The Trichlorogermanite(II) Anion and its Gold(I) Complexes

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Germanium(II), Trichlorogermanite(II), Gold-Germanium Compounds, Arsine Complexes, Germylene Insertion

Tetraphenylphosphonium trichlorogermanite(II) (1) has been prepared (as a reference compound) from Ph_4P^{\dagger} Cl⁻ and GeCl₂(dioxane) in tetrahydronaphthalene. Its structure has been determined by single crystal X-ray methods. The lattice contains independent monomeric $GeCl_3^-$ anions (Ge-Cl distances between 2.290 and 2.320 Å, Cl-Ge-Cl angles between 95.33 and 98.27°). Treatment of (Ph₃As)AuCl with GeCl₂(dioxane) affords (Ph₃As)AuGeCl₃ in high vields as a germylene insertion product (2). The complex is a dimer in the crystal with a short Au--Au contact of 2.9415(4) Å and bent As-Au-Ge axes [169.353(13)°]. The GeCl₃ ligand has shorter Ge-Cl bonds [2.175 to 2.183 Å] and wider Cl-Ge-Cl angles than in the free anion [100.9 to 101.9°]. The analogous reaction with CH₂(AsPh₂AuCl)₂ leads only to a mono-insertion product in the form of a salt with $\{[CH_2(AsPh_2)_2Au]\}_2^{2+}$ dications and two $[ClAuGeCl_3]^-$ anions (3). In the lattice these three ions form a centrosymmetrical tetranuclear unit through short Au--Au contacts. The resulting z-shaped Au--Au--Au-Au chain has distances of 3.0499(6) (twice) and 3.1613(8) Å and angles of 118.833(8)° (twice). The geometry of the GeCl₃ units is similar to that in 2. $\{(Et_3N)Au[P(o-Tol)_3]\}^+ PF_6^-$ (4) was obtained as a by-product in several reactions with the bulky phosphine and where NEt₃ was used as a base. The crystals contain two crystallographically independent cations with a similar core structure, but different conformations of the substituents. Both the P-Au and the N-Au bonds are elongated owing to steric effects.

Introduction

The trichlorogermanite(II) anion $[\text{GeCl}_3]^-$ is isoelectronic with arsenic(III) chloride $[\text{AsCl}_3]$ and can act as a soft donor ligand for low-valent, late transition metals. The structures of the two species are expected to be very similar both as a free anion/molecule and in analogous complexes. Structural studies of trichlorogermanate(II) salts are few in number, and most of the examples reported in the literature feature aggregates { $[\text{GeCl}_3]_n$ }^{*n*-}, as *e. g.* in the classical case of Cs[GeCl₃]. It was only in the lattice of salts with large cations, as in the benzyl(triethyl)ammonium salt, that isolated [GeCl₃]⁻ anions could be investigated, and in fact very close structural analogies between [GeCl₃]⁻ and AsCl₃ have been confirmed [1].

Results and Discussion

In the course of the present study we have discovered another example of "free" [GeCl₃]⁻ in the form of its tetraphenylphosphonium salt, which was prepared in order to provide new reagents for the introduction of the trichlorogermanite(II) ligand into coinage metal complexes. Following earlier work [2, 3] on prototypes like Ph₃P-Au-GeCl₃, we have also included a case where Ph₃P is replaced by Ph₃As in order to match the isoelectronic combination (AsX_3/GeX_3^{-}) . Following the same line, a polynuclear complex of bis(diphenylarsino)methane Ph₂AsCH₂AsPh₂ (dpam) has also been prepared, which was anticipated to complement the data on the bis(diphenylphosphino)methane Ph₂PCH₂PPh₂ (dppm) [3 - 5]. A novel stoichiometry and structure involving the anion [Cl-Au-GeCl₃]⁻ was found, however, which illustrates the diversity of structural principles in this system.

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The influence of a typical hard donor as compared to the soft arsine and germanite(II) ligands was briefly investigated by a study of the cationic complex $[(o-Tol)_3P-Au-NEt_3]^+$ obtained as a byproduct in a different context [6].

Tetraphenylphosphonium trichlorogermanite(II)(**1**)

The reaction of equivalent quantities of tetraphenylphosphonium chloride and dichlorogermanium(II)(dioxane) in tetrahydronaphthalene at 90°C leads to a virtually quantitative conversion of the components into the 1:1 complex (99% yield, m. p. 186°C) as a colourless crystalline salt. The product can be recrystallized from dichloromethane to give triclinic single crystals, space group $P\bar{1}$, containing two formula units in the unit cell.

$$\begin{split} [Ph_4P]^+Cl^- + GeCl_2(dioxane) \\ & \longrightarrow dioxane + [Ph_4P]^+GeCl_3^- \end{split}$$

The lattice contains no solvent molecules and is composed of independent $[Ph_4P]^+$ cations and $[GeCl_3]^-$ anions. The cation has a standard molecular geometry which deserves no further comment in this context. The individual $[Ph_4P]^+$ units are stacked in columns with no sub-van der Waals contacts.

In the parallel strings of [GeCl₃]⁻ anions the individual units are also well separated from each



Fig. 1. Molecular structure of compound **1** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge-Cl1 2.3201(8), Ge-Cl2 2.2900(8), Ge-Cl3 2.3030(8), P-C11 1.786(2), P-C21 1.794(2), P-C31 1.789(2), P-C41 1.792(2); Cl1-Ge-Cl2 95.38(3), Cl1-Ge-Cl3 95.33(3), Cl2-Ge-Cl3 98.27(3).

other, with all Cl---Cl and Cl---Ge contacts exceeding 4.774 Å. The anion has no crystallographically imposed symmetry, but the geometry closely approaches the requirements of a threefold axis, with Ge-Cl distances of 2.2900(8), 2.3030(8) and 2.3201(8) Å, and Cl-Ge-Cl angles of 95.33(3), 95.38(3) and 98.27(3)° (Fig. 1). These parameters resemble those reported for other known examples with free [GeCl₃]⁻ anions [1]. There is also a close relation to the structural data of AsCl₃ (in both the gas phase and in the crystal lattice) and of [SeCl₃]⁺, following the isoelectronic principle [1].

(Triphenylarsine)gold(I) trichlorogermanite(II) (2)

Treatment of (triphenylarsine)gold(I) chloride with equimolar quantities of dichlorogermanium(II)(dioxane) in tetrahydrofuran at room temperature and under reflux conditions gives high yields (90%) of the expected 1:1 complex as a colourless, crystalline compound (m. p.183°C).

$$(Ph_3As)AuCl + GeCl_2(dioxane) \rightarrow dioxane + (Ph_3As)AuGeCl_3$$

The crystals are monoclinic, space group C2/c, with four formula units in the unit cell. The compound is hence isomorphous with the triphenylphosphine analogue [2]. In the lattice the molecules are arranged in pairs with the monomeric units crossing their principal molecular axes and with a remarkably short intermolecular Au--Au contact of 2.9415(4) Å (Fig. 2). The arsine ligand has a standard molecular geometry which is not discussed any further.

The trichlorogermanite(II) ligand shows significant deviations from the geometry of the free anion (above). All three Ge-Cl distances are shortened very considerably upon complexation [to values of 2.1750(10), 2.1782(10) and 2.1829(10) Å], and the angles Cl-Ge-Cl are widened to 100.91(4), 100.97(4) and 101.90(4)°. In the gold(I) complex the structure is thus closer to the tetrahedral geometry of regular four-coordinate germanium, and its Ge-Cl bond lengths indicate a significant strengthening through the concomitant rehybridization of the germanium atom.

The axis Ge-Au-As is strongly bent away from linearity [bond angle $169.353(13)^{\circ}$] which facilitates the intermolecular approach and the aurophilic Au-Au contact. In this respect the situation is



Fig. 2. Molecular structure of compound 2 (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au-Ge 2.3884(4), Au-As 2.4117(4), Au-Au' 2.9415(4), As-C11 1.927(3), As-C21 1.926(3), As-C31 1.930(3), Ge-Cl1 2.1829(10), Ge-Cl2 2.1782(10), Ge-Cl3 2.1750(10); Ge-Au-As 169.353(13), Cl1-Ge-Cl2 100.91(4), Cl1-Ge-Cl3 101.90(4), Cl2-Ge-Cl3 100.97(4), Cl1-Ge-Au 116.90(3), Cl2-Ge-Au 117.75(3), Cl3-Ge-Au 115.73(3).

again generally quite similar to the structure of Ph₃PAuGeCl₃[2].

$Bis[bis-\mu,\mu'(diphenylarsinomethane)gold(I)](2+)$ bis[Chloro(trichlorogermanito)gold(I)(1-)] (3)

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Bis(diphenylarsino)methane (dpam) is readily converted into its bis[chlorogold(I)] complex (dpam)(AuCl)₂ by reaction with two equivalents of chloro(dimethyl sulfide)gold(I) in tetrahydrofuran at ambient temperature. Treatment of the resulting clear solution with two equivalents of GeCl₂(dioxane) at room temperature affords colourless crystals (53% yield, m.p. 155°C). After drying in a vacuum the analytical data of the weathered crystals indicate a net composition of (dpam)₂Au₄Ge₂Cl₈. Longer reaction times (20 h) did not lead to any changes in the composition. Upon work-up of the mother liquor a yellow sticky mass was obtained which could not be characterized.



Fig. 3. Molecular structure of compound 3 (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1…Au1' 3.1613(8), Au1…Au2 3.0499(6), Au1-As1 2.4040(8). Au1-As2 2.4066(8), Au2-Ge 2.3235(10), Au2-Cl 2.297(2), Ge-Cl1 2.171(2), Ge-Cl2 2.166(2), Ge-Cl3 2.151(3); As1-Au1-As2 168.52(3), Ge-Au2-Cl 173.87(6).

 $CH_2(AsPh_2)_2 + 2 (Me_2S)AuCl$ $\rightarrow 2 \text{ Me}_2\text{S} + \text{CH}_2(\text{AsPh}_2\text{AuCl})_2$

 $2 CH_2(AsPh_2AuCl)_2 + 2 GeCl_2(dioxane)$

 $\rightarrow 2$ (dioxane)

+ { $[CH_2(AsPh_2Au)_2]_2$ }²⁺ 2 [ClAuGeCl₃]⁻

Single crystals (monoclinic, space group $P2_1/c$, Z = 4) were obtained upon layering the solution of the compound in tetrahydrofuran with hexane containing a few drops of benzene. An X-ray diffraction analysis showed that these clear crystals (not dried in a vacuum) contain both tetrahydrofuran and benzene in the lattice.

The main component of the lattice is a centrosymmetrical unit composed of a dication $\{[(dpam)Au]_2\}^{2+}$ flanked by two $[ClAuGeCl_3]^{-}$ anions which have short interionic contacts Au1--Au2/Au1'--Au2' = 3.0499(6) Å (Fig. 3). Together with the transannular contact Au1--Au1' = 3.1613(8) Å, the four gold atoms form a Z-shaped tetraatomic sequence [Au2--Au1--Au1' 118.833(14)°]. Under the influence of these gold-gold interactions, the axes As1-Au1-As2 [168.52(3)°] and Ge-Au2-Cl [173.87(6)°] deviate strongly from the 180° standard, and are "crossed" with an dihedral angle Cl-Au2--Au1-As1 of 110.7°. The eight-membered ring of the dication is in an elongated chair conformation.

The trichlorogermanite(II) ligand in the anions has Ge-Cl distances [2.151(3), 2.166(2), 2.171(2) Å] and Cl-Ge-Cl angles [101.09(11), 101.15(11), 102.29(11)°] in narrow ranges. The latter are slightly larger than those in (Ph₃As)AuGeCl₃ (above), and the distances are significantly shorter, indicating a stronger trans influence of the chloride ligand as compared to the arsine ligand, shifting both parameters a little closer to the tetrahedral standards (as in GeCl₄).

It is very surprising that the [Cl-Au-GeCl₃]⁻ anions are not undergoing insertion of a second equivalent of GeCl₂ available in the above 1:2:2 reaction mixture. The symmetrical anion [Cl₃Ge-Au-GeCl₃]⁻ is a known species and has been structurally characterized [3] as a component of the tetranuclear salt {[(PhMe₂P)₂Au]⁺ [Au(GeCl₃)₂]⁻}₂. Even a tricoordinate complex [Au(GeCl₃)₃]²⁻ was observed in a salt with [(dppm)Au]₂²⁺ counterions [4]. Attempts to force the above reaction by heating to reflux temperature lead to decomposition.

It is unclear why the reaction is not proceeding to completion in the (dpam) system. The failure of synthetic attempts may be ascribed to steric congestion in the tetranuclear complex, implying that the ion-triple is very tightly bonded and that none of the anions is released from the cluster for further insertion. The results of recent measurements of the bond energy associated with aurophilic interactions (8 - 11.5 kcal/mole) [5] are indeed indicative of very significant bond strengths in related aggregates, however, and therefore this conclusion is not unreasonable.

(*Triethylamine*)[*tri*(*o*-*tolyl*)*phosphine*]*gold*(*I*) *hexafluorophosphate* (**4**)

Mixed ligand complexes of gold(I) with a combination of hard and soft Lewis-base donor molecules are rare. An early example has been the (quinocludine)(triphenylphosphine)gold(I) tetrafluoroborate, with an N-Au-P axis [7]. In the course of the present and some earlier studies, a similar complex with NEt₃ and (o-tolyl)₃P was isolated and structurally characterized. This compound was obtained when phosphine complexes were treated with various reagents in the presence of triethylamine as a base [6].



Fig. 4. Molecular structure of the cation of compound **4** (ORTEP drawing with 50% probability ellipsoids, Hatoms omitted for clarity; only one of the two crystallographically independent cations is shown, the corresponding values of the second cation are given in parentheses). Selected bond lengths [Å] and angles [°]: Au1-P1 2.256(2) [2.243(2)], Au1-N1 2.134(5) [2.119(5)]; P1-Au1-N1 176.7(2) [179.6(2)].

Suitable crystals (colourless, triclinic, space group $P\bar{I}$, Z = 4) could be grown with $[PF_6]^-$ as the counterion. The lattice contains no solvent. It is composed of two crystallographically independent cations $[(Et_3N)Au(o-Tol)_3]^+$ (Fig. 4) and anions $[PF_6]^-$. The two anions have a standard octahedral geometry with very similar dimensions.

A superposition of the two cations shows several significant differences in the conformation of the amine and phosphine ligands. Only the $C_3N-Au-PC_3$ cores are very similar with almost perfectly linear axes P1-Au1-N1 176.7(2) and P2-Au2-N2 179.6(2)°. The two phosphine ligands are both in a propeller-type conformation with opposite directionality (left- and right-handed). However, the two triethylamines show approximate threefold (N2) and mirror symmetry (N1), respectively, as demonstrated in the projection of the two cations along their principal molecular axes (Fig. 5).

As expected for a bulky $(o-\text{Tol})_3\text{P}$ ligand, the Au-P distances are rather long [2.243(2) and 2.256(2) Å], and even the Au-N distances, in the trans position, still show a distinct lengthening [2.134(5) and 2.119(5) Å], at least as compared to gold(I) complexes of ammonia. However, the data for the quinuclidine analogue are similar [Au-N 2.11(1), Au-P 2.240(4) Å] [7].



Fig. 5. Projection of the two cations of compound 4 along their principal molecular axes, showing the approximate threefold (N2) (left) and mirror symmetry (N1) (right) of the two triethylamines.

Experimental Part

General: All experiments were routinely carried out in an atmosphere of dry purified nitrogen. Standard equipment was used throughout. Starting materials were purchased except for GeCl₂(dioxane) [8] and (Ph₃As)AuCl [9, 10].

Tetraphenylphosphonium trichlorogermanite(II) (1)

A slurry of GeCl₂(dioxane) (1.90 g, 8.2 mmol) and Ph₄P⁺Cl⁻ (3.08 g, 8.2 mmol) in 20 ml of tetrahydronaphthalene was heated to 90 °C for 15 min. Dioxane liberated during the reaction was stripped off in a vacuum (10^{-2} mm Hg), and the evaporation was continued for 12 h with stirring to ensure the complete removal of the dioxane. The white precipitate was filtered off in the cold, washed three times with 10 ml of pentane and dried in a vacuum. The product was recrystallized from CH₂Cl₂ (yield 4.20 g, 98.8%, m. p. 186 °C). – MS (FAB): *m/e* = 338.9 [100%, Ph₄P⁺], 261.7 [2.8%, Ph₃P].

 $C_{24}H_{20}Cl_3GeP(518.31)$

Calcd	C 55.61	H 3.89	Cl 20.52%,
Found	C 55.79	H 3.91	Cl 20.43%.

(Triphenylarsine)gold(I) trichlorogermanite(II) (2)

To a solution of $(Ph_3As)AuCl (0.42 g, 0.76 mmol)$ in 25 ml of tetrahydrofuran 0.18 g (0.77 mmol) of solid $GeCl_2(dioxane)$ was added at 20 °C and the mixture was heated to reflux for 5 h. The product was precipitated by addition of hexane. Crystallization from hexane/chloroform [2:1] resulted in 4.7 g (90% yield) of product (m. p. 183°C with decomposition). – NMR: ¹H

 $(CDCl_3) \delta 7.37 - 7.52 (m, Ph).$ ¹³C $\{^{1}H\} \delta 133.28, 131.88, 131.28, 129.76 (all s, meta, ipso, para, and ortho).$

C₁₈H₁₅AsAuCl₃Ge (682.13) Calcd C 31.69 H 2.20 Au 28.88 Cl 15.59%, Found C 32.00 H 2.28 Au 28.70 Cl 15.52%.

Bis{[bis(diphenylarsino)methane]gold(I)}(+2) bis[chloro(trichlorogermanito)gold(I)] (-1) · 2 benzene · 2 tetrahydrofuran (**3**)

To a suspension of (Me₂S)AuCl (0.24 g, 0.81 mmol) in 15 ml of tetrahydrofuran was slowly added a solution of (Ph₂As)₂CH₂ (0.19 g, 0.40 mmol) in the same amount of the same solvent and the mixture stirred for 2 h at 20°C to give a clear solution. Solid GeCl₂(dioxane) (0.19 g, 0.81 mmol) was added to the solution and the mixture was again stirred at 20 °C for 20 h. The resultant solution was layered with hexane and a few drops of benzene to crystallize the product, which after short evacuation was free of solvents (0.23 g, 53.5 % yield, m. p. 155°C). – NMR: ¹H (CD₃CN) δ 2.72 (s. 2H, CH₂), 7.30 - 7.48 (m, 20 H, Ph). ${}^{13}C{}^{1}H{}\delta$ 140.8, 132.7, 128.5 (all s, para, meta, ortho; ipso and CH₂ not observed). MS (FAB): m/e 1606 [100%, (dpam)₂Au₃Cl₂], 1373 [40%, (dpam)₂Au₂Cl], 900.9 [87%, (dpam)Au₂Cl], 669 [10%, (dpam)Au].

C₅₀H₄₄As₄Au₄Ge₂Cl₈ (2161.27)

Calcd C 27.79 H 2.03 Au 36.46 Cl 13.40%, Found C 28.00 H 2.10 Au 36.51 Cl 13.12%.

(*Triethylamine*)[*tri(o-tolyl)phosphine*]gold(*I*) *hexafluorophosphate* (**4**)

The preparation and isolation of the compound was first reported in Ref. [6].

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Table I.	. Crystal	data.	data co	llection	and	structure	refinement
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^[a] $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; |b| wR2 = [\Sigma w(F_0^2 - F_c^2) / \Sigma w(F_0^2)^2]^{1/2}; w = 1/[\sigma^2(F_0^2) + (ap)^2 + bp]; p = (F_0^2 + 2F_c^2)/3; a = 0.0442$ (1), 0.0262 (2), 0.0528 (3), 0.0752 (4); b = 1.00 (1), 0.00 (2), 8.57 (3), 9.59 (4).

Crystal structure determinations

Specimens of suitable quality and size were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo-K_{α} radiation, λ (Mo-K_{α}) = 0.71073 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Lp correction was applied, and data of **2**, **3**, and **4** were corrected for absorption. The structures were solved by direct methods (SHELXS-86) [11] and completed by full-matrix-least squares techniques against F^2 (SHELXL-93) [12]. The thermal motion of all nonhydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5 \times U_{eq}$ of the attached C atom). Further information on crystal data, data collection and structure refinement are summarized in Table I. Important interatomic distances and angles are shown in the corresponding Figure Captions. Anisotropic thermal parameters, tables of interatomic distances and angles, and atomic coordinates have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD-408892 (1), -408894 (2), -408891 (3), and -408893 (4).

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