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Self-Assembly of $[(Me_2PhP)_2Au]^+[Au(GeCl_3)_2]^-$ into Linear Ion Quadruples with an Unusual [+ − − +] Sequence

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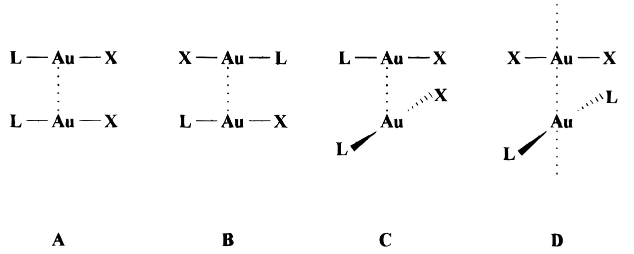
The supramolecular aggregates of two-coordinate gold(I) complexes of the type L−Au−X (L = neutral donor ligand, X = anionic ligand) have a multifaceted structural chemistry,[1−4] including dimers and higher oligomers, as well as one-, two-, and three-dimensional polymers. In all cases the association is based on sub van der Waals Au--Au contacts (auriophilicity)[5] with distances and bond energies in the order of 3.0 Å and 7 kcal/mol,[6−9] respectively, with variations depending on the nature and steric requirements of L and X. These parameters place auriophilicity in the same category as hydrogen bonds.[1]

Structurally, the intermolecular contacts between L−Au−X molecules occur perpendicular to the main molecular axis, and with the monomers in an eclipsed (parallel/ antiparallel: **A/B**) or staggered orientation (**C**), and in chain-type aggregates these modes may be alternating following different sequential patterns.[1,4,10−13]

It was noted in some of the earlier structural studies already, that an isomerization of the neutral complexes L−Au−X through ligand redistribution may lead to ionic species of the general type $[L_2Au]^+[AX_2]^-$, the components of which can again form oligomers through Au--Au contacts (**D**). Examples in case are $\{[(\text{tetrahydrothiophene})_2Au]^+ [AuI_2]^-\}_n$ and $\{[Pyr_2Au]^+ [AuBr_2]^-\}_n$.[14,15] As probably expected, the sequence of ions in the chains follows the pattern [+ − + − + − + −] largely dictated by electrostatic forces. To the best of our knowledge there is only one exception[15,16] to this concept, $\{[Pyr_2Au]^+[AuX_2]^-\}_2$ (X = Cl, Br, I), where *tetramers* were found, with a *nonalternating sequence of ions* [− + + −], which is clearly at variance with the simple rules of Coulomb forces.

Chart 1



During our continuing studies of the auriophilicity phenomenon[1−3] we now discovered another extravagant case of ion association with a nonalternating sequence of ions but with the unprecedented pattern [+ − − +].

(Dimethylphenylphosphine)gold(I) chloride was found to react with the germanium dichloride dioxane complex in tetrahydrofuran at −78 °C to give a bright yellow, highly photoluminescent, crystalline product (mp 167 °C, dec) of the net composition $(Me_2PhP)AuGeCl_3$, **1**, as confirmed by elemental analysis.[17] $GeCl_2$ insertion into an Au−Cl bond has recently also been carried out with $(Ph_3P)AuCl$, and the product was shown to be indeed the expected (phosphine)gold−trichlorogermyl complex $(Ph_3P)AuGeCl_3$.[18] This compound is associated into *dimers* with a staggered configuration in the crystal (type **C**).

$$4(Me_2PhP)AuCl + 4GeCl_2(\text{dioxane}) \xrightarrow[-4\text{dioxane}]{\text{thf}} \{[(Me_2PhP)_2Au]^+[Au(GeCl_3)_2]^-\}_2 \quad (1)$$

Unexpectedly, the field desorption mass spectrometric investigation of compound **1** showed the cations $[(Me_2PhP)_2Au]^+$ as the parent peak (100%), which suggested a redistribution of the phosphine ligands already in solution. This assumption was corroborated by the NMR data of $CDCl_3$ solutions of the complex: The ^1H and ^{13}C resonances exhibit second order splitting associated with strong coupling of the two phosphorus atoms across the Au center to give $H_6PP'H'_6$ and CPP′ spin systems for the methyl hydrogen and carbon atoms, respectively.[19] Such a splitting should be absent in L−Au−X complexes but is compatible with the ionic formula $[L_2Au]^+[AuX_2]^-$.

The X-ray analysis of a single crystal of **1** (from $CHCl_3$/hexane, monoclinic, space group $P2_1/c$, $Z = 4$) confirmed the ionic structure of the compound.[20] The ionic components are arranged in *tetramers*; however, with a quasi-linear sequence of gold atoms built from a pair of very closely spaced anions in the center [Au2−Au3 2.881(1) Å], and two terminal cations [Au1−Au2 2.981(1), Au3−Au4 2.976(1) Å] (Figure 1). The conformation of the tetramer is all-staggered, and the coordination geometry is close to linear at all four gold atoms.

This structure is noteworthy because it demonstrates that auriophilicity-based bonding is strong enough to overrule Coulomb repulsion between two anions. The Au--Au distance

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[17] $(Me_2PhP)AuCl$ (0.50 g, 1.43 mmol) and $GeCl_2$(dioxane) (0.33 g, 1.43 mmol) in 20 mL of tetrahydrofuran were stirred for 2 h at −78 °C. The resulting yellow solution was allowed to warm to room temperature, and the product was precipitated by addition of pentane. Crystallization from chloroform−hexane (1:1) yielded 0.61 g of **1** (83%), mp 167 °C (dec); $^{31}P\,\{^1H\}$ NMR ($CDCl_3$) δ 15.4 (s); ^1H NMR ($CDCl_3$) δ 2.06 ($A_6XX'A'_6$, $N = 10.3$ Hz, 12 **H**, CH_3), 7.51−7.67 (m, 10 **H**, $C_6\mathbf{H}_5$). Anal. Found: C, 18.64; H, 2.18; Cl, 20.40. $C_8H_{11}AuCl_3GeP$ (514.09) requires C, 18.69; H, 2.16; Cl, 20.69. Mass spectrometry (FD): $m/z = 473$ ($[(Me_2PhP)_2Au]^+$, 100%).

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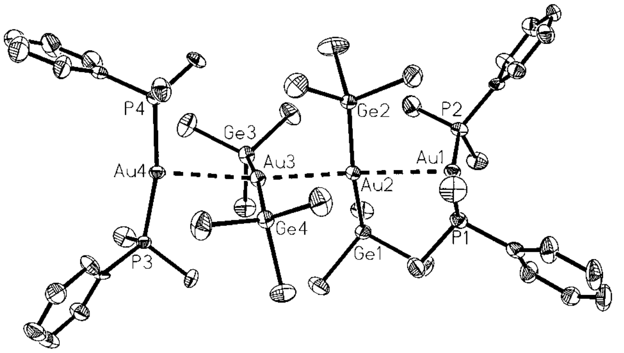

Figure 1. Molecular structure of compound **1** with atomic numbering (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). The tetranuclear unit has no crystallographic symmetry. Selected bond lengths (Å) and angles (deg): Au1−Au2 2.981(1), Au2−Au3 2.881(1), Au3−Au4 2.976(1), Au2−Ge1 2.416(1), Au2−Ge2 2.417(1), Au3−Ge3 2.409(1), Au3−Ge4 2.414(1), Au1−P1 2.313(2), Au1−P2 2.311(2), Au4−P3 2.304(2), Au4−P4 2.306(2), Ge1−Au2−Ge2 169.98(4), Ge3−Au3−Ge4 169.20(4), P1−Au1−P2 170.06(9), P3−Au4−P4 168.38(8).

between the anions is even shorter than in metallic gold [2.889(1) Å] and is also shorter than between anion and cation [Au1−Au2, Au3−Au4, above]. As noted previously, the effect of a germanium substituent appears to be particularly favorable for reasons not yet properly understood.[18]

$$2(o\text{-Tol}_3\text{P})\text{AuCl} + 2\text{GeCl}_2(\text{dioxane}) \xrightarrow[-2\text{dioxane}]{\text{thf}} \{(o\text{-Tol}_3\text{P})\text{AuGeCl}_3\}_2 \quad (2)$$

Large ligands L are required to finally quench the inherent Au--Au attraction. The product of the GeCl_2 insertion into the Au−Cl bond of (o-Tol_3P)AuCl is a stable trichlorogermyl gold compound (o-Tol_3P)AuGeCl_3 (**2**, mp 242 °C, dec), which has spectroscopic data indicative of a "regular" L−Au−X structure.[21] A single crystal X-ray study (from CHCl_3/hexane, colorless, monoclinic, space group $P2_1/c$, $Z = 4$)[22] confirmed this assumption. Close inspection shows, however, that there is evidence for another type of weak aggregation to give a centrosymmetrical *dimer* (Figure 2): The coordination geometry at the gold atom is not really linear [P−Au−Ge 167.9(1)°], and there are sub van der Waals-contacts Au′--Cl2 [3.299(3) Å]. This result suggests that Au--Au contacts are superior in energy to Au--Cl contacts in the aggregation of L−Au−X molecules, the latter gaining ground only as steric effects make metal−metal contacts impossible.

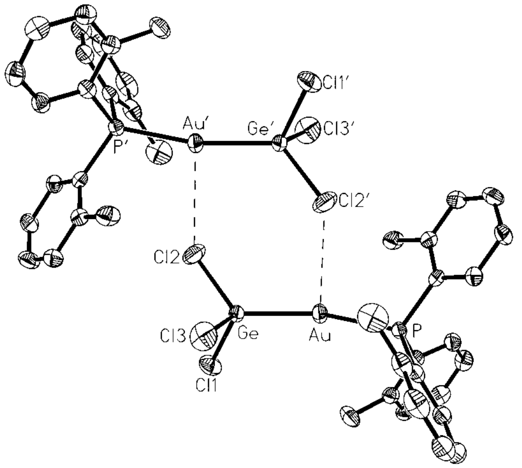

Figure 2. Molecular structure of compound **2** (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). The dimer has a center of inversion, as indicated by the atomic numbering. Selected bond lengths (Å) and angles (deg): Au−Ge 2.376(1), Au−P 2.302(1), Au′−Cl2 3.299(3), Ge−Cl1 2.163(2), Ge−Cl2 2.171(2), Ge−Cl3 2.172(2), Ge−Au−P 167.9(1).

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Supporting Information Available: Table 1 containing ^{13}C NMR data of **1** and **2** and Tables 2−12 containing crystal data, bond lengths, bond angles, atomic coordinates and thermal parameters for both compounds (20 pages). Ordering information is given on any current masthead page. Atomic coordinates, bond lenghts, bond angles and thermal parameters have also been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 59403.

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(20) Crystal data of compound **1**: monoclinic, space group $P2_1/c$, a = 16.669(2) Å, b = 16.191(2) Å, c = 20.312(2) Å, β = 94.70(1)°, V = 5464(1) Å^3, crystal dimensions 0.25 × 0.30 × 0.35 mm, Z = 4, d_{calcd} = 2.500 g/cm^{-3}, F(000) = 3776 e, Enraf Nonius CAD4 diffractometer, Mo K_α radiation (λ = 0.71069 Å), T = −68 °C. Data were corrected for Lorentz and polarization effects as well as for absorption [empirical, $T_{\min}$ = 0.4825, $T_{\max}$ = 0.9983, μ(Mo K_α) = 135.94 cm^{-1}]. 10024 reflections measured, 9717 unique reflections from which 8148 [$F_o \geq 4\sigma(F_o)$] were observed. Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were calculated in idealized geometry and included with isotropic contributions. Refined parameters (505) wR_2 [unique data] = 0.0900, R_1 [$F_o \geq 4\sigma(F_o)$] = 0.0388 $\{wR_2 = [\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$, $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o$, $w = q/2\sigma^2(F_o^2) + (ap)^2 + bp$, $p = (F_o^2 + 2F_c^2)/3$; a = 0.0501, b = 26.1687$\}$, ρ_{final} = +1.74/−1.88 e Å^{-3} [located at the heavier atoms]. The structure was solved by direct methods and refined by full matrix least-squares calculations (SHELXTL-93).[23]

(21) (o-Tol_3P)AuCl (0.32 g, 0.57 mmol) and GeCl_2(dioxane) (0.13 g, 0.57 mmol) in 10 mL of tetrahydrofuran were stirred for 3 h at room temperature. The product was precipitated by addtion of pentane. Crystallization from chloroform−hexane (1:1) yielded 0.26 g of **2** (67%), mp 242 °C (dec); ^{31}P $\{^1$H$\}$ NMR (CD_2Cl_2) δ 19.9 (s); ^{1}H NMR (CD_2Cl_2) δ 2.70 (s, 3 **H**, C**H**$_3$), 6.93−7.54 (m, 4 **H**, C_6**H**$_4$). Anal. Found: C, 36.99; H, 2.94; Cl, 15.89. $\text{C}_{21}\text{H}_{21}\text{AuCl}_3\text{GeP}$ (680.31) requires C, 37.08; H, 3.11; Cl, 15.63.

(22) Crystal data of compound **2**: monoclinic, space group $P2_1/c$, a = 11.548(1) Å, b = 11.004(1) Å, c = 18.424(2) Å, β = 99.34(1)°, V = 2310.2(5) Å^3, crystal dimensions 0.25 × 0.35 × 0.38 mm, Z = 4, d_{calcd} = 1.973 g/cm^{-3}, F(000) = 1296 e, Enraf Nonius CAD4 diffractometer, Mo K_α radiation (λ = 0.71069 Å), T = −62 °C. Data were corrected for Lorentz and polarization effects as well as for absorption [empirical, $T_{\min}$ = 0.6771, $T_{\max}$ = 0.9992, μ(Mo K_α) = 81.01 cm^{-1}]. 5072 reflections measured, 4309 unique reflections from which 3832 [$F_o \geq 4\sigma(F_o)$] were observed. Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were calculated in idealized geometry and included with isotropic contributions. Refined parameters (244) R (R_w) = 0.0267 (0.0289) $\{R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o) + k(F_o)^2$, k = 0.000 16$\}$, ρ_{final} = +0.91/−1.05 e Å^{-3} [located at the heavier atoms]. The structure was solved by direct methods and refined by full matrix least-squares calculations (SHELXTL-PLUS).[24]

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