Are Tetra[gold(I)]phosphonium Cations $[(LAu)_4P]^+$ Non-obedient to the LeBel-van't Hoff Rule?

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Recent theoretical studies of the molecular and electronic structure of tetra[(phosphine)gold(I)]-phosphonium cations, $[(H_3PAu)_4P]^+$, gave contradictory results favoring either a classical tetrahedral or a unique square-pyramidal structure of the PAu_4 unit. A tetrahedral structure had previously been confirmed for the corresponding ammonium cations $[(Ph_3PAu)_4N]^+$, while a square-pyramidal structure was discovered for the corresponding arsonium cations $[(Ph_3PAu)_4As]^+$, but there is as yet no unequivocal experimental evidence for the structure of phosphonium cations like $[(Ph_3PAu)_4P]^+$ in an innocent environment. – In this account the structural chemistry of this class of onium salts and related species is reviewed. The data accumulated to date provide virtually compelling evidence that the phosphonium cations should have a ground state with a *square pyramidal* PAu_4 core unit, provided that no external constraints are imposed. For large central elements (P, As), aurophilic interactions appear to drive the reorganization from tetrahedral to square-pyramidal skeletons in which a maximum number of short Au---Au contacts can be maintained. For the small central element N, similar interactions are already realized in the tetrahedral structure.

Key words: Aurophilicity, Phosphonium Salts, Poly(gold)phosphonium Salts,
Poly(gold)ammonium Salts, Poly(gold)arsonium Salts

Introduction

In experimental work carried out about three decades ago [1 – 3] it has been demonstrated that tetra[gold(I)]*ammonium* salts of the type $[(LAu)_4N]^+$ X^- have the expected tetrahedral configuration of the central nitrogen atom (**I** in Scheme 1*). By contrast, it has later been found that the corresponding *arsonium* salts of the type $[(LAu)_4As]^+$ X^- have cations in which the arsenic atom is located at the apex of an $AsAu_4$ square pyramid (**III** in Scheme 1) [3]. In these formulae, L and X^- represent a tertiary phosphine, like Ph_3P, and a non-coordinating anion, like BF_4^-, respectively. In the *ammonium* cation, the N atom occupies the central void of a tetrahedron of gold atoms, but in the *arsonium* cation the arsenic atom is capping a square of gold atoms. All gold atoms are linearly two-coordinate (P–Au–N/As *ca*. 180°).

It is obvious that the tetrahedral structure of the *ammonium* cation is in obedience to the van't Hoff model [4] established for the analogous carbon compounds and reflecting the close (isoelectronic) relation between the ammonium cation NH_4^+ and the methane molecule CH_4. However, the strict structural analogy expected for ammonium, phosphonium and arsonium cations according to the Valence Shell Electron Pair Repulsion (VSEPR) and Ligand Close Packing rules and their predecessors [5a – c] for a species with an "octet" of valence electrons appears to be invalid: The square-pyramidal structure of the *arsonium* compound is not in agreement with these models and violates the rules derived there from, and it is indeed without precedent in the structural chemistry of arsonium cations [6]. It is needless to say, that no quaternary ammonium salt with a square-pyramidal structure has ever been reported, even though this model had originally also been considered in the evolution of the concepts of molecular structure of substituted methanes and their analogs in the late 18th century [5d].

In an attempt to qualitatively rationalize the structural phenomena in aurated onium salts, the newly introduced concept of aurophilic bonding [3, 7 – 9] was applied, because it was noticed that in both structures

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[*] All formulae presented in this article are schematic representations of cations and molecules. For details of the experimentally determined structures (**I**, **III**, **IV**, **1** – **5**) the reader is referred to the original publications.

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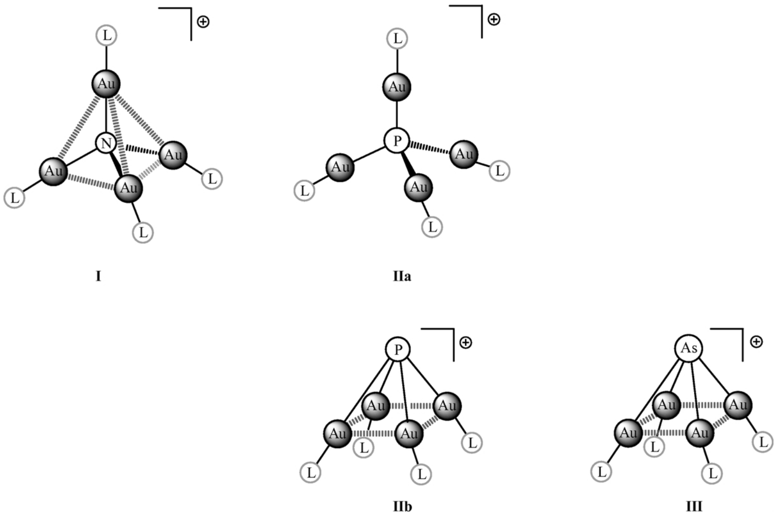


Scheme 1.

(the ammonium and the arsonium cations) the intracationic Au---Au distances are within the range of 2.8 – 3.5 Å which is typical for attractive contacts between gold(I) centers. It is easily recognized that in the tetrahedron of gold atoms of the ammonium cation – owing to the small size of the N atom – the Au---Au edges are short enough (3.32 Å average) to allow for aurophilic bonding, while with the large arsenic atom this would not be true. (For an Au–As distance of 2.50 Å and tetrahedral angles, the edges Au---Au are calculated to be 4.08 Å long.) The Au–As–Au angles in the square pyramidal arsonium salt are as small as 71° (average) indicating a very steep pyramid.

The at first sight unexpected rearrangement of the arsonium cation from tetrahedral to square pyramidal thus appears to follow the mutual attraction of the gold atoms which reaches a maximum for an $AsAu_4$ pyramid based on a square of gold atoms with short edges of only 2.90 Å (average).

The obvious question arose in this context, if the corresponding *phosphonium* salts $[(LAu)_4P]^+$ X^- would show cations with a tetrahedral or a square-pyramidal cation (**IIa, IIb** in Scheme 1). The latter would be in agreement with the geometrical argument that the size of the phosphorus atom (r_{cov} 1.10 Å), which is not much smaller than the arsenic atom (r_{cov} 1.21 Å), but much larger than a nitrogen atom (r_{cov} 0.70 Å), would require the formation of the pyramidal structure in order to secure efficient aurophilic bonding. In the absence of direct experimental proof, it therefore was predicted that the tetra[gold(I)]*phosphonium* cations should also have a pyramidal structure if there were no special influences from the ligand L and the counterion X^- [3, 7]. Such a structure was also unprecedented in the structural chemistry of phosphonium salts [10].

Very recently, the structures of the above family of onium cations in general, and that of the *phosphonium* case in particular, were revisited in theoretical investigations using state-of-the-art quantum chemical calculations. Surprisingly, the authors arrived at conflicting results, with one group favoring the tetrahedral structure (**IIa**) [11], but the other group confirming the square pyramidal structure (**IIb**) originally proposed on the basis of the aurophilicity concept [12].

From a study of these two contributions [11, 12] it appeared that in the discussion of the theoretical results not all experimental evidence compiled to date has been considered. It is therefore worthwhile to give a comprehensive account of the structural information available for the species in question and discuss these in the context of the chemistry of closely related compounds.

Successful and Unsuccessful Attempts to Synthesize Tetra[gold(I)]phosphonium Salts

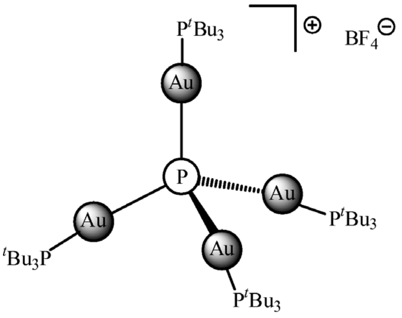
Preparative work oriented at synthesizing the elusive tetra[gold(I)]*phosphonium* salts $[(LAu)_4P]^+$ X^- was first carried out with L = Ph_3P as the most common auxiliary ligand and under a variety of experimental conditions (ambient and low temperature, various solvents, different anions, different stoichiometry). From none of these experiments a salt with the cation $[(Ph_3PAu)_4P]^+$ could be obtained. Instead, products with unexpected stoichiometries were isolated [13]. Three of these could be identified and were shown to contain the species $[(Ph_3P)_8Au_9P_2]^{3+}$, $[(Ph_3P)_6Au_5P]^{2+}$ and $[(Ph_3PAu)_5P]^{2+}$, respectively [14–16]. Their structures are discussed below.

From the above results it was concluded that the cation $[(Ph_3PAu)_4P]^+$ most probably formed as an intermediate in these reactions must be a highly reactive species which undergoes rapid and irreversible reactions with other components of the reaction mixture or even with the solvent [7, 13]. This assumption was supported by the experimental observation that tetra[gold(I)]*methanes* are extremely nucleophilic molecules [7, 17, 18], a good example of the $C-P^+$ "diagonal relation" in the Periodic Table ("Phosphorus – the Carbon Copy") [19].

This nucleophilic character of tetrahedral $[(LAu)_4C]$ molecules and $[(LAu)_4P]^+$ cations is very unusual as there is no lone pair of electrons localized at the central atom (or, more general, no obvious nucleophilic center in the molecule or cation, respectively). Nucleophilicity could indeed arise only upon rearrangement from the tetrahedral to a square-pyramidal species [7].

In order to lower the reactivity of the phosphonium cation, efficient steric protection of the nucleophilic center and enhanced steric repulsion between ligands L was sought in order to avoid any secondary reactions. This strategy was successful when L = ^{t}Bu$_3$P was chosen as a ligand (**1**) [20].

The cation of $[(^tBu_3PAu)_4P]^+\ BF_4^-$ (**1**) has a *quasi*-tetrahedral structure, and the onium center is fully covered by the four ligand umbrellas making any nucleophilic activity and any structural rearrangement all the way from tetrahedral to square pyramidal impossible. However, the molecular geometry of the cation is far from regular tetrahedral, with Au–P–Au angles in the broad range from 96.1° to 139.5°. The shortest Au---Au contact is 3.44 Å which means that virtually no stabilizing contribution can be gained from aurophilic interactions. The structural details suggest that the energy profile of Au–P–Au bending and related movements is rather flat and that quite distorted configurations are tolerated.



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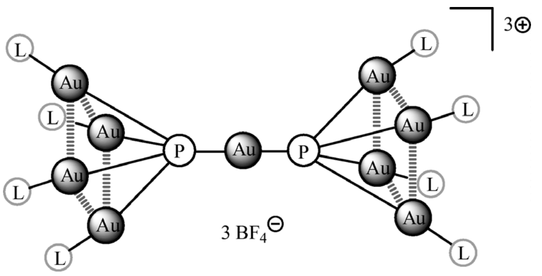
It should be mentioned that the same strategy – introduction of large umbrella-type ligands – has made possible the isolation of the first $[(R_3PAu)_4C]$ molecules (R = cyclohexyl, *o*-tolyl) [21]. The geometry of the products is also distorted.

The results of this *preparative* work are proof that stable tetra[gold(I)]phosphonium salts with a *quasi*-tetrahedrally coordinated phosphorus atom can be isolated provided that suitable protective measures are taken. In one of the two recent *theoretical* studies, the results of which seem to favor the tetrahedral over the square pyramidal structure (**IIa**) [11], the P–Au distances calculated for the model cation with the simple ligand L = PH$_3$ are similar to the experimental ones, but a more detailed comparison is pointless because of the restraints imposed on the geometry (point group T_d) in the calculations (Au–P–Au 109.5°).

Adducts of Tetra[gold(I)]phosphonium Salts

Three adducts of tetra[gold(I)]phosphonium cations have been structurally characterized. They all contain more or less distorted square-pyramidal $[(LAu)_4P]^+$ cations as donor units attached to the acceptor centers $[Au]^+$, $[LAu]^+$ and $[L_2Au]^+$ in the stoichiometries 2 : 1, 1 : 1 and 1 : 1, respectively, and with L = Ph$_3$P in all cases (**2**–**4**).

The tricationic 2 : 1 complex $\{[(LAu)_4P]_2Au\}^{3+}$ (in **2**) has a central Au atom linearly coordinated to two P atoms each of which is the apex of a PAu$_4$ square pyramid [15]. In the tetragonal crystals, the trications have crystallographic D_{4h} symmetry. The Au–P–Au angles in the two symmetry-equivalent pyramids are as small as 76.6° resulting in close Au---Au contacts of 2.93 Å at the eight base edges of the



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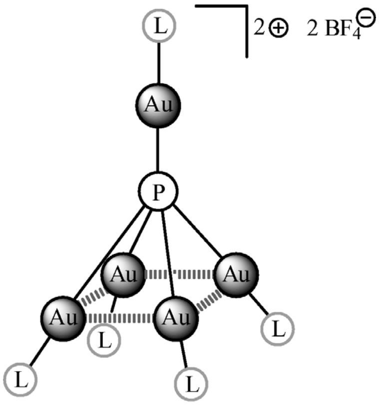

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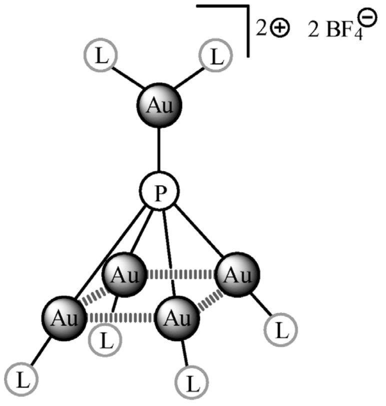

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two pyramids which can be taken as strong evidence for very significant aurophilic bonding. According to results of low-temperature NMR studies (A$_4$XX'A'$_4$ spin system), the structure appears to be maintained in dichloromethane solution.

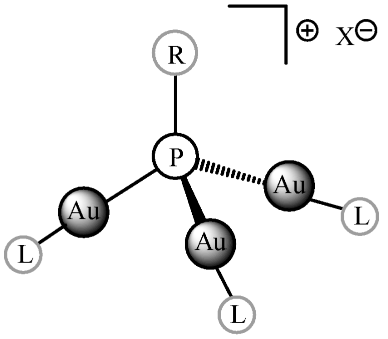
The dicationic 1 : 1 complex $\{[(LAu)_4P]AuL\}^{2+}$ (in **3**) has the simplified net stoichiometry $[(LAu)_5P]^{2+}$ but the geometry of its structure in the crystal clearly suggests that it is indeed the 1 : 1 adduct of cations $[LAu]^+$ and $[(LAu)_4P]^+$: Four LAu units are grouped closely together while the fifth LAu unit has a "*trans*" orientation at the central P atom (*quasi*-C_{4v} symmetry) [16]. This structure illustrates very nicely the stability of the compact $[(LAu)_4P]^+$ unit. In solution (CD_2Cl_2), the molecule is fluxional such that in the NMR spectra the ^{31}P signals (doublet/sextet) show five virtually equivalent LAu units even at −80 °C. This is in agreement with the dynamic behavior of many pentacoordinate phosphorus compounds in solution. The same result was obtained with L = ^{t}Bu$_3$P [13, 22].

Finally, the dicationic 1 : 1 complex $\{[(LAu)_4P](AuL_2)\}^{2+}$ (in **4**) has the $[(LAu)_4P]^+$ unit attached to the Au atom of a bent $[LAuL]^+$ cation [14]. This bending of the P–Au–P angle in the $[L_2Au]^+$ unit is indicative of a donor-acceptor interaction with the tetranuclear cation $[(LAu)_4P]^+$. The geometry is not unlike that in L_2AuCl or $[L_3Au]^+$ where Cl^- and L, respectively, are the donor units (L = Ph$_3$P) [23, 24]. In the crystal of $\{[(LAu)_4P](AuL_2)\}(BF_4)_2$, there are two independent dications with similar structures. The geometry of the $[(LAu)_4P]^+$ core units shows different deviations from the square-pyramidal reference with large variations in the Au–P–Au angles and, concomitantly, of the Au---Au contacts. For solutions in CD_2Cl_2, variable temperature NMR studies have also demonstrated fluxionality and even dissociation into the components at ambient temperature (broad unresolved resonances even at −90 °C).

The three adducts **2** – **4** show consistently that the cation $[(LAu)_4P]^+$ is a strong donor ligand comparable in its donor capacity to a tertiary phosphine. This donor capacity originates from the reorganization of the four LAu substituents at the central P atom from tetrahedral to square pyramidal with a concomitant rehybridization generating a lone pair of electrons at the central P atom (**IIa** → **IIb**). The reorganization is largely driven by the extra gain in energy for the cation from aurophilic bonding [7].

It should be pointed out that all the aggregations to form **2** – **4** take place against strong Coulomb repulsion between two or three cations. Even if these repulsions are in part compensated by the influence of the anions in the crystal and mediated by solvent dipoles in solution, the donor-acceptor affinity must be quite strong to overcome these net repulsive forces. Owing to the efficient shielding of the core units by large tertiary phosphines, the charge concentrations in the cations are low in all cases such that repulsive forces may be comparable for anion:cation ratios 1 : 1 (AB in **IIb**), 2 : 1 (A$_2$B in **3**, **4**) or 3 : 1 (A$_3$B in **2**).

Finally, there is also firm experimental evidence for the existence of trications of the type $[(LAu)_6P]^{3+}$ from extensive preparative and spectroscopic studies (L = ^{i}Pr$_3$P, ^{t}Bu$_3$P, Ph$_3$P, *o*-Tol$_3$P) [13, 25]. In the above formalism, these trications are 2 : 1 adducts of $[LAu]^+$ and $[(LAu)_4P]^+$ units in which the central P atom is associated with six LAu groups. No crystal structure of any of their salts has been determined, but there is little doubt that these *phosphorus*-centered trications have an octahedral structure, similar to the *carbon*-centered



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dications $[(LAu)_6C]^{2+}$ [7, 17, 26, 27].

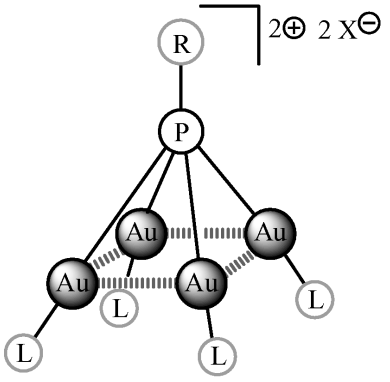
Organo-tri[gold(I)]-phosphonium Cations

The auration of primary phosphines RPH_2 (R = alkyl, aryl) leads to organophosphonium salts of the type $[RP(AuL)_3]^+$ X^- (**5**). For several members of this series the crystal and molecular structures have been determined [22, 28]. The cations have a tetrahedral configuration with the organic groups R (alkyl, aryl) in the *quasi*-apical position. The Au–P–Au angles are close to the tetrahedral standard, and therefore the peripheral Au---Au contacts are long (> 3.65 Å) ruling out significant contributions from aurophilic bonding.

Organo-tetra[gold(I)]-phosphonium Dications

The reorganization of the $[RP(AuL)_3]^+$ cations from tetrahedral to apically substituted square-pyramidal species is induced by the *electrophilic* attack of $[LAu]^+$ agents which are added to form dications $[RP(AuL)_4]^{2+}$ (in **6**). Examples are known for primary phosphines with R = cyclohexyl, *o*-tolyl, mesityl, and 2,4,6-tri(^{t}butyl)phenyl [13, 29], and for a diprimary phosphine derived from *p*-xylene [29]. The central P atom(s) can be described as rehybridized to become donor centers for the incoming electrophile. The geometry of the di-/tetra-cations indicates several close contacts between gold atoms which assist in stabilizing the bonding between the components which notably again occurs against Coulomb repulsion between two cations. The Au–P–Au angles are in the range 75.3° to 79.0° associated with Au---Au contacts in the range 2.89 – 3.01 Å (for R = *o*-tolyl [29]).

It should be noted that formation of compounds with pentacoordinated P atoms from phosphonium cations and *nucleophiles* is a standard reaction pattern. An example in case is the conversion of tetraphenylphosphonium cations $[Ph_4P]^+$ into pentaphenylphosphorane Ph_5P using phenyllithium PhLi [30]. In $[(LAu)_4P]^+$ cations, however, pentacoordination can be reached by addition of an $[LAu]^+$ *electrophile*. In this process in principle a system with electron-deficient bonding is produced (eight valence electrons for five bonds). It appears that the polyaurated products are particularly stable because the incoming unit is not only able to become involved in – say – conventional 3-center-2-electron bonding, but also to participate in a system of multicentered aurophilic bonding.



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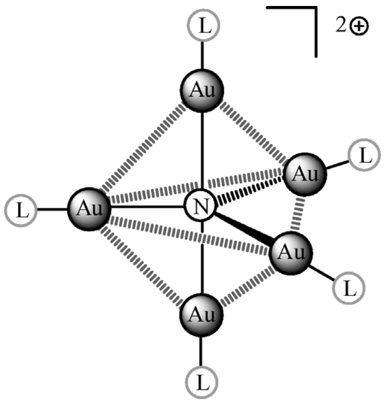
For this pattern of reactivity there are also parallels in the analogous *carbon* chemistry [32]: Tetra-[gold(I)]methanes $[(LAu)_4C]$ are attacked by $[LAu]^+$ electrophiles to give pentanuclear $[(LAu)_5C]^+$ or even hexanuclear (di)cations $[(LAu)_6C]^{2+}$ [17]. Molecules $RC(AuL)_3$ can be converted into $[RC(AuL)_4]^+$ cations for cases where R = H with L = Ph_3P [18], or R = Me with L = ^{c}Hex$_3$P [33]. In both cases, the $[C(AuL)_4]$ unit has an apically substituted square-pyramidal structure.

From the experimental point of view it is still an open question if $[C(AuL)_4]$ molecules have a tetrahedral or a square-pyramidal ground state structure. The former has only been observed for molecules with very bulky ligands L (above, [21]), while no example has been confirmed as yet for the pyramidal structure in the presence of small ligands L. Theoretical calculations have also indicated a preference for the pyramidal structure (for models with L = PH_3) [12, 34, 35].

Structural Anomalies in Tetra- and Penta[gold(I)]ammonium Cations

Tetrakis(triphenylphosphinegold)ammonium cations (**I**) were crystallized with fluoride, tetrafluoro-



IV

borate and hexafluorophosphate anions [1–3]. In all three cases the NAu$_4$ tetrahedra are significantly distorted in different ways. For the BF$_4^-$ and PF$_6^-$ salts, the Au–N–Au angles cover the large range from 94.4° to 120.8° associated with Au---Au edges in the range 3.01 to 3.50 Å. In the F$^-$ salt, the cation has C_{3v} symmetry with Au---Au contacts of 3.23 and 3.35 Å. It is thus obvious that the structure of the NAu$_4$ core unit is rather flexible and that configurations with at least a few shorter Au---Au contacts are preferred.

The *pentakis*(triphenylphosphinegold)ammonium dications (**IV**) have pentacoordinate nitrogen atoms with *quasi*-trigonal bipyramidal geometries of the NAu$_5$ core unit, but the deviations from this idealized structural model are again quite significant. In a tetrahydrofuran solvate of the BF$_4^-$ salt, the equatorial Au–P–Au angles in the dication are in the range from 109.6° to 129.0° while the axial Au atoms form an Au–N–Au angle of 174.9° [36, 37]. A dichloromethane solvate contains three independent dications with mutually similar geometries showing even greater deviations from standard trigonal-pyramidal or square-pyramidal models. In all cases at least some short Au---Au contacts are maintained [38]. An almost undistorted trigonal-bipyramidal unit [(Me$_3$PAu)$_5$P]$^{2+}$ is present in a dicationic 2 : 1 adduct with Me$_3$PAuCl (as the tetrafluoroborate salt) [39]. Several quantum-chemical studies on these and related systems were carried out [40–45].

Summary and Conclusions

Even though there is not yet any direct experimental proof for a square-pyramidal structure (**IIb**) of tetra[gold(I)]phosphonium cations [(LAu)$_4$P]$^+$ in an "innocent environment", the existing wealth of data collected from all kinds of derivatives supports a firm belief that this molecular geometry is in fact the ground state of these species. Surprisingly strong peripheral and internal multicenter aurophilic interactions clearly contribute very significantly to the overall bonding and thus co-determine the structure of molecules and ions of this type. They may overrule other contributions and thus give rise to molecular geometries unexpected on the basis of conventional rules established for the description of molecular structures.

It appears that for obtaining meaningful theoretical predictions based on quantum chemical calculations the methods and parameters (basis sets) have to be carefully chosen in order to be able to reliably account for dispersion forces [12]. Since aurophilic interactions rank among the most powerful dispersion forces, their contribution often has a striking influence on configurations and conformations of molecular units leading to just these non-conventional geometries and to gross violations of standard laws of bonding and structure, including the LeBel-van't Hoff rule. The chemistry of mono- and polynuclear gold compounds has already provided us with some of the most unusual examples, and probably many more are to be discovered.

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