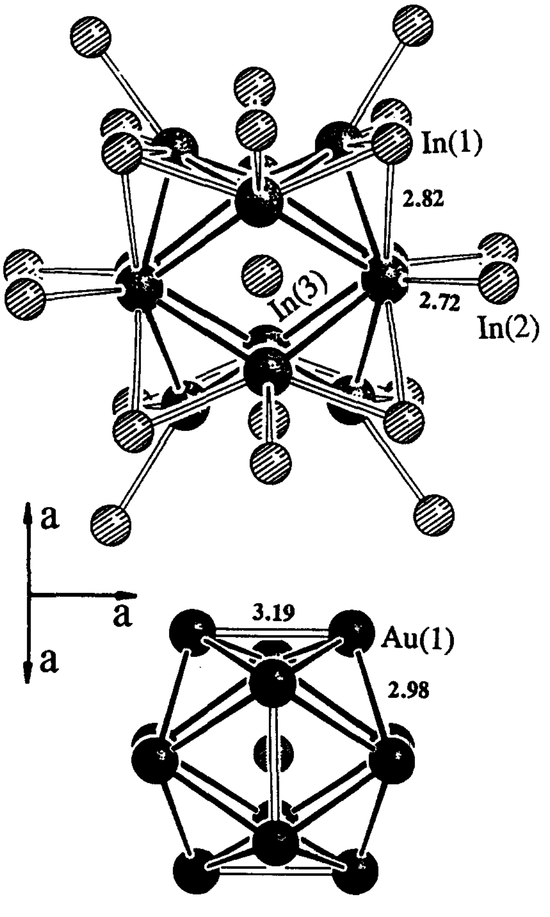

Fig. 3. [In(3)Au(1)$_{12}$In(1)$^i_8$]In(2)$^a_{12}$ building unit in Na$_2$Au$_6$In$_5$.

The indium environment of the distorted In(3)Au(1)$_{12}$ icosahedron (Fig. 3) can also be designated by the notation for transition metal clusters [22]. Eight triangular faces of the icosahedron are capped by one $In(1)^i$ atom and Au(1) has one exo-bonded $In(2)^a$ atom. So, the structural unit is designated $[In(3)Au(1)_{12}In(1)^i_8]In(2)^a_{12}$. The distances d(Au(1)–Au(1)) = 2.98 and 3.19 Å of the icosahedron edges are also significantly longer than in metallic gold.

The gold environment of the interconnecting In(1) and In(2) atoms is shown in Figs. 4(a) and 4(b). In(1) is coordinated by a slightly distorted trigonal prism of three Au(1) and three Au(2) atoms. Each In(1) connects the triangular faces of one $In(3)Au(1)_{12}$ and one $Au(2)_6$ unit. The In(2) atoms are surrounded by a tetrahedron of two Au(1) and two Au(2) atoms. So each In(2) connects two $In(3)Au(1)_{12}$ icosahedra and two $Au(2)_6$ octahedra. The $In(2)Au(1)_2Au(2)_2$ tetrahedra are connected by a common edge of Au(2) atoms. The relatively short distance within the resulting $In(2)_2$ dumb-bell has already been discussed above. The interconnecting pattern of gold icosahedra and octahedra can be formulated as $\{[In(3)Au(1)_{12}In(1)^{i-i}_{8/2}]In(2)^{a-a}_{12/4}\}$ $\{[Au(2)_6In(1)^{i-i}_{8/2}](In(2)_2)^{a-a}_{6/4}\}_{8/8}$, according to Schäfer and von Schnering's [22] notation for transition metal clusters.

The sodium atoms are surrounded by a CN16 polyhedra of six Au(1), two Au(2), four In(1) and four In(2). Two of these CN16 polyhedra are connected to dimers by a common hexagon face (Fig. 5). Consequently, there is a short Na–Na distance of 3.18(4) Å. This value is close to the Na–Na distances of the ionic compound Na_2O (d(Na–Na) = 3.20 Å) [24] and the Zintl–Klemm compound NaIn (d(Na–Na) = 3.16 Å [25]. The Na–Au(1) distances (Table 4) are shorter than the sum of the metallic radii d(Na–Au) = 3.35 Å (for CN12) [26]. Comparable short Na–Au distances occur in the compound $NaAu_2$ [1] with d(Na–Au) = 3.24 Å, whereas the distances d(Na–Au(2)) = 3.91 Å are significantly longer. The Na–In(1) and Na–In(2) distances (Table 4) are shorter than the sum of the metallic radii d(Na–In) = 3.57 Å (for CN12) [26]. Comparable short Na–In distances are also found in the Zintl–Klemm compounds NaIn (d(Na–In) = 3.16 Å) [25] and Na_2In (d(Na–In) = 3.31–3.71 Å) [12].

The molar volume of $Na_2Au_6In_5$ (158.6 $cm^3\,mol^{-1}$) is 13.2% smaller than the sum of the elemental atomic volumes according to Biltz [27] (182.8 $cm^3\,mol^{-1}$). This volume shrinking, the brittleness of $Na_2Au_6In_5$ and the above-mentioned short Na–In and Na–Au distances lead to the assumption of partially positively

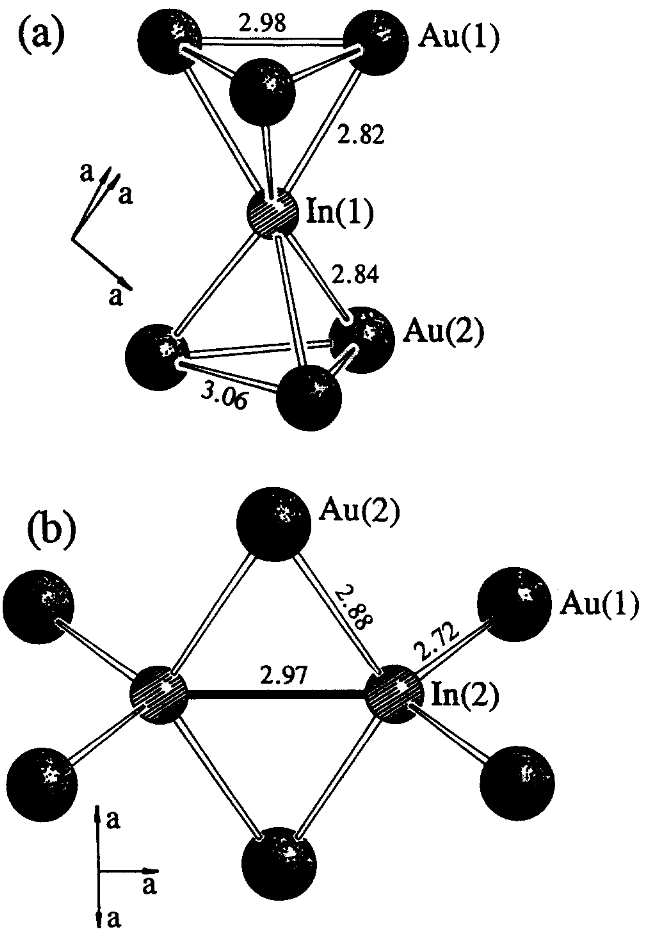

Fig. 4. Gold environment of (a) In(1) and (b) In(2) in $Na_2Au_6In_5$.

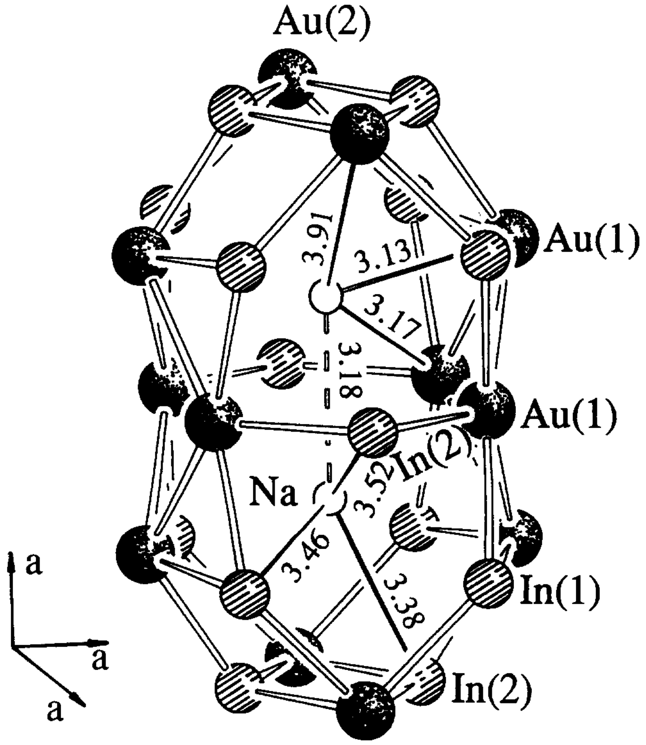

Fig. 5. Gold and indium environment of sodium in $Na_2Au_6In_5$. Two CN16 polyhedra are connected to dimers by a common hexagon face.

charged sodium together with negatively charged In(1), In(2) and Au(1) atoms within the gold indium framework.

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