The Auophilicity Phenomenon: A Decade of Experimental Findings, Theoretical Concepts and Emerging Applications

Hubert Schmidbaur

Anorganisch-chemisches Institut, Technische Universität München, D-85747 Garching, Germany

Dedicated to the memory of William S Rapson

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The term ‘auophilicity’ was introduced in 1989 to describe phenomena in the structural chemistry of gold which could not be readily rationalized by conventional concepts of chemical bonding. In the following decade the auophilicity concept has been widely applied and supported by the results of many experimental as well as theoretical studies. It will be carried over into the new millennium as a continued incentive for investigations that will help in the understanding of the unique properties of gold.

For the first half of the 20th century, the knowledge of the chemistry of gold remained very limited (1, 2), but growth of the coordination and organometallic chemistry of gold was more rapid than in the decades after World War II owing to emerging applications in modern technologies (3). It was, in particular, the advent of crystal structure analysis as a convenient tool for the straightforward determination of molecular structures in the 1960s, which provided a rapidly growing wealth of information on the structural chemistry of gold (4).

Careful inspection of the details of the new results revealed that the structural chemistry of gold was in many ways surprisingly different from the standard molecular characteristics of compounds of related metals: there is the clear preference not only for short and strong bonds suggesting a small atomic/ionic radius and a high electronegativity, but also for small coordination numbers (2 and 4). There is also ready access to various higher (Au^{2+} , Au^{3+} , Au^{5+}) and lower (Au^-) oxidation states not encountered in silver or mercury chemistry (5).

These experimental findings coincided with a growing awareness by chemists of the significance of relativistic effects in chemistry (6). As physicists learned to communicate with chemists about this subject, many of the peculiarities of gold could be rationalized and turned into heuristic concepts. Good

examples are the strong bond in the diatomic molecule Au_2 , the high electron affinity of gold atoms (responsible for the stability of Au^-), and the small ionic and covalent radius of gold. Gold atoms were actually found to be smaller than silver atoms, exactly as predicted by the ‘relativistic contraction’ of orbitals (7).

However, perhaps the most striking phenomenon in the structural chemistry of gold was the tendency of the low-coordinate compounds of gold(I) to associate into dimers, oligomers or even uni- and multidimensional polymers *via* direct gold-gold contacts (4, 5). Surprisingly, this aggregation occurs through a novel type of bonding between formally closed-shell metal centres ($5d^{10}$ configuration for Au^+). The metal atoms approach each other to an equilibrium distance of between 2.7 and 3.3 Å. This range includes the distance between gold atoms in gold metal and approaches, or even overlaps with, the range of distances established for the few authentic Au-Au single bonds in a pair of Au^{2+} cations (with a $5d^9$ configuration) (8).

Similar contacts have also been discovered within polynuclear molecules where the gold atoms appear to be drawn together to reach the ‘magic’ distance of *ca* 3 Å. Some molecules of this type were thus found to adopt unusual conformations, in which the gold atoms

can become nearest neighbours (9). The gain in stability through these non-classical interactions was obviously also the reason for unexpected multiauration processes which lead to a gathering of gold atoms at certain functions of a substrate (5, 10). While polymetallation of molecular functions is often difficult to achieve with other metals, there is an almost spontaneous clustering of gold atoms/cations at virtually any donor site (halides, hydroxides, mercaptides, amines, phosphines, arsines, methane, benzene, activated methyl etc.) (5b).

THE AUROPHILICITY CONCEPT

The structural phenomena suggested a new type of chemical bonding with the following characteristics (5): (a) at two-coordinate gold(I) centres, the interactions appear to occur perpendicularly to the molecular axis independent of the radial direction; (b) steric effects permitting, the metal-metal distances are clearly shorter than the sum of two van der Waals radii (3.7 Å), in favourable cases as short as 2.7 Å, but generally around 3 Å; (c) several gold atoms can gather at a given gold centre in a polynuclear species, to form triangles, squares or lozenges of gold atoms *etc*; (d) the bond energy associated with the interaction is generally small, but higher than the energy of standard van der Waals contacts; (e) when dissolved in a donor solvent, solvation of the monomers predominates in most cases

Scheme 1 Tetraauromethanes $C(AuL)_4$ with small ligands L are unstable in the classical tetrahedral configuration (A) and rearrange to the square pyramidal structure with short intramolecular $Au...Au$ contacts (B). This isomer is an extremely strong carbon base which is readily protonated even in the presence of a competing amine base. The resulting cations $[HC(AuL)_4]^+$ (C) dimerize via further intermolecular aurophilic interactions (D) (28).

Scheme 2 Bis(trimethylsilyl)methane (A) is readily aurred to give not only a bis(trimethylsilyl)-bis(gold)methane molecule (B), but also the triply aurred cation with pentacoordinate carbon atoms (C) (27).

over the intermolecular interactions of a species which is an oligomer in the crystal - intramolecular Au-Au contacts are generally not affected by solvation; (f) although virtually ubiquitous in gold chemistry, the phenomenon is much less common in the structural chemistry of the congeners copper and silver and of the neighbours platinum or mercury.

In an attempt to stimulate interest in this new type of bonding, which is intermediate between conventional covalent/ionic and van der Waals interactions, the term 'aurophilicity' was coined (5, 10). When this proposal was published ten years ago, the name was intended to express the specificity of the unexpected attraction between two or more gold centres in compounds where the metals are already chemically saturated according to conventional valence concepts: gold atoms always interact with the gold atoms in neighbouring functions or molecules, ignoring all other potential donor or acceptor sites. In its most simplistic form, the message reads: 'gold is drawn to gold'. The idea was also publicized in an essay in *Gold Bulletin* by the late Dr W. S. Rapson who held that there was great promise in the new concept (11). It was hoped that 'aurophilicity' would be sufficiently provocative to trigger a series of activities in preparative and structural gold chemistry and – equally important – in the theoretical treatment of the phenomenon by state-of-the-art calculations.

Ten years later it can be seen that these activities have been very successful (2). 'Aurophilicity' was adopted very quickly and has become a popular subject of research. A literature survey for the first decade indicates that there are hundreds of publications on this topic (!), and the conclusions drawn from these contributions are all in support of the concept. Previous findings were confirmed and a plethora of new examples were discovered. In summary, 'aurophilicity' appears to be real. For gold chemists it is essential to be familiar with the concept, because it now provides additional guidance for research.

Scheme 3 Free rotatory motion of the molecular units in the trifunctional phosphine ligand **A** is impeded by strong Au...Au interactions in the trinuclear gold complex **B**. The temperature required to restore freedom of movement on the NMR time scale is a measure for the strengths of the Au...Au bonding. Internal rotation is not impeded by sulfurization (**C**) (33a).

EXPERIMENTAL CONTRIBUTIONS

Gold Clustering in Polynuclear Compounds

The most convincing results of 'aurophilicity at work' are found in polyaurated molecules (5b). Double-auration at halide anions to give V-shaped cations with small angles and short Au-Au distances are now known for chlorine and bromine (12). Oxide and alkoxide anions have been shown to accept up to four gold atoms to give V-shaped, trigonal pyramidal and even tetrahedral complexes (5b, 13, 14). Sulfide (selenide, telluride) (5b, 14d) and thiolate (selenolate (5b), telluride (14c)) anions can reach coordination numbers from 2 to 6, and the resulting polynuclear cations have cluster structures clearly determined by Au-Au interactions. Nitrogen becomes up to pentacoordinate (15) in homoleptic $[\text{N}(\text{AuL})_5]^{2+}$ while for phosphorus hexacoordinate species $[\text{P}(\text{AuL})_6]^{3+}$ are reached (16). Work was also successful with polyaurated hydrazines (17) and hydroxylamines (18), amines (19), imines (20), phosphinimines (21), sulfoximines (22), and amides (23). Tetraaurated arsine has a non-classical square-pyramidal structure (24), and the corresponding phosphonium cations $[\text{P}(\text{AuL})_4]^+$ are part of several more complicated aggregates (16b, 25). Polyauration is also easily accomplished at non-metal or metalloid atoms (P, As, S, Se) of heteroclusters and at pure metal clusters (26a, b). Clustering at carbon was one of the early phenomena that attracted greatest interest (10). C-centred homoleptic polyhedra were complemented by examples with mixed substituents including, for example, the trigonal-bipyramidal $[(\text{Me}_3\text{Si})_2\text{C}(\text{AuPPh}_3)_3]^+$ (27), (Scheme 2) and – most spectacularly – the square pyramidal $[\text{HC}(\text{AuPPh}_3)_4]^+$ with pentacoordinate carbon

atoms (28), (Scheme 1). It should be noted that there is no comparable clustering phenomenon for silver at any of these nucleation centres, and mercuration never exceeds the standard valence or coordination numbers of nitrogen, carbon or other partner elements.

Intramolecular Aurophilic Interactions Between Distant Gold(I) Functions

Gold atoms at a common element centre, as in the examples given above, are in fixed positions and their interaction becomes obvious mainly from angle distortions. If the gold atoms are further apart and attached to a flexible molecular skeleton, their interaction leads to the adoption of unusual conformations which allow the mutual approach to reach the optimum equilibrium distance (ca 3 Å) (9).

This effect was found in a large number of molecules where two or more X-Au-Y units are, for example, at the ends of hydrocarbon chains: a folding into the cis-conformations is observed which brings the ends into close proximity, and the ends are thus fixed in a non-standard configuration by Au-Au bonding (2). The energy associated with the cleavage of the aurophilic bonding can be estimated or – in favourable cases – measured by variable temperature NMR spectroscopy [9, 29 - 33]. To date the results are remarkably consistent and put the effect in the same category as standard hydrogen bonding (7-12 kcal/mole). Already one such small contribution to the total energy of a given system is sufficient to stabilize unusual molecular conformations and configurations, to induce polyauration at an atom or at neighbouring atoms (33b), and to cause aggregation of gold(I) complexes (opposite), Scheme 3).

The effect is becoming more pronounced with the larger gold clusters, where the number of interactions is greatly increased. Aurophilic interactions are also

Scheme 4 Gold(I) complexes L-Au-X with small ligands L and X (halide) oligomerize to give dimers (**B**), trimers (**C**), tetramers (**D**), chain polymers (**E**), or layers with short Au...Au contacts (2, 4, 5, 35, 36).

Scheme 5 Self-assembly of catena-complexes induced by Au...Au interactions. A: the hexanuclear complex $[(\text{AuC}\equiv\text{C}^t\text{Bu})_6]_2$ (42a), and B: the dinuclear complex $[(\text{CH}_2)_4\{\text{PPh}_2\text{-Au-C}\equiv\text{CCH}_2\text{OC}_6\text{H}_4\}_2\text{CMe}_2]$ as catena dimers (42b).

most effective in di- or polymetallic ring compounds, where transannular bonding is possible without much loss of entropy. Consequently the number of examples is most numerous for auracyclic compounds (2).

However, all aurophilic interactions may easily be prevented by steric hindrance which cannot be overcome by the rather weak aurophilic forces. Where experimentalists have failed to observe the expected Au-Au bonding it was almost always due to steric effects. When steric effects are present, *intramolecular* bonding may not occur and it may be replaced by *intermolecular* bonding which leads to aggregation of molecules.

Aggregation of Gold(I) Complexes via Aurophilic Bonding

All two-coordinate gold(I) complexes with small ligands were found to be associated in the solid state (2). The aggregates may be dimers, open-chain trimers and tetramers, rings, chains, or layers. As a rule, complexes with the smallest ligands form the highest-dimensional aggregates. Thus $(\text{CO})\text{AuCl}$ or $(\text{MeNC})\text{AuCN}$ have the 'slim' CO, CN and isonitrile ligands and form two-dimensional layers (34), but $[(\text{PhCH}_2)_2\text{S}]\text{AuCl}$,

$(\text{Me}_3\text{P})\text{AuCN}$ and $(\text{Me}_3\text{P})\text{AuCl}$ form chains (35); $(\text{Me}_3\text{P})\text{AuOCOCF}_3$ is a trimer (36), *etc.*, (Scheme 4).

The contacts between the molecules are almost always regioselective, *ie* solely *via* the gold atoms at distances around 3 Å. In a very few, but important number of cases the association of independent units is maintained in solution, as detected by absorption spectroscopy and luminescence effects (see below).

The heteroleptic L-Au-X molecules may also undergo ligand redistribution in solution and group together upon crystallization in homoleptic isomeric forms $[\text{L}_2\text{Au}]^+[\text{AuX}_2]^-$ which again form aggregates (37). The sequence of ions in these aggregates may vary against all intuition by placing ions of like charge next to each other, *eg* in patterns $-++-$ or $++--$ instead of $+-+-$ expected for tetramers [38, 39]. This result indicates that in a favourable lattice environment aurophilic bonding may overrule Coulomb repulsion.

Design in Supramolecular Chemistry via Aurophilicity

For a few years now, aurophilicity has been recognized as a major concept which is useful for the design of supramolecular structures (40) and has been placed in the arsenal of building principles together with hydrogen bonding and coordinative bonding. Like hydrogen bonding, it is easily reversible and geometrically flexible. Apart from the construction of oligomers, rings or chains through a tailoring of the ligand bulk (see above), more complicated structures could be realized employing Au-Au interactions between the components. Chains could be interwoven like braids (41), in which the strings are fixed to each other periodically as gold atoms appear in neighbouring positions, (Scheme 6).

Most recently, the synthesis of catena-molecules (rings-in-rings) has been achieved by placing gold atoms into macrocycles (42). Guided by aurophilicity, an apparently magic self-assembly of the components leads to high yields of true molecular chains, *ie* interpenetrating ring molecules, (Scheme 5).

Synergism of Aurophilic and Hydrogen Bonding

Hydrogen bonding is determining the nature of many molecular structures (40). Although associated with only minor energy contributions, it affects molecular conformations as well as intermolecular aggregations. There are many parallels between hydrogen bonding and aurophilic bonding, and this is reflected in cooperativity phenomena if systems are designed where both types of bonding can be present. In recent work from several laboratories a whole range of such dual systems have been prepared and structurally characterized (43-45). Again

dimers and larger oligomers as well as polymers were obtained with alternating sequences of the two types of interactions. It appears that this field can offer a particularly rich variety of new structural features.

Physical Properties Associated with Auophilic Bonding

Auophilic bonding is associated with small energy contributions (7-12 kcal/mole) (29 - 33). The interactions are thus easily reversible with temperature and sensitive to many other influences in a competitive situation arising, for example, from steric bulk of neighbouring substituents, packing forces in crystals, concentration and solvation in solution, change of state of aggregation, *etc.*

The presence of auophilic contacts may be recognized not only from short metal-metal distances and unusual conformations and configurations of molecules, but also from Raman spectra (46), and electronic absorption and emission spectroscopy. Many Au-Au bonded species show intense photoluminescence in the UV/vis region if investigated in the solid state (47, 48). This effect may vanish in solution, but there are favourable cases where the luminescence is retained at least for high concentrations in a suitable solvent. The assignment of the luminescence to specific transitions is not always unambiguous, but there is a growing number of cases where it is becoming sufficiently clear that the Au-Au bonding is responsible for the relevant transitions. Luminescence has thus become an important diagnostic tool for auophilicity.

In a spectacular experiment it has been demonstrated that luminescence of gold complexes can also be triggered by solvation of the donor-free solid substrate either from the vapour phase or by dissolving the material in a solvent [49]. It is obvious that phenomena of this kind hold great potential for analytical applications.

Argentophilicity, Numismophilicity and Metallophilicity

Several early observations have been documented in the literature where the lighter coinage metals (silver, copper) are in close, mainly intramolecular metal-metal contacts. With the advent of a plethora of pertinent examples in gold chemistry, many of these classical cases have been revisited and a search began for new compounds specifically designed for this type of bonding. Based on the term 'numisma' for coin, the search was on for 'numismophilicity' (50), or – in general – for 'metallophilicity' (51). Mercury in particular also became the subject of pertinent studies because Hg^{2+} is

isoelectronic with Au^+ and both have a preference for low coordination numbers which should be favourable for extra metal-metal bonding. All these studies proved that silver (52) and mercury (53) compounds can be found which show convincing evidence for such closed-shell interactions. In many of the examples the metal-metal contacts are enforced by the ligands to give what is called ligand-supported interactions. The number of unsupported contacts is extremely limited (52b) and estimations of the energies involved give values of only a few kcal, close to those of standard van der Waals interactions. Nevertheless it is clear that there are small contributions from metallophilic bonding which should not be ignored.

THEORETICAL CONTRIBUTIONS

Bonding between closed-shell atoms was successfully traced in several early theoretical investigations by extended Hückel quantum chemical calculations (54, 55). Based on the hybridization concept the nature of the bonding interaction could be qualitatively rationalized in the language of chemists. It was recognized that this type of interaction must be a general phenomenon but it was less obvious in which cases it should be most prominent.

The introduction of relativistic effects in more advanced calculations in the 1970s has shown that bonding between closed-shell metal atoms or ions may be strongly enhanced by these effects (56-62). Since relativistic effects have been known to be particularly strong for the heavy elements in the Periodic Table in general, and to reach a local maximum for gold in particular (6, 7), auophilicity was accepted as a logical

Scheme 6 Interwoven structures of dinuclear gold complexes derived from ditertiary phosphines: the dinuclear complex $[\text{IAuPh}_2\text{P}(\text{CH}_2)_6\text{PPh}_2\text{AuI}]$. Small circles represent the gold atoms, short lines the Au...Au contacts, and long lines the PC_6P chains (41).

Scheme 7a Photoluminescence of Au...Au bonded complexes and luminescence induced by solvation.

Scheme 7b The trinuclear compound $[\text{AuN}(\text{Me})=\text{C}(\text{OMe})_3]_3$ (a) exhibits the emission spectra shown in (49).

consequence of these contributions (5). For some time, aurophilic bonding was even called 'relativistic bonding', but this clearly unrealistic term was soon abandoned and replaced by more adequate descriptions (60).

Current literature qualifies aurophilic bonding as an effect based largely on electron correlation of the closed-shell components, somewhat similar to van der Waals interactions, but unusually strong and therefore tentatively addressed as 'super van der Waals interactions' (60). All the studies have consistently shown that calculations will reproduce the attractive forces between the gold atoms really well only if relativistic effects are included. It is therefore not surprising that for lighter elements, where relativistic effects are less pronounced, metallophilic bonding is absent or difficult to detect. For the heavy elements platinum, mercury, thallium and lead the effect is often masked by a more extended set of ligands (Pt^0), by a higher positive charge (Hg^{2+}) or by the inert pair of electrons (Tl^+ , Pb^{2+}).

It is perhaps a new case of irony in science that the weak, seemingly negligible metallophilic force between copper(I) atoms in cuprous oxide (Cu_2O) may have very recently provided the first direct experimental observation of an orbital (63): the interactions between closed-shell copper(I) centres ($3d^{10}$) in this oxide lead to 'holes' in the formally filled set of d-orbitals, and this deficit could be visualized in charge-density maps.

Scheme 7b (See caption for Scheme 7a)

Based on experiments combining electron and X-ray diffraction for the investigation of domains of a perfect crystal of Cu_2O , an image of a $d(3z^2-1)$ [or – in its common abbreviation – a $d(z^2)$] orbital appeared which is clearly reminiscent of the drawings in introductory chemistry textbooks.

We may therefore conclude this section with an euphoric statement, *ie* that metallophilicity or closed-shell interactions have at last been visualized even for one of the weaker examples (copper), and this lends great support to the concept proposed for the heavy congener (gold) where relativistic effects make such interactions even more effective. It is important, however, to note that aurophilicity effects are often absent or negligible for gold(III) compounds, and there are convincing arguments to explain this trend (64).

APPLICATIONS

Aurophilicity is a useful concept in current and future preparative chemistry. This is not only true for the clustering of gold atoms in homo- and heteronuclear aggregates around core elements, but also for the construction of more extended systems. The main advantages for the design of molecular structures are (a) the versatility and flexibility of the geometrical characteristics of the aurophilic interactions, and (b) the low bond energy of the individual interactions which makes aggregation readily reversible. Like hydrogen bonding, aurophilic bonding is a powerful force in a collective set of interactions, however weak the individual bonding may be. It provides a reliable basis for reversible self-assembly of components into products with a variety of structures including porous materials and mesogenic phases. The aggregates may be quite sensitive and respond to other weak forces exerted by donor molecules on the molecular level or by crystal packing forces or solvation on a collective level. The changes in the electron characteristics of the gold atoms and its ligands upon aggregation (assembly) lead to new physical, photophysical and photochemical properties which will make gold(I) compounds the target of detailed investigations as sensors or related devices.

ABOUT THE AUTHOR

Prof Dr Hubert Schmidbaur has the Chair of Inorganic and Analytical Chemistry and is Head of the Inorganic Chemistry Institute at the Technical University of Munich. He has ca 750 publications, with research papers and review articles on a wide range of inorganic topics including gold chemistry. He has received a significant number of international awards and honours, including endowed lectureships, and recently edited a book entitled 'Gold: Progress in Chemistry, Biochemistry and Technology', the starting point for which was an international conference in Hanau which he chaired (see *Gold Bulletin*, 1996, **29**, 105; 1998, **31**, 134).

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Note: The literature survey in this account is not meant to be comprehensive. A set of very recent papers have been included which can be used as a guide to earlier contributions (See also reference 2).

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