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# The Tetrachloridoaurates(III) of Zinc(II) and Cadmium(II)

Christian Landvogt<sup>[a]</sup> and Johannes Beck\*<sup>[a]</sup>

Dedicated to Prof. Hartmut Bärnighausen on the Occasion of his 85. Birthday

Abstract: The first salt-like compounds of dications with [AuCla]anions are reported. The compounds Zn[AuCl<sub>4</sub>]<sub>2</sub>·(AuCl<sub>3</sub>)<sub>1.115</sub> (1) and  $Cd[AuCl_4]_2$  (2) are obtained from reactions of  $MCl_2$  (M = Zn, Cd) and elemental gold in liquid chlorine at ambient temperature under autogenous pressure and subsequent annealing at 230 °C. The structure of 1 represents an incommensurately modulated composite (superspace group  $C2/c(\alpha 0y)0s$ ) built of two subsystems. The first subsystem contains chains of zinc(II) tetrachloridoaurate(III), which feature a slightly distorted octahedral coordination of Zn and can be second subsystem consists of Au<sub>2</sub>Cl<sub>6</sub> molecules, which are located in channels built up by the first subsystem. The structural parameters of the hosted Au<sub>2</sub>Cl<sub>6</sub> molecules show only small deviations from neat AuCl<sub>3</sub>. The crystal structure of  $Cd[AuCl_4]_2$  (2) consists of chains built of Cd2+ ions coordinated by bridging [AuCl4] anions and alternating Cd-Au sequence. Cd has a distorted octahedral coordination environment.

#### Introduction

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Gold(III) halides are Lewis acids and readily form salts with alkali halides. A large number of salts with alkali cations have been reported [1]. However, the number of known compounds for salts with dications is dramatically smaller. Only salts of tetrafluoridoaurate(III) anions with alkaline earth and divalent transition metal cations  $(M[AuF_4]_2 \text{ with } M = Mg, Ba, Ni, Pd, Ag,$ Au, Zn, Cd, Hg) have been reported [2], but compounds of the heavier halogen homologues of the formula type M[AuX<sub>4</sub>]<sub>2</sub> with X = CI, Br, or I are unknown. The literature holds two compounds, which come close to this formula type. In 1988 Jones et al. reported a zinc(II) tetrachloroaurate disolvate [3] and more recently, in 2007, the tetraamminepalladium salt [Pd(NH<sub>3</sub>)<sub>4</sub>][AuCl<sub>4</sub>]<sub>2</sub> was reported by Plyusnin et al. [4]. However, in both compounds additional ligands are present in the coordination sphere of the respective dication besides the chloride anions of the tetrachloridoaurate(III) anion. Looking for even higher charged cations a single exception is again found for tetrafluoridoaurate(III). In 1996 Graudejus et al. reported the synthesis and crystal structure of La[AuF<sub>4</sub>]<sub>3</sub> [5].

This work describes the synthesis and the crystal structures of the first salts of tetrachloridoaurate(III) with dications:  $Zn[AuCl_4]_2 \cdot (AuCl_3)_{1.115}$  (1) and  $Cd[AuCl_4]_2$  (2). Compound 1 is

found to have an incommensurately modulated composite structure.

### **Results and Discussion**

The properties and crystal structure of Zn[AuCl<sub>4</sub>]<sub>2</sub>. (AuCl<sub>3</sub>)1.115 (1)

Zn[AuCl<sub>4</sub>]<sub>2</sub>·(AuCl<sub>3</sub>)<sub>1.115</sub> (1) forms air-sensitive transparent orange crystals. DSC measurements heating up from -50 °C show no thermal effect up to the decomposition of the compound at about 250 °C, which coincidences with the decomposition temperature of neat AuCl<sub>3</sub>. The single crystal diffraction pattern of this compound cannot be fully indexed with three indices *hkl*. However, *hklm* indexing as a 3+1D modulated compound succeeded. Additionally, Fourier maps from initial structure solution attempts suggested that the crystal is best described as an incommensurately modulated composite crystal with two subsystems in the monoclinic superspace group  $C2/c(a0\gamma)$ 0s. Table 3 holds the crystallographic data for 1, unit cell data for both subsystems is shown in Table 4. Further details are available in the Supporting Information.

The first subsystem contains zinc(II) tetrachloridoaurate(III), the second subsystem contains gold(III) chloride in form of discrete Au<sub>2</sub>Cl<sub>6</sub> molecules. The asymmetric unit of the first subsystem consists of one zinc atom and two halves of the anion, the asymmetric unit of the second subsystem contains one gold atom and a terminal and a bridging chlorine atom, respectively. The zinc(II) tetrachloridoaurate(III) substructure forms chains, which run along the (101) direction (Figure 1). In these chains, zinc(II) is coordinated by three tetrachloridoaurate anions, which act as mono- or bis-chelating ligands resulting in a distorted octahedral ZnCl<sub>6</sub> coordination sphere. One of the [AuCl<sub>4</sub>]<sup>-</sup> anions is coordinated terminally, while the other two are bridging between Zn cations, resulting in zig-zag chains with alternating Zn-Au sequence. The Zn-Cl distances for the three surrounding anions differ slightly. The shortest distance is present between the chlorine atoms of the terminal  $[{\rm AuCl}_4]^-$  anions and the  ${\rm Zn}^{2+}$ cations (roughly 2.40 Å), while the bridging [AuCl<sub>4</sub>]<sup>-</sup> ligands are slightly farther away from the Zn<sup>2+</sup> cations (Zn-Cl distances between 2.46 Å and 2.52 Å). The distortion of the octahedron is reflected best by its CI-Zn-CI angles, which range from 80° to 100° and thus deviate substantially from rectangularity.

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**Figure 1.** Section of the zinc(II) tetrachloroaurate(III) chain taken from the crystal structure of **1** at *t* = 0. The chain runs along the (101) direction and can be described by the Niggli formula  $\frac{1}{4}$ {Zn[AuCl<sub>4</sub>]<sub>1/1</sub>[AuCl<sub>4</sub>]<sub>2/2</sub>}. Symmetry codes for equivalent atoms have been omitted. The displacement ellipsoids represent a probability of 90 %.

The arrangement of the zig-zag chains builds up a honeycomblike structure when viewed along the crystallographic c axis. This honeycomb structure generates flat channels within the crystal packing running along the c axis (see Figure 2). These channels are filled by the second subsystem.



**Figure 2.** Network built up by subsystem I in the crystal structure of 1. Structural detail taken at t = 0. The displacement ellipsoids represent a probability of 90 %.

The second subsystem consists of planar dinuclear  $Au_2Cl_6$ molecules, which show almost identical geometric parameters in comparison to the molecules present in neat  $AuCl_3$  [6]. The bond lengths and angles found for  $Au_2Cl_6$  in both compounds are very similar, Table 1 compares their structural features. In the structure of 1, the dimeric molecules are stacked with their longer "rectangle edge" next to each other along the channels built up by the first subsystem. These channels, however, seem slightly too wide to perfectly house the  $Au_2Cl_6$  molecules, which allows the molecules to tilt towards each other (Figures 3 and 4).

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**Figure 3.** Au<sub>2</sub>Cl<sub>6</sub> molecules taken from the crystal structure of **1** at t = 0. The channel built by subsystem I is slightly too large, the molecules are oriented in different directions. The Cl(6)···Cl(6) distances between adjacent molecules are a function of *t* (Figure 4). Symmetry codes for equivalent atoms have been omitted. The displacement ellipsoids represent a probability of 90 %.



**Figure 4.** *t*-Plot of the distance between the terminal chlorine atom of adjacent  $Au_2Cl_6$  molecules in the modulated crystal structure of **1**. The longer distances around *t* = 0.8 correspond to sections where the tilting direction switches.

**Table 1.** Comparison of the structural features of the second subsystem of1 to neat gold(III) chloride. For AuCl<sub>3</sub> all symmetrically independent valuesare listed, the value ranges for subsystem II are taken from *t*-plots.

	AuCl <sub>3</sub> <sup>[a]</sup>	Subsystem II of 1
d(Au – Cl <sub>term</sub> )	2.245(2) Å; 2.251(2) Å	2.23 Å – 2.27 Å
d(Au –Cl <sub>bridge</sub> )	2.333(2) Å; 2.343(2) Å	2.32 Å – 2.38 Å
d(Au – Cl <sub>ax</sub> )	3.454(2) Å; 3.460(2) Å	3.25 Å – 3.26 Å
<(Cl <sub>bridge</sub> – Au – Cl <sub>bridge</sub> )	85.71(6)°	85° – 87°
<(Cl <sub>bridge</sub> - Au - Cl <sub>term</sub> )	91.58(6)°; 92.40(6)°	90° – 93°
<(Cl <sub>term</sub> – Au – Cl <sub>term</sub> )	90.31(7)°	89° – 92°

[a] We redetermined the crystal structure of AuCl<sub>3</sub> based on single crystal date recorded at 123 K with the lattice constants: a = 6.5316(5), b = 10.9011(7), c = 6.4072(5) Å and  $\beta = 113.477(4)^{\circ}$  (see Supporting Information). The atomic coordinates are in good agreement with those already published based on room temperature data [6].

Usually, compounds with square-planar coordinated gold(III) cations show an extended 4+2 or at least 4+1 coordination sphere for the gold atom. In the crystal structure of **1**, this distorted octahedral coordination is likewise found. Examining the coordination of the gold atoms of the second subsystem, contacts to the chlorine atoms of the terminal anions of the first subsystem are revealed (Figure 5). These contacts range from

3.25 Å to 3.60 Å (Figure 6 *top*). There are always at least two contacts below 3.60 Å. In the first half of the modulation (t < 0.5) the close contacts are present between Au(3) and Cl(2), for the second half they are present between Au(3) and Cl(1). The extended coordination sphere for Au(III) around t = 0.5 even shows up to four additional contacts as close as 3.75 Å, which is a feature not observed for neat AuCl<sub>3</sub>.

The closer the contact between the  $Au_2Cl_6$  dimer and the chlorine atom, the better is the interaction between the dimer and the first subsystem. Therefore, fixing of the dimer inside the channel should be stronger for short contacts. Indeed, this is reflected by the maximal anisotropic displacement parameters of the gold atoms shown in *bottom* of Figure 6. The maximal displacement is larger for longer contacts and smaller for closer contacts.

Both independent gold atoms of the first subsystem also exhibit an extended 4+2 coordination sphere (pink contacts in Figure 5). The gold atoms of the bridging anions have contacts between 3.30 Å and 3.60 Å to the terminal chlorine atoms of the Au<sub>2</sub>Cl<sub>6</sub> dimers. Finally, the gold atoms of the terminally bound [AuCl<sub>4</sub>]<sup>-</sup> anions fulfill their 4+2 coordination inside their own subsystem, with contacts from 3.40 Å to 3.60 Å to chlorine atoms of the symmetrically equivalent ligands belonging to the chains above and below.



**Figure 5.** Extended coordination of the gold atoms (depicted as dashed lines) in the crystal structure of 1 at t = 0. All three independent gold atoms show the 4+2 coordination usually found for gold(III) compounds. The blue and orange coloured contacts are those depicted in the *t*-plot in Figure 6. The displacement ellipsoids represent a probability of 90 %.

With this property in mind the necessity for an incommensurately modulated composite crystal structure is revealed. The reason for the intercalated  $Au_2Cl_6$  dimers lies in the extended coordination sphere of the gold(III) cations. In the first subsystem only one of the two independent gold atoms is able to achieve the 4+2 coordination without the intercalated guest molecules. A different conformation of the Zn[AuCl\_4]<sub>2</sub> chain might be sterically hindered by the small size of the zinc(II) cation. Finally, the translation period of the stacked dimers does not fit with the translation period of the stacked chains, because

the Au<sub>2</sub>Cl<sub>6</sub> molecules are tilted towards each other to improve the space filling instead of a uniform arrangement. With the extended coordination in mind, the tilting may also be interpreted as an attempt of the Au<sub>2</sub>Cl<sub>6</sub> molecules to optimize their 4+2 coordination interaction with the first subsystem. This is supported by the fact that the elongation of the displacement ellipsoids of the Au<sub>2</sub>Cl<sub>6</sub> molecules increases with the length of the distance between the Au atom and the additional chlorine ligands, indicating a less tight fixation of the dimers inside the channel (Figure 6 *bottom*).



**Figure 6.** *t*-Plot of the intersubsystem Au(3)····Cl(1/2) contacts (*top*) and the maximal anisotropic displacement parameter (ADP) of Au(3) (*bottom*) in the modulated crystal structure of **1**. There are always at least two Au···Cl contacts below 3.60 Å to complete the 4+2 coordination sphere. The ADP parameter for Au(3) behaves accordingly: for shorter contacts (t = 0.25; 0.75) the displacement ellipsoid is smaller, while it is higher for longer contacts (t = 0.0; 0.5).

#### Supercell approximation of 1: Zn<sub>9</sub>Au<sub>28</sub>Cl<sub>102</sub>

The modulation vector of **1** is close to (2/3; 0; 1/9), which would open the opportunity for a supercell description as a 27-fold superstructure. However, refinement as a commensurately modulated structure yields significantly worse *R* values. By omitting part of the diffraction pattern, an acceptable nine-fold superstructure can be solved and refined in 3D space. All general features of the modulated structure are present. The most noticeable error is the exact description of the Au<sub>2</sub>Cl<sub>6</sub> molecules as is evident from their large displacement ellipsoids (Figure S9). Full data for this approximant is given in the Supporting Information.

#### The crystal structure of Cd[AuCl4]2

The compound Cd[AuCl<sub>4</sub>]<sub>2</sub> (**2**) forms orange-yellow crystals and crystallizes in the monoclinic space group I2/a (Table 3). The asymmetric part of the unit cell contains half the formula unit. The gold atom of the tetrachloridoaurate(III) anion in the first coordination sphere – as usual for gold(III) – is in an almost perfect square-planar arrangement. The Au-Cl bond lengths range between 2.26 Å and 2.32 Å, and the Cl-Au-Cl angles between 89° and 91° (see Table 2). The coordination around the

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cadmium cations, on the other hand, is in form of heavily distorted octahedra, which is reflected by the wide range of Cl-Cd-Cl angles from 76° to 101°. The Cd-Cl distances however, are almost identical between 2.62 Å and 2.63 Å. The six chlorine atoms belong to four different [AuCl<sub>4</sub>]<sup>-</sup> anions, which requires two anions to act as bidentate ligands. All anions bridge two adjacent Cd<sup>2+</sup> cations, while one cation is always coordinated in bidentate and the other one in monodentate fashion. This means in turn, that one chlorine atom of each anion is not part of the cadmium coordination sphere. The role of this chlorine atom will be discussed later. The site symmetry requires that pairs of two anions are co-planar with a Au-Au distance of 4.04 Å. The bridging anions connect the cations to chains, which run along the crystallographic *c* axis (Figure 7).



**Figure 7.** Chain running along the crystallographic *c* axis in the crystal structure of **2.** Displacement ellipsoids represent a probability of 90 %. Superscripts indicate symmetry generated atoms: (i) -x, - $\frac{1}{2}$ +y,  $\frac{1}{2}$ -z; (ii) x,  $\frac{1}{2}$ -y, - $\frac{1}{2}$ +z; (iii)  $\frac{1}{2}$ -x, y, -z; (iv)  $\frac{1}{2}$ -x,  $\frac{1}{2}$ -y,  $\frac{1}{2}$ -z.

As was discussed for compound 1, the gold(III) coordination sphere is usually extended to an elongated octahedron in a 4+2 coordination. In the crystal structure of 2, again two additional chlorine atoms are present to fulfill the extended coordination. One of these two atoms is the "non-coordinating" Cl(1) belonging to an adjacent chain with a Au---Cl distance of 3.33 Å, the other atom is Cl(3) belonging to a neighboring co-planar [AuCl<sub>4</sub>]<sup>-</sup> anion. Here, the Au---Cl distance is larger and amounts to 3.53 Å (Figure 8, dashed lines). This extended coordination is Au-Cl within reflected by the distances the tetrachloridoaurate(III) anions. The shortest Au-CI bond is present for the chlorine atom, which is not part of the cadmium coordination sphere, while the longest Au-Cl bond is found for the chlorine atom, which is part of the extended 4+2 coordination of an adjacent gold atom.



**Figure 8.** Extended unit cell of **2** viewed along the crystallographic *c* axis. The extended gold coordination sphere is indicated by dashed lines. Displacement ellipsoids represent a probability of 90 %.

Atoms	Distance / Å	Atoms	Distance / Å
Au—Cl(1)	2.261(3)	Cd—Cl(2)	2.623(2)
Au—CI(2)	2.293(1)	Cd—Cl(3) <sup>ii</sup>	2.622(2)
Au—Cl(3)	2.316(3)	Cd—Cl(4) <sup>ii</sup>	2.630(3)
Au—CI(4)	2.286(2)	Au…Cl(1) <sup>i</sup>	3.338(2)
Au…Au <sup>ii</sup>	4.0400(6)	Au…Cl(3) <sup>iv</sup>	3.532(2)
Atoms	Angle / °	Atoms	Angle / °
Cl(1)—Au—Cl(2)	90.30(7)	Cl(2)—Cd—Cl(2) <sup>iii</sup>	77.64(8)
CI(2)—Au—CI(3)	89.87(7)	Cl(2)—Cd—Cl(3) <sup>iv</sup>	93.28(6)
Cl(3)—Au—Cl(4)	89.60(7)	Cl(2)—Cd—Cl(4) <sup>ii</sup>	90.11(6)
Cl(4)—Au—Cl(1)	90.24(7)	Cl(2)—Cd—Cl(4) <sup>iv</sup>	100.36(6)
CI(3) <sup>ii</sup> —Cd—CI(3) <sup>iv</sup>	99.29(9)	$CI(1)\cdots Au\cdots CI(1)^i$	101.44(7)
CI(3) <sup>iv</sup> —Cd—CI(4) <sup>ii</sup>	94.97(6)	Cl(1)…Au…Cl(3) <sup>iv</sup>	82.17(7)
CI(3) <sup>ii</sup> —Cd—CI(4) <sup>ii</sup>	76.26(6)		

Table 3. Crystallographic data and details of the structure refinement for

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Zn[AuCl <sub>4</sub> ] <sub>2</sub> ·(AuCl <sub>3</sub> ) <sub>1.115</sub> ( <b>1</b> ) brackets refer to the last s	and Cd[AuCl₄] <sub>2</sub> ( <b>2</b> ). Standard ignificant digit.	d deviations given in	
Compound	Zn[AuCl4] <sub>2</sub> ·(AuCl <sub>3</sub> ) <sub>1.115</sub> ( <b>1</b> ) Cd[AuCl4] <sub>2</sub> ( <b>2</b> )		
$M_r$ / g·mol <sup>-1</sup>	1081.12	789.93	
Temperature / K	123(2)		
Crystal system	Monoclinic		
Space group	$C2/c(\alpha 0\gamma)0s$	<i>l</i> 2/ <i>a</i> (No. 15)	
Lattice constants		a = 12.2612(7)  Å b = 7.3511(4)  Å c = 12.8244(8)  Å $\beta = 95.403(5)^{\circ}$	
Volume / ų	1668.3(9)	1150.8(2)	
Ζ	4	4	
Calc. density / g cm <sup>-3</sup>	4.304	4.559	
Radiation	Mo-K <sub><math>\alpha</math></sub> radiation $\lambda$ =	= 0.71073 Å	
Crystal size / µm <sup>3</sup>	$86\times70\times46$	$88\times58\times2$	
Theta range	$0.92^{\circ} \leq \theta \leq 47.43^{\circ}$	$3.2^\circ \leq \theta \leq 27.5^\circ$	
Completeness	98 % for $\theta$ = 26.62°	100 % for $\theta$ = 25.24°	
Limiting indices	$ h  \le 17;  k  \le 37;$ $ l  \le 12;  m  \le 4$	<i>h</i>  ≤21;   <i>k</i>  ≤9;   <i>l</i>  ≤15	
Reflections. collected / unique	117367 / 29752	9785 / 1319	
Absorption correction / Abs. coefficient / mm <sup>-1</sup>	SADABS / 30.502	MULTISCAN / 29.060	
Max. / min transmission	0.4357 / 0.2649	0.1822 / 0.0802	
Refined parameters / against	433 / F	51 / <i>F</i> <sup>2</sup>	
$R_1$ ; w $R_2$ (all data) <sup>[a]</sup>	0.1721; <i>wR</i> = 0.0631	0.0375; 0.0569	
<i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub> (obs) <sup>[a]</sup>	0.0555; wR = 0.0576 n(l > 3σ) = 11923	0.0270; 0.0545 $n(l > 4\sigma) = 1112$	
R <sub>1</sub> main / 1 <sup>st</sup> / 2 <sup>nd</sup> R <sub>1</sub> 3 <sup>rd</sup> / 4 <sup>th</sup> (obs)	3.46 % / 5.66 % / 7.98 % 14.09 % / 21.19 %	<u>v</u> _	
Goodness-of-Fit	1.57	1.092	
Largest peak / hole / e <sup>-</sup> Å <sup>-3</sup>	+14.44 / -16.48 (3+1D) integr. charge: +2.23 / -3.47	+1.329 / -1.731	

[a] Weighting scheme for 1:  $w = [\sigma^2 F_o + 0.0001 F_o^2]^{-1}$ and for 2:  $w = 1/[\sigma^2 F_o^2 + (0.0083P)^2 + 7.7789P^2]$  with  $P = \frac{1}{3} (F_o^2 + 2F_c^2)$ 

	Subsystem I	Subsystem II
Composite matrix W <sup>v</sup>	[1 0 0 0;	[1 0 0 0;
	0100;	0100;
	0010;	0011;
	0001]	0011]
space group	C2/c(α0γ)0s	C2/m(α0γ)0s
Lattice constants	a = 9.2485 Å	a = 10.5213 Å
	b = 23.7995 Å	b = 23.7995 Å
	c = 7.5926 Å	<i>c</i> = 6.8136 Å
	$\beta = 93.405^{\circ}$	β = 118.661°
	q = (0.6600; 0;	q = (-0.5923; 0;
	0.1143)	0.8974)
Volume / ų	1668.3	1497.1
Contents	Zn[AuCl4]2	1/2 Au2Cl6
Z	4	4

#### Conclusions

Two salt-like compounds of dications with  $[AuCl_4]^-$  anions were synthesized. The use of liquid chlorine as solvent was crucial to obtain crystalline products. The single crystal structures of  $Zn[AuCl_4]_2 \cdot (AuCl_3)_{1.115}$  (1) and  $Cd[AuCl_4]_2$  (2) exhibit an extended 4+2 coordination sphere around the Au(III) cation. In the structure of 2 this elongated octahedral coordination is achieved by building chains which are arranged in a pseudo-hexagonal rod packing. In the structure of 1,  $Au_2Cl_6$  molecules are intercalated as guest molecules into its honeycomb-like network to complete the gold coordination sphere. The resulting intricate crystal structure is best described as an incommensurately modulated two-sublattices composite structure.

#### **Experimental Section**

**Zn[AuCl<sub>4</sub>]<sub>2</sub>•(AuCl<sub>3</sub>)<sub>1.115</sub> (1):** Gold powder, precipitated by reduction with gaseous SO<sub>2</sub> from HAuCl<sub>4</sub> solution (104 mg, 0.53 mmol) and ZnCl<sub>2</sub>, prepared from elemental zinc and hydrogen chloride at 700 °C (21.1 mg, 0.16 mml) were charged in a borosilicate ampoule (~10 cm length, 12.9 mm diameter, 2.2 mm wall thickness). Chlorine (Praxair, Düsseldorf, 99.9 %), was condensed onto the mixture (filling level 25 %). The chlorine was frozen with liquid nitrogen and the ampoule was sealed under reduced pressure and placed vertically for four weeks at ambient temperature. The ampoule was opened, the excess of chlorine evaporated and the orange powder was sealed under reduced pressure in a glass ampoule (length 20 cm) having an additional constriction. The

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ampoule was placed asymmetrically in the temperature gradient of a tube furnace for one week at 230 °C to sublimate off the excess of gold(III) chloride into the colder part. The constriction was sealed to separate AuCl<sub>3</sub> and **1**, which remains in the warmer part. Longer reaction times for the first step improved yield and crystallinity.

**Cd[AuCl<sub>4</sub>]**<sub>2</sub> (2): The synthetic procedure follows the protocol described for the synthesis of 1. Gold powder (58.8 mg, 0.30 mmol) and CdCl<sub>2</sub> (27.4 mg, 0.15 mmol), synthesized from elemental cadmium and hydrogen chloride at 450 °C, were used.

**Crystal Structure Determinations:** Crystals of **1** and **2** suitable for X-ray analysis were selected in perfluorinated polyether (FOMBLIN Y HVAC 140/13, Solvay, Brussels, BE) and transferred to a Bruker Nonius kappaCCD diffractometer equipped with graphite-monochromatized Mo-K<sub>a</sub> radiation and an Oxford Cryostream 700 crystal cooling device. Cell determination and data collection were carried out at 123 K. The data collection was performed by COLLECT [7]. Data integration for **1** was performed by APEX2 [8], followed by a semi-empirical absorption correction as implemented in SADABS [8]. The initial, modulated structure solution was achieved by charge flipping as implemented by SUPERFLIP [9], interpretation of the resulting electron density and further structure refinement was done with JANA2006 [10]. Diamond [11] was used for structure visualisation.

Data integration for **2** was done using DENZO [12], followed by a semiempirical absorption correction suitable for area detectors as proposed by Blessing [13] (implemented in PLATON [14]). The structure was solved by charge flipping using SUPERFLIP and refined with anisotropic displacement parameters for all atoms with SHELXL 2014 [15]. The setting *I*2/*a* was chosen to avoid an extreme monoclinic angle in the standard setting *C*2/*c* (lattice constants of the C2/*c* cell: *a* = 16.8876(10), *b* = 7.3511(4), *c* = 12.2612(7) Å,  $\beta$  = 130.885(2)°).

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, E-mail: crysdata@fiz-karlsruhe.de, on quoting the CSD number CSD-433230 for Cd[AuCla]2 (2) and CSD-433229 for AuCl<sub>3</sub> (123 K). Modulated data for Zn[AuCla]2 •(AuCl<sub>3</sub>)<sub>1.115</sub> (1) have been deposited under the CSD number CSD-433327, the commensurate approximant Zn<sub>9</sub>Au<sub>28</sub>Cl<sub>102</sub> is available under CSD-433231.

### **Supporting Information**

Supporting Information is available for this article (15 pages): DSC data, diffraction images, additional *t*-plots and positional parameters of **1**, positional parameters and thermal displacement parameters of **2**, complete crystallographic data of the structure of AuCl<sub>3</sub> at 123 K, crystallographic data of the supercell approximation of **1**.

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**Keywords:** Tetrachloridoaurate • Zinc • Cadmium • Incommensurate structure • Composite crystal

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# FULL PAPER

The first salt-like compounds of divalent metal cations with [AuCl<sub>4</sub>]<sup>-</sup> anions are reported. The compounds  $Zn[AuCl_4]_2 \cdot (AuCl_3)_{1.115}$ (1) and Cd[AuCl<sub>4</sub>]<sub>2</sub> (2) are obtained from reactions of  $MCI_2$  (M = Zn, Cd) and elemental gold in liquid chlorine. 1 is incommensurately modulated an composite built of polymeric zinc(II) tetrachloridoaurate(III) and embedded Au<sub>2</sub>Cl<sub>6</sub> molecules. 2 consists of chains of  $Cd^{2+}$  ions bridged by  $[AuCl_4]^-$  anions. Both M<sup>2+</sup> cations posses a distorted octahedral coordination environment.



Christian Landvogt, Johannes Beck\*

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The Tetrachloridoaurates(III) of Zn(II) and Cd(II)

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