Caesium Tetrachlorido Aurate(III), $CsAuCl_4$

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The crystal structure of caesium tetrachlorido aurate(III), $CsAuCl_4$, is presented. The compound crystallizes in the form of orange, needle-shaped single crystals in the monoclinic space group $C2/c$ with a = 12.923(2), b = 6.1715(9), c = 96512(13) Å, β = 105.049(13)°, V = 743.34(19) Å^3, and Z = 4. As expected, the compound consists of isolated Cs^+ cations and square planar $AuCl_4^-$ anions.

Key words: Caesium, Gold, Chloride

Introduction

Alkali metal tetrahalido aurates(III) have been studied crystallographically in some detail, but for $CsAuCl_4$ only the lattice parameters have been given [1 – 3]. Here we present the X-ray single-crystal structure of $CsAuCl_4$.

Results and Discussion

$CsAuCl_4$ crystallizes in the monoclinic space group $C2/c$ and is isotypic to $RbAuCl_4$. The Cs cation and the Au atom reside on the 4e and 4c Wyckoff positions, respectively, whereas the chloride anions reside on the common 8f position. As expected, Au(III) is coordinated square-planar by the chloride ions according to its [Xe] 5d^8 electron configuration (Fig. 1). However, the planarity is also required by the site symmetry of $\bar{1}$ of the Au atom. The Au–Cl distances are 2.2718(13) and 2.2838(13) Å, so their deviation from a perfect square is small. For detailed atomic distances and angles see Table 1. The Cl(1)–Cl(2) and Cl(1)–Cl(2)#1 distances are 3.2034(19) and 3.2387(21) Å. The coordination number of the Cs cation is ten. It is coordinated by six $AuCl_4^-$ anions, four of them coordinate with two chlorine atoms, and two $AuCl_4^-$ anions coordinate with one chlorine atom. The Cs–Cl distances are found in the range from 3.48 to 3.77 Å. Fig. 2 shows the unit cell of $CsAuCl_4$, and Table 2 holds some crystallographic details.

Table 1. Selected atomic distances and angles of the title compound[a].

Atoms	Distance (Å)	Atoms	Angle (deg)
Au(1)–Cl(1)	2.2718(13)	Cl(1)$^{\#1}$-Au(1)–Cl(1)	180
Au(1)–Cl(2)	2.2838(13)	Cl(1)$^{\#1}$-Au(1)–Cl(2)$^{\#1}$	89.38(5)
Au(1)–Cs(1)$^{\#2}$	4.4743(7)	Cl(1)–Au(1)–Cl(2)$^{\#1}$	90.63(5)
Au(1)–Cs(1)$^{\#4}$	4.5158(6)	Cl(1)$^{\#1}$-Au(1)–Cl(2)	90.62(5)
Cs(1)–Cl(1)$^{\#6}$	3.4813(14)	Cl(1)–Au(1)–Cl(2)	89.38(5)
Cs(1)–Cl(1)$^{\#8}$	3.5400(17)	Cl(2)$^{\#1}$-Au(1)–Cl(2)	180
Cs(1)–Cl(2)$^{\#7}$	3.6957(13)		
Cs(1)–Cl(2)	3.7746(14)		

[a] Symmetry operations for the generation of equivalent atoms: $^{\#1}$ $-x+1/2$, $-y+1/2$, $-z$; $^{\#2}$ x, $y-1$, z; $^{\#4}$ $-x+1$, $-y+1$, $-z$; $^{\#6}$ $x+1/2$, $y+1/2$, z; $^{\#7}$ $-x+1/2$, $y+1/2$, $-z+1/2$; $^{\#8}$ $x+1/2$, $-y+3/2$, $z+1/2$.

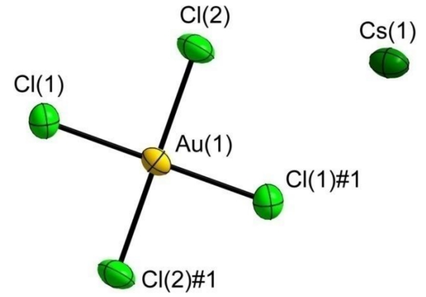

Fig. 1. The $[AuCl_4]^-$ anion and the Cs^+ cation of the title compound. Displacement ellipsoids are shown at the 70 % probability level at 150 K. Symmetry transformations for the generation of equivalent atoms: $^{\#1}$ $-x+0.5$, $-y+0.5$, $-z$.

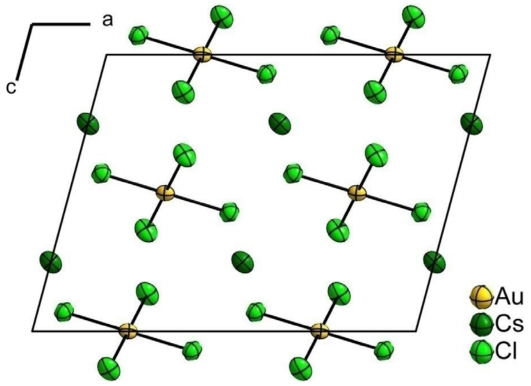

Fig. 2. A projection of the unit cell of the title compound onto the *ac* plane. Displacement ellipsoids are shown at the 70 % probability level at 150 K.

Table 2. Crystal structure data for the title compound $CsAuCl_4$.

Formula	$AuCl_4Cs$
M_r	471.68
Crystal system	monoclinic
Size, mm^3	$0.3 \times 0.02 \times 0.02$
Space group	$C2/c$
a, Å	12.923(2)
b, Å	6.1715(9)
c, Å	9.6512(13)
β, deg	105.049(13)
V, Å^3	743.34(19)
Z	4
ρ_{calc}, g/cm^3	4.22
λ, Å	0.71073
T, K	150
μ(MoK_α), mm^{-1}	25.9
R_{int}/R_σ	0.0566 / 0.0192
Data / parameters / restraints	874 / 31 / 0
$R(F)^a$ $[I \geq 2\sigma(I)]$ / all data	0.0241 / 0.0253
$wR(F^2)^a$ $[I \geq 2\sigma(I)]$ / all data	0.0633 / 0.0636
Extinction	0.0029(2)
GoF (F^2, all data)^b	1.126
$\Delta\rho_{max/min}$, e Å^{-3}	2.47 / −1.57

[a] $R1(F) = \|F_o| - |F_c\|/\Sigma|F_o|$, $wR(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, for the compound: $w = [\sigma^2(F_o{}^2) + (0.0428P)^2 + 1.6646P]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2,0) + 2F_c{}^2)/3$; [b] $GoF = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

A comparison of the Au–Cl bond lengths with those of the tetrachloroaurate(III) compounds MAuCl$_4$ (M = K, Na, Rb, NH$_4$, pyridinium, Ph$_4$As, and others) shows a very good agreement. Jones reported that the average Au–Cl distances for the anion are 227(1) Å [4]. In fact, the Au–Cl bond lengths of $CsAuCl_4$ are the same within standard deviation as in the isotypic $RbAuCl_4$. The Cs–Cl distances are approximately 0.1 Å longer than the respective distances in $RbAuCl_4$. The influence of these two cations on the anion is thus very similar. For crystallographic reasons, the space group of $RbAuCl_4$ was chosen as $I12/c1$ [3]. Transforming the space group to the standard setting $C12/c1$ yields the lattice parameters a = 12.512, b = 5.902, c = 9.76 Å, β = 102.42°, V = 703.84 Å^3. Therefore we observe an expansion of the a parameter by 3.3, of the b parameter by 4.6, of the angle by 2.6 and of the volume by 5.6 % when going from $RbAuCl_4$ to $CsAuCl_4$. The c parameter however is contracted by 1.1 %. If the Biltzsche Rauminkremente are used to calculate the volume gain when going from the Rb to Cs compound, a value of 5.8 % is obtained, which is in good agreement with the observed volume increase [5]. In summary we present the crystal structure of $CsAuCl_4$ which features the square planar $AuCl_4{}^-$ anion and is isotypic to $RbAuCl_4$ [1–3].

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), http://www.fiz-karlsruhe.de/icsd.html, on quoting the depository number CSD 423233 for the compound, the name of the author, and the citation of the paper.

Experimental Part

All work was carried out in air at ambient conditions. Gold-containing laboratory waste was worked up with aqua regia. Upon driving off the nitrate with hot, concentrated hydrochloric acid, $CsAuCl_4$ crystallized in the form of orange needles upon cooling. A crystal was selected and mounted on the diffractometer using the MiTeGen MicroLoop system. The structure was solved using Direct Methods and refined on F^2 [6, 7]. All atoms were localized by Fourier cycling methods and refined anisotropically.

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