An *ab initio* study of the aggregation of LAuX molecules and $[LAuL]^+[XAuX]^-$ ions

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Pseudopotential *ab initio* calculations on dimers and tetramers of formula $\{[(H_3P)_2Au]^+[AuCl_2]^-\}_n$ (*n* = 1, 2) which are the products of a ligand distribution of systems $(H_3PAuCl)_{2n}$, show that the different experimentally observed structures are actually energetically quite comparable.

Many neutral gold(I) complexes of the type LAuX (L = neutral donor, X = anionic ligand) undergo facile ligand scrambling: NMR data on solution equilibria,[1,2] and solid-state structural data (*e.g.* L = C_5H_5N, X = halide;[3] L = C_4H_8Se, X = I;[4] L = PMe_2Ph, X = $GeCl_3$;[5] L = $Ph_2C{=}NH$, X = Cl, Br[6]), suggest that the energy differences associated with the ligand exchange according to eqn. (1) are very small, but there are no calculations to support this assumption.

$$2\,LAuX \rightleftharpoons (L_2Au)^+ + (AuX_2)^- \qquad (1)$$

It appears that solvation of the species in solution and aggregation of the components in the crystal play an important role in determining the equilibria.

When examining the details of the supramolecular chemistry of representative examples in the solid state, very unexpected modes of aggregation have been discovered[5] including non-standard ion sequences following the pattern [−++−] or [+−−+], instead of [+−+−], for tetramers of the formula $[LAuX]_4 = \{[L_2Au]^+[AuX_2]^-\}_2$.

In order to analyse the effects governing the aggregation modes, both Hartree–Fock (HF) and second-order Møller–Plesset (MP2) calculations (Table 1) were performed for di- and tetra-nuclear species of this type, and the previous $(H_3P)AuCl$ model, using GAUSSIAN 94 and either 11 or 19 valence-electron (11- or 19-VE) pseudopotentials.[7] We have pointed out earlier the importance of correlation and relativistic effects[8–10] for the underlying $\mathrm{Au^I\cdots Au^I}$ interactions.[11] The use of a PH_3 group to model the structures with higher PR_3 groups was found to be acceptable,[12] although this approach at the semiempirical level has been criticised.[13] At *ab initio* MP2 level, PMe_3 gives the same interaction depth, but larger R_e,[14] as PH_3.

The dihedral angles (P–Au–Au–Cl, Cl–Au–Au–Cl or P–Au–Au–P) were fixed at 90° in the dimers $(\mathbf{1})_2$, **2** and linear tetramers **3**, **4**, **6** (Fig. 1 and Table 2). The Au_4 geometry in cyclic tetramers **5** [(**5a**)$_2$], was assumed to be rectangular with a parallel arrangement of all PAuP and ClAuCl axes. The Au···Au distance, R_{intra}, established for the dimers was kept constant in the tetramers. The 19-VE geometries of the monomers **1**, **2a** and **2b** (Table 1) were adopted for the 11-VE calculations.

Table 1 Optimized monomer properties at the 19-VE MP2 level. Distances in pm, energies in E_h ($E_h = 4.35975 \times 10^{-18}$ J)

System	Au–P/pm	Au–Cl/pm	P–H/pm	Au–P–H/°	$-E$
$(H_3P)AuCl$ **1**	224.3	226.3	141.3	117.42	158.47013 56.69561[a]
$Au(Ph_3)_2^+$ **2a**	233.0	—	141.1	115.39	151.58419 49.81742[a]
$AuCl_2^-$ **2b**	—	228.8	—	—	165.21778 63.45385[a]

[a] 11-VE energies with the optimized 19-VE geometry.

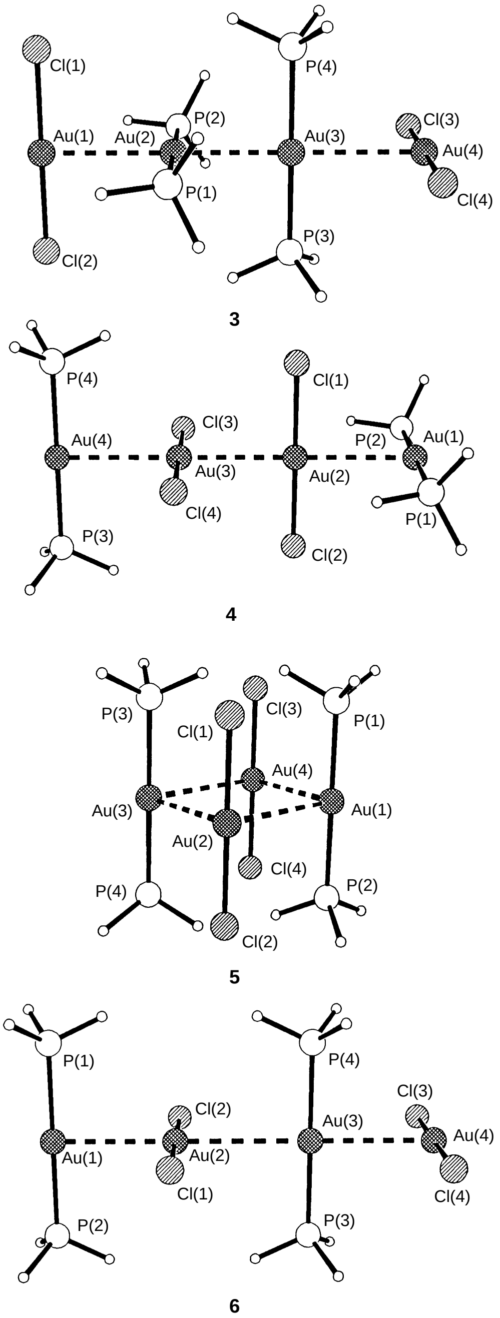

Fig. 1 The different linear-chain and cyclic tetramers on which the calculations were performed

Table 2 Calculated 'intramolecular' Au···Au distances,R_{intra}, of the ion pair $[\mathrm{Au(PH_3)_2}^+\mathrm{AuCl_2}^-]$ **2**, 'intermolecular' distances, R_{inter}, of the tetranuclear species, and the corresponding energy changes relative to molecular $[\mathrm{(H_3P)AuCl}]_2$ dimers. A counterpoise correction is included (E_{h} = 627.5095 kcal mol^{-1})[a]

System	R_{intra}	R_{inter}	ΔE/ kcal mol^{-1}	Pseudopotential
$[\mathrm{(H_3P)AuCl}]_2$ (**1**)$_2$	320.9	—	0	19 VE
	321.7	—	0	11 VE
[+−], **2**	289.5	—	+9.5	19 VE
	294.2	—	−0.9	11 VE
[−++−], **3**	294.2	313.1	−6.6	11 VE
[+−−+], **4**	294.2	306.7	−5.4	11 VE
[+−], **5a**	324.1	—	−3.4	11 VE
$\begin{bmatrix}+ & - \\ - & +\end{bmatrix}$, **5**	324.1	366.8	−32.3	11 VE
[+−+−], **6**	294.2	313.7	−11.4	11 VE

[a] 1 cal = 4.184 J.

The energies and gold··gold distances obtained for the di- and tetra-meric systems are summarized in Table 2. The former were calculated starting from the monomeric units (**1**, **2a**, **2b**), complemented by their interaction energies as obtained by subtracting the value for monomers (dimers) from those of the dimer (tetramer), including a counterpoise correction.

In all three linear tetramers a short R_{inter} Au···Au contact is observed. The shortest distance is found for the [+−−+] system followed by [−++−] and finally [+−+−]. A similar result is observed experimentally for the compound $[\mathrm{(Me_2PhP)_2Au^+}$-$\mathrm{Au(GeCl_3)_2}^-]$ {sequence [+−−+]} which indeed shows the shortest Au···Au contact between the two anions. This result is clearly at variance with Coulomb's law. However, focussing on the natural bond orbital (NBO) populations of the Au atoms, it is easier to understand the insensitivity of the total energy to the ionic arrangement. All gold atoms of $\mathrm{AuCl_2}^-$ have charges between 0.53320 and 0.57567 (0.60541 in the monomeric $\mathrm{AuCl_2}^-$, **2b**, and 0.56730 in the dimer [+−], **2**), and those in cations between 0.473 59 and 0.494 71 {0.442 63 in the monomeric $\mathrm{Au(PH_3)}^+$, **1a**, and 0.47359 in the dimer [+−], **2**}. The Mulliken Au populations vary more and are in the ranges 0.26500–0.39708 and −0.02241–0.13594 for anions and cations, respectively.

It should be mentioned that the R_{intra} values of the dimers were kept constant in every tetramer, and therefore the geometries obtained may not be the absolute minima on the energy surfaces. We have also not attempted a full-crystal simulation, and it should finally be noted that a short Au···Au contact does not necessarily correlate with the lowest energy. The main point is that all curves in Fig. 2 are evidence for attractive interactions and that the distances in Tables 2 and 3 are comparable.

The cyclic tetramer shows a larger R_{inter} distance probably due to the steric repulsion between the hydrogen and the chlorine atoms, which come very close together in the parallel arrangement of the individual units. Nevertheless this oligomer has the lowest energy as compared to the linear-chain tetramers. The optimum arrangement for two dipoles [+−] and the occurrence of one additional Au···Au interaction between dimers may be the reasons for this preference.

In conclusion, we have found that the molecular and ionic dimers of the type $[\mathrm{(H_3P)AuCl}]_2$ and $[\mathrm{(H_3P)_2Au^+AuCl_2}^-]$ are closely comparable in energy. This is made plausible by the close similarity of the gold atom NBO charges in the anion, cation and neutral monomer.

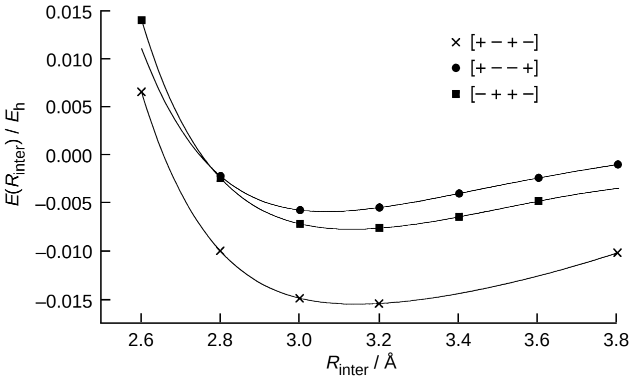

Fig. 2 Calculated bond energies for the intermolecular gold···gold contacts in the linear-chain tetramers using the 11 VE pseudopotential at MP2 level

Table 3 R_{intra} and R_{inter} distances of some experimentally known compounds

Compound	R_{intra}/pm	R_{inter}/pm
(py)AuCl, type **3** and **5**[3b]	324.9(3)	341.6(4)
(py)AuBr, type **6**, infinite chain[3a]	330.2(2)	356.3(2)
(py)AuBr, type **3**[3a]	324.6(1)	349.6(2)
(py)AuI, type **3**[3b]	299.0(1)	329.1(1)
$[\mathrm{(Me_2PhP)_2Au}]^+[\mathrm{Au(GeCl_3)_2}]^-$, type **4**[5]	297.9 av.	288.1(1)
$[\mathrm{(Ph_2CNH)_2Au}]^+[\mathrm{AuCl_2}]^-$, type **5**, Z-shaped[6]	319.44(5)	360.4(1)

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