Inorg. Chem. **2007**, *46*, 6444–6451

Inorganic Chemistry
Article

Au···Au Interactions: *Z′* > 1 Behavior and Structural Analysis

Kirsty M. Anderson,* Andrés E. Goeta, and Jonathan W. Steed

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.

Received March 9, 2007

The tendency of molecules containing an Au···Au interaction to crystallize with more than one molecule in the asymmetric unit (i.e., *Z′* > 1) and the geometry of the Au···Au interaction in X–Au–Y species have been investigated. Au-containing compounds exhibiting Au···Au interactions are shown to form *Z′* > 1 structures in 25.0% of cases, compared with 7.8% for Au-containing species where no Au···Au interactions exist and 8.8% for the Cambridge Structural Database as a whole. This propensity toward high *Z′* behavior is investigated by considering the nature of the packing of the compounds as well as the characteristics of the ligands and, in particular, the difference in sizes of the X and Y ligands. The geometry and conformation of molecules linked by an Au···Au interaction is also analyzed, taking into account the steric and electronic characteristics of the ligands.

Introduction

Gold···gold or "aurophilic" interactions[1,2] are a key factor in the self-assembly of many two-coordinate gold(I)-containing compounds. Complexes containing aurophilic interactions can show interesting physical properties such as enhanced luminescence,[3] and they are also an important synthon in crystal engineering.[4–8] Aurophilic interactions, with Au···Au distances ranging from 2.9 to 3.32 Å (i.e., less than twice the van der Waals radius of gold(I)), are thought to arise from a combination of relativistic and correlation effects and have been shown to have an interaction energy of between 20 and 50 kJ mol^{-1}, comparable with that of a hydrogen bond.[9–11]

Molecules containing groups with a preference for assembling via strong intermolecular interactions such as hydrogen bonding are known to show a preference to form structures with more than one molecule in the asymmetric unit (i.e., *Z′* > 1).[12,13] Recent work by us[14] has shown that the combination of a molecule with a resolved chiral center together with a strongly directional supramolecular synthon with a preference for centrosymmetry leads to *Z′* > 1 structures in over 60% of cases, compared with 8.8% for the Cambridge Structural Database (CSD)[15,16] as a whole. It is thought[14] that the motifs generated by these robust interactions do not always conform to one of the 230 space group symmetries, and hence, the molecule is forced to adapt its packing (e.g., by including another molecule in the asymmetric unit) as a result.

In view of the fact that the strength of the closed shell gold···gold interaction is of similar magnitude to a hydrogen bond we were interested in whether Au···Au-containing compounds would show similar high *Z′* behavior to hydrogen-bonded species. Similarities between hydrogen-bonded systems and those containing aurophilic interactions are not unprecedented; for example, it has been shown[17] that RNCAuCl ($R = C_nH_{2n+1}$; $n = 2-12$) complexes form tilted bilayer structures in almost identical fashion to that of the geometrically similar primary alcohols, with O−H···O

---

* To whom correspondence should be addressed. E-mail: k.m.anderson@durham.ac.uk.

(1) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, *24*, 391.
(2) Schmidbaur, H. *Nature* **2001**, *413*, 31.
(3) Vickery, J. C.; Balch, A. L. *Inorg. Chem.* **1997**, *36*, 5978−5983.
(4) Mohr, F.; Jennings, M. C.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 969−971.
(5) Smyth, D. R.; Hester, J.; Young, V. G.; Tiekink, E. R. T. *CrystEngComm* **2002**, 517−521.
(6) Brandys, M. C.; Puddephatt, R. J. *Chem. Commun.* **2001**, 1280−1281.
(7) Chen, J. X.; Zhang, W. H.; Tang, X. Y.; Ren, Z. G.; Li, H. X.; Zhang, Y.; Lang, J. P. *Inorg. Chem.* **2006**, *45*, 7671−7680.
(8) Madalan, A. M.; Avarvari, N.; Andruh, M. *Cryst. Growth Des.* **2006**, *6*, 1671−1675.
(9) Zank, J.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1998**, 323−324.
(10) Pyykko, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133−138.
(11) Schmidbaur, H.; Graf, W.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417−419.
(12) Steed, J. W. *CrystEngComm* **2003**, *5*, 169−179.
(13) Anderson, K. M.; Goeta, A. E.; Hancock, K. S. B.; Steed, J. W. *Chem. Commun.* **2006**, 2138.
(14) Anderson, K. M.; Afarinkia, K.; Yu, H. W.; Goeta, A. E.; Steed, J. W. *Cryst. Growth Des.* **2006**, *6*, 2109−2113.
(15) Allen, F. H. *Acta Crystallogr., Sect. B* **2002**, *58*, 380.
(16) *Cambridge Structural Database*, version 5.27; Nov 2005.
(17) Bachman, R. E.; Fioritto, M. S.; Fetics, S. K.; Cocker, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 5376−5377.

10.1021/ic700466y CCC: $37.00

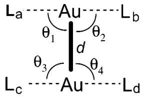


Figure 1. Fragment used in the CSD search. L = any non-hydrogen atom, and Au is restricted to being two-coordinate. The dashed lines indicate "any" bond type, and the thick continuous line indicates a contact of $3.00 \leq d \leq 4.00$ Å.

interactions in the alcohols replaced by gold⋯gold interactions in the *n*-alkylisonitrile gold(I) chloride complexes. This comparison is of particular interest in the present study as mono-alcohols are already known to exhibit interesting high Z' behavior.[18−20]

Experimental Methods

Data were obtained from the Nov 2005 version of the CSD. Gold⋯gold distances (d) were defined to be either as $3.00 \leq d \leq 4.00$ Å (for the geometric analysis) or with d less than the sum of the van der Waals radius (3.32 Å) for other searches. Au⋯Au distances shorter than the lower limit of 3.00 Å were considered to be formal covalent bonds for the purpose of this study. In view of the fact that we are interested in high Z' structures (which frequently have poor R values and large bond esd's) no restrictions on R value or other refinement parameters were enforced in the search, although hits where there are no three-dimensional coordinates deposited in the CSD have been disregarded. Redeterminations of structures were also omitted. *X-Seed*[21,22] was used to calculate the molecular volumes of the ligands.

Results and Discussion

Geometry Analysis. In 1993, Pathaneni and Desiraju undertook a geometry analysis of gold⋯gold interaction;[23] however, at that time only 17 examples of linear L−Au−L species (from a total of 82 129 structures in the 1990 version of the CSD) were available. We carried out a similar search of the CSD (349 661† structures; structures with Z′ entered as zero were removed) for the fragment shown in Figure 1 and found 336 compounds with short Au⋯Au distances (i.e., with $3.00 \leq d \leq 4.00$ Å). Two types of motif are observed, discrete Au⋯Au bonded aggregates containing 2−4 gold atoms and infinite chains held together by Au⋯Au interactions. For each fragment, the Au⋯Au distance as well as the four L−Au−Au angles (θ_1, θ_2, θ_3, and θ_4) and the L−Au−Au−L torsion angles (four in all) were recorded.

A plot of the L−Au−Au−L torsion angle vs d is shown in Figure 2. There are four L−Au−Au−L torsion angles per Au⋯Au contact, and therefore, there are 1152 points in all compared with 136 from the earlier study.[23] It was previously found that the Au⋯Au contacts have "highly specific" angular geometries corresponding to either the eclipsed (L−Au−Au−L angle ≈ 0° or ±180°) or staggered (L−Au−Au−L angle ≈ ±90°) conformations.[23] The eclipsed conformation, which was actually observed more frequently (48 vs 80 data points), was typically found at larger d values (where presumably steric hindrance is less of an issue) compared with the staggered conformation, which adopts smaller d values. The remaining eight data points were found at L−Au−Au−L angles ≈ ±60° and ±120°, corresponding to the structure $[\mathrm{Au(PEt_3)Cl)}]$[24] (SATTEM, $Z' = 2$), which was suggested as an intermediate in the transformation between eclipsed and staggered conformations.

Figure 2 shows that our results are broadly in agreement with the previous study. There are two reasonably distinct categories corresponding to a preference for staggered and eclipsed conformations; however, unlike the previous study, there is a much larger spread of intermediate values with L−Au−Au−L values ranging from ±50° to ±140°. All of these structures can be thought of as intermediates in the transformation from eclipsed to staggered orientations.

It is also interesting to note the Z' dependence of the L−Au−Au−L torsion angle and d. As Figure 2 shows, structures with $Z' \neq 1$ tend to have lower values of d and prefer the staggered conformation. Structures with $Z' = 1$ have a much larger spread of d and a greater proportion of eclipsed structures. The Z' behavior will be examined in more detail later (vide infra).

The L−Au−L angle (ϕ) is also of interest as the approach of a gold atom to the L−Au−L species can be considered a preliminary step in the reaction shown below in Scheme 1.[23]

It is therefore expected that as d decreases ϕ will increase. It is important to note that measuring the L−Au−L angle itself is not sufficient, as there are two possible conformations, both with $\phi < 180°$ (see Scheme 2, ϕ_a and ϕ_b); therefore, the L−Au−Au angles (θ_n) have been measured and the parameter $(\theta_1 + \theta_2) = \phi_a$ or ϕ_b is used instead.

As can be seen in Figure 3, as d decreases, $(\theta_1 + \theta_2)$ increases, suggesting a distortion away from the linear geometry. There appear to be no significant differences in the spread of data for different values of Z', although the $Z' = 1$ data points appear slightly more scattered than the $Z' < 1$ or $Z' > 1$ data.

A closer look at some of the structures with large d values (i.e., $d > 3.32$ Å) from the previous set showed that around 60% of them have slightly skewed Au⋯Au interactions; i.e., θ deviates significantly from 90°. While these can still be considered aurophilic interactions for the purposes of the geometric study above, for the investigation into the Z' behavior of these species, we are most interested in the strongest and most directional interactions, as it is likely to be these which direct the self-assembly of the structures; therefore, a cutoff point of $d < 3.32$ Å (the sum of the van der Waals radii) was chosen rather than $d < 4.00$ Å, as used previously. Repeating the search with the Au⋯Au contact distance constrained to <3.32 Å gives 184 hits, which were used for the remainder of the studies.

Z' Behavior. Table 1 shows the distribution of Z' values for the CSD as a whole as well as the subset of X−Au−Y-containing structures with Au⋯Au $d < 3.32$ Å. A search was also carried out for compounds that contain linear gold

---

(18) Brock, C. P.; Duncan, L. L. *Chem. Mater.* **1994**, *6*, 1307−1312.
(19) Brock, C. P.; Dunitz, J. D. *Chem. Mater.* **1994**, *6*, 1118−1127.
(20) Gavezzotti, A.; Fillippini, G. *J. Phys. Chem.* **1994**, *98*, 4831−4837.
(21) Barbour, L. J. *J. Supramol. Chem.* **2001**, *1*, 189.
(22) Atwood, J. L.; Barbour, L. J. *Cryst. Growth Des.* **2003**, *3*, 3.
(23) Pathaneni, S. S.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 319−322.
(24) Tiekink, E. R. T. *Acta Crystallogr., Sect. C* **1989**, *45*, 1233.

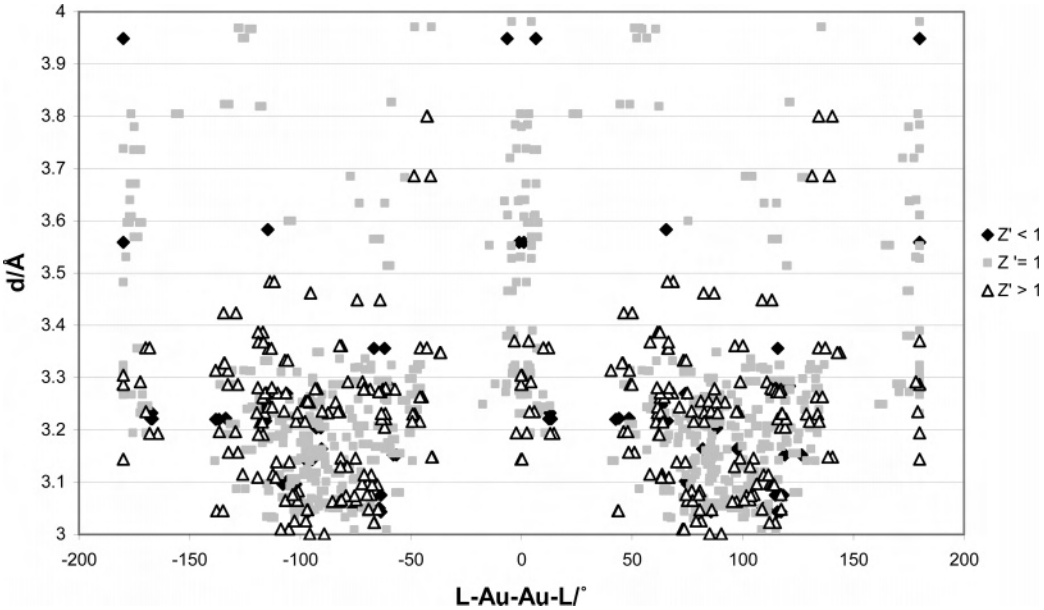
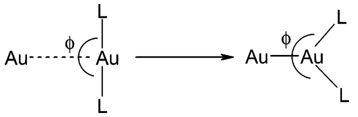
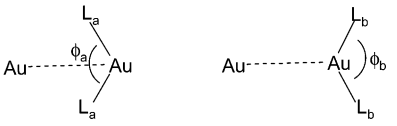


Figure 2. Scatterplot of L−Au−Au−L vs *d*. Data points are located mainly at the eclipsed (0°, 180°) and staggered (±90°) conformations

Scheme 1



Scheme 2



centers that do *not* participate in Au···Au contacts, the results of which are also presented in Table 1.

The results show that, as predicted, molecules containing an Au···Au interaction show a strong preference for forming structures with $Z' > 1$, with 25.0% of structures having $Z' > 1$ compared with 8.8% for the database overall and 7.8% for Au-containing compounds with no Au···Au interactions. Structures with $Z' < 1$ represent special cases where the molecule also exhibits internal symmetry and therefore these have not been studied further.

Closer examination of the $Z' = 1$ dataset indicates that 70 structures have more than one gold center with the Au···Au interaction between two unique gold(I) centers rather than between two symmetrically equivalent species. Five of these 70 structures have two half-molecules in the asymmetric unit (i.e., $Z' = 2 \times {}^1/_2 = 1$)[25] with the Au···Au interaction between the Au atoms on different half-molecules.

Six structures have $Z'' > 1$,[26] i.e., more than one chemically unique unit in the asymmetric unit, and again, the Au···Au interaction is between two unique gold centers.

Interestingly, 10 of the 116 $Z' = 1$ species have potentially misassigned or ambiguous Z' values. Z' is strictly defined as the number of formula units in the unit cell divided by the number of independent general positions; however, sometimes the definition of the formula unit can be ambiguous and several different values of Z' are technically correct.[27] For example, CSD refcodes IHIQEV,[28] LUSSUN,[29] QAJMIX,[30] XIMNUC,[31] YESQES[32] and YESQIW[33] all contain interlocked Au-containing rings held together by Au···Au interactions. Despite the fact the dimers are interlinked and therefore inseparable without breaking bonds, they are essentially two unique molecules and may be better described as $Z' = 2$. The same principle could also be applied to CIVBIS[34] (from the $Z' > 1$ subset), which is in the CSD formally as $Z' = 2$ but has two such "dimers" and therefore could be better described as $Z' = 4$. $[PPh_3AuSe(CH_2Ph)AuPPh_3][SbF_6]$[35] (LECVEU), $[Au(SC_6H_4COO)_2][K_6]$[36] (XEBVEF), and $[Au_3(MeN{=}COEt)_3]$[37] (XICVAG) are currently described as $Z' = 1$ Au−Au bonded dimers, but all have Au···Au interactions of > 3 Å and therefore may be more accurately described as $Z' = 2$ systems. Perhaps the most interesting misassignment is $[Au(\mu\text{-4-Me-pz})]_3$[38] (MUTLAO), which actually exhibits an astonishing 15 unique

---

[25] Anderson, K. M.; Steed, J. W. *CrystEngComm* **2007**, *9*, 328.

[26] van Eijck, B. P.; Kroon, J. *Acta Crystallogr., Sect. B* **2000**, *56*, 535−542.

[27] See *http://www.durham.ac.uk/zprime/not.html*.

[28] Mohr, F.; Eisler, D. J.; McArdle, C. P.; Atieh, K.; Jennings, M. C.; Puddephatt, R. J. *J. Organomet. Chem.* **2003**, *670*, 27.

[29] Mohr, F.; Jennings, M. C.; Puddephatt, R. J. *Eur. J. Inorg. Chem.* **2003**, 217.

[30] McArdle, C. P.; Vittal, J. J.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3819.

[31] McArdle, C. P.; Van, S.; Jennings, M. C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 3959.

[32] Wiseman, M. R.; Marsh, P. A.; Bishop, P. T.; Brisdon, B. J.; Mahon, M. F. *J. Am. Chem. Soc.* **2000**, *122*, 12598.

[33] Wiseman, M. R.; Marsh, P. A.; Bishop, P. T.; Brisdon, B. J.; Mahon, M. F. *J. Am. Chem. Soc.* **2000**, *122*, 12598.

[34] McArdle, C. P.; Irwin, M. J.; Jennings, M. C.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3376.

[35] Eikens, W.; Kienitz, C.; Jones, P. G.; Thone, C. *J. Chem. Soc., Dalton Trans.* **1994**, 83.

[36] Nomiya, K.; Noguchi, R.; Sakurai, T. *Chem. Lett.* **2000**, 274.

[37] Olmstead, M. M.; Jiang, F.; Attar, S.; Balch, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 3260.

[38] Yang, G.; Raptis, R. G. *Inorg. Chem.* **2003**, *42*, 261.

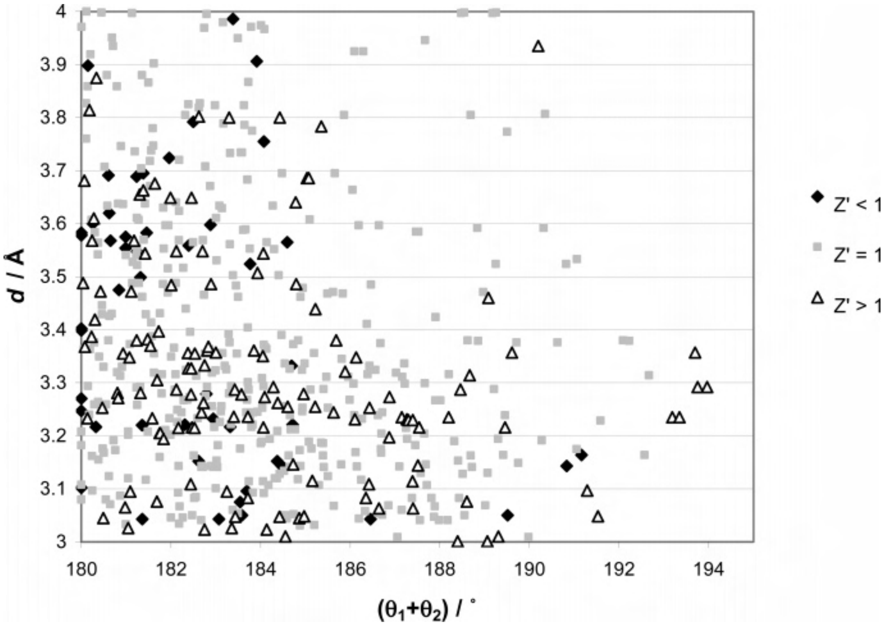


Figure 3. Scatterplot of ($\theta_1 + \theta_2$) vs *d*.

Table 1. Comparison of Distribution of *Z*′ Values for CSD as a Whole and Au···Au-Containing Species

Z′	CSD as a whole	X−Au−Y-containing species with Au···Au $d < 3.6$ Å	X−Au−Y-containing species with no Au···Au interaction(s) with Au···Au $d < 3.6$ Å
total	349 661[a]	184[b]	1749
$Z' < 1$	87 035 (24.9%)	22 (12.0%)	485 (27.7%)
$Z' = 1$	232 095 (66.4%)	116 (63.0%)	1127 (64.4%)
$Z' > 1$	30 608 (8.8%)	46 (25.0%)	137 (7.8%)

[a] Hits numbering 5403 with *Z*′ entered as zero (i.e., there is not enough information to determine the value of *Z*′) were removed. [b] Four redeterminations were removed.

molecules in the asymmetric unit. Compounds with such a high *Z*′ value are extremely rare (there are only 11 reliable structures in the CSD with $Z' > 12$),[39] and therefore, MUTLAO is of particular interest, especially as it is the first reliable example of a species with $Z' = 15$. The 15 molecules arrange themselves into one 16-membered aggregate (Figure 4, purple) consisting of 8 of the independent molecules (plus their symmetry generated counterparts) and 1 dimer (Figure 4, green), with the remaining 5 independent molecules (Figure 4, yellow) showing no short Au···Au interactions.

The molecules are almost planar, and the backbone of the pyrazolate is relatively sterically unhindered, allowing the close approach of another molecule, unlike in [Au(μ-3-Me-5-Ph-pz)]$_3$,[38] for example, where the bulky phenyl group prevents the close approach of another molecule and a $Z' = 1$ structure is observed with no short Au···Au contacts. Effects other than sterics are obviously also important, however, as [Au(pz)]$_3$[38] itself has two slightly skewed Au···Au contacts and also has $Z' = 1$.

Of the 46 $Z' > 1$ structures, *Z*′ values range from 1.250 to 6, with the majority (33, 71.7%) having $Z' = 2$. Nineteen of the 46 structures have more than 1 gold atom per molecule and 3 have more than one unique gold species in the asymmetric unit (i.e., $Z'' > 1$).[26] In all of these 21 cases, the gold···gold interaction is between two independent gold atoms.

As mentioned earlier, the Au···Au-containing structures form two types of extended arrangements in the solid state, discrete Au···Au bonded arrays and infinite chains held together by Au···Au interactions. Table 2 shows the distribution of these packing arrangements for $Z' = 1$ and $Z' > 1$ structures.

In addition to the dimer and infinite chain motifs observed for the $Z' = 1$ species, the $Z' > 1$ species form two additional motifs, namely, trimers and tetramers (i.e., three or four molecules respectively held together by Au···Au interactions either in a chain or in a discrete unit). These discrete arrangements account for more than four-fifths (80.4%) of the molecules, with only a small number (19.6%) forming infinite chains. In seven of these cases, there is more than one discrete unit per asymmetric unit; e.g., [PhC≡CAuPMe$_3$] (FIRWEJ)[40] has two trimers as its unique component.

Ligand Effects. When trying to rationalize the geometries or *Z*′ behavior of L−Au−L species, it is obviously imperative to consider the steric and electronic characteristics of the ligands.

In order to investigate the steric effects of the ligands on the geometry and *Z*′ behavior of the overall complex, the molecular volumes (i.e., the space taken up by overlapping van der Waals radii spheres of the atoms that make up the ligand) of ligands X and Y were calculated using *X-Seed*.[21,22] For comparison purposes, the ligand X is defined as the ligand with the smaller molecular volume and ligand Y that of the larger molecular volume. This convention is adopted throughout the remainder of this work. For both the $Z' = 1$ and $Z' > 1$ datasets, structures with more than one gold atom or more than one gold-containing species as well as structures

---

(39) See *http://www.durham.ac.uk/zprime*.

(40) Schuster, O.; Liau, R.-Y.; Schier, A.; Schmidbaur, H. *Inorg. Chim. Acta* **2005**, *358*, 1429.

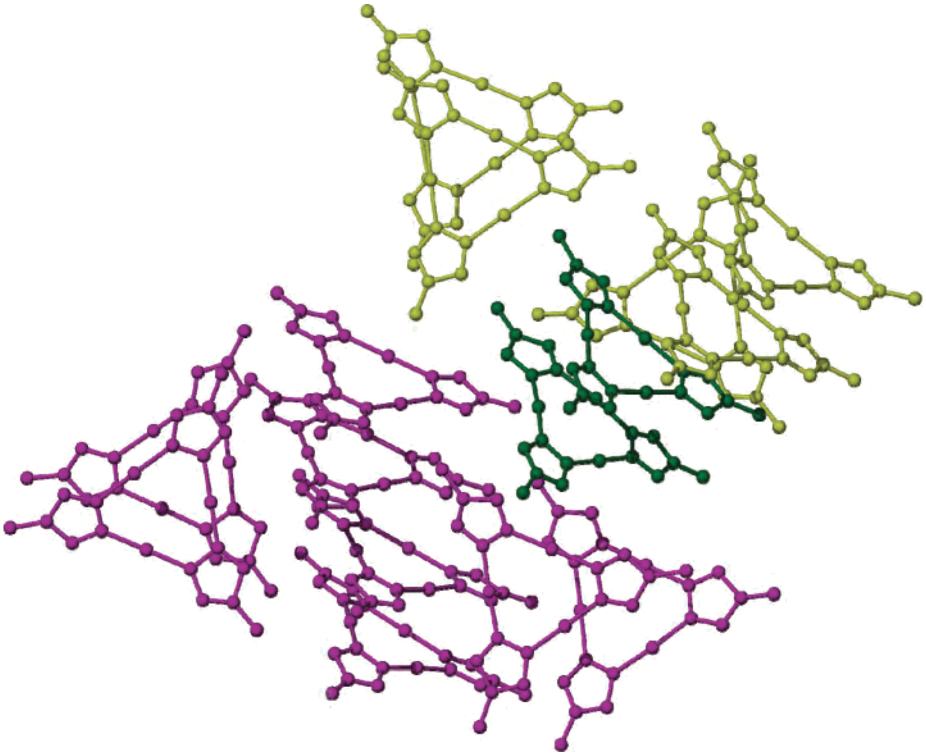


Figure 4. The asymmetric unit of [Au(μ-4-Me-pz)$_3$] showing the symmetry-independent part of the 16-membered aggregate (purple), the dimer (green), and the five independent molecules (yellow).

Table 2. Distribution of Packing Arrangements for Compounds Containing Au···Au Interactions

	$Z' = \mathbf{1}^a$	$Z' > 1$
dimers	65 (56.5%)	30 (65.2%)¶
trimers	0	5 (10.9%)
tetramers	0	2 (4.4%)
infinite chains	50 (43.5%)	9 (19.6%)

[a] MUTLAO is not considered.

where the value of Z' is somewhat ambiguous have been discounted, leaving 39 structures from the $Z' = 1$ dataset and 24 for the $Z' > 1$ dataset, which were considered further.

Figure 5 shows both the molecular volume of X vs the X−Au−Au−X torsion angle and the molecular volume of Y vs the Y−Au−Au−Y torsion angle. The data is further subdivided by the Z' value.

The plot shows that there is essentially no correlation between molecular volume and torsion angle. The overall Pearson correlation coefficients[41] are −0.104 for X and −0.185 for Y. This means that the orientation of the gold centers with respect to one another is not influenced by the steric bulk of the individual ligands. There also does not appear to be any particular trend in the Z' behavior, although it appears that eclipsed torsion angles (i.e., angles greater than 140°) occur mainly for $Z' = 1$ species with just two $Z' > 1$ exceptions, [EtN≡CAu(NO$_3$)] (JOCBIM)[42] and [O$_2$-NC$_6$H$_4$C≡CAuC≡N^{t}Bu] (XAKGIZ).[43] Closer examination of these two structures shows that for XAKGIZ, while there are two independent molecules in the asymmetric unit, the Au···Au interaction formed is not between the two independent species but is actually between two symmetry-related molecules; hence, for the purposes of this study, it could be thought of as a $Z' = 1$ structure as the second independent molecule in the asymmetric unit displays no short Au···Au contacts. JOCBIM, on the other hand, does have two independent molecules that show a short Au···Au interaction between one another; however, X and Y in this case are the smallest multi-atom ligands found in this study. This may allow closer approach of the ligands, and hence, the steric hindrance will be much reduced and the eclipsed conformation may be more favorable.

We were also interested in the difference in molecular volumes of the two ligands. Figure 6 shows a plot of the difference in the molecular volumes for X and Y.

It can clearly be seen that the $Z' = 1$ and $Z' > 1$ datasets have different maxima, separated by around 70 Å^3. This difference is also reflected in the two average values (97.24 Å^3 for $Z' = 1$ and 52.15 Å^3 for $Z' > 1$). This suggests that $Z' > 1$ structures occur more frequently when the ligands are of similar sizes, whereas ligands of different sizes form $Z' = 1$ structures more readily.

While the above results show that the molecular volume of a ligand fragment is a good way of representing the steric considerations of the ligand as a whole, the reality of the situation is somewhat more complex. When the approach of two species which may interact via gold−gold interactions is considered, steric congestion around the gold center is of vital importance. Figure 7 shows that two ligand fragments

---

(41) Excel; Microsoft Office Professional Edition, 2003.
(42) Mathieson, T. J.; Langdon, A. G.; Milestone, N. B.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* **1999**, 201.
(43) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Ramirez de Arellano, M. C.; Jones, P. G.; Humphrey, M. G.; Cifuentes, M. P.; Samoc, M.; Luther-Davies, B. *Organometallics* **2000**, *19*, 2968.

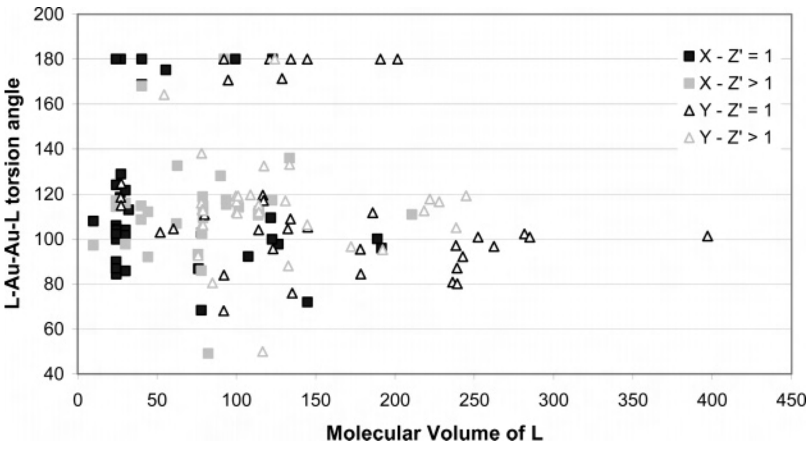


Figure 5. Molecular volume (Å^3) of L vs L−Au−Au−L angle (deg).

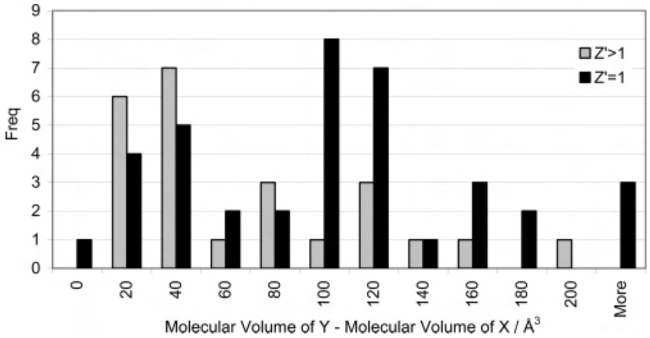


Figure 6. Difference in molecular volumes for X and Y.

Figure 7. Difference ligand shape makes on steric congestion around a gold center.

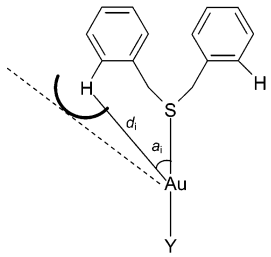


Figure 8. Diagram showing the parameters needed for calculation of a cone angle for ligand Y in [BrAuS(CH$_2$Ph)$_2$][46] (CIBLUU). The bold arc indicates the van der Waals radius of the atom.

with the same molecular volume can exert entirely different steric constraints upon the gold centers.

In view of this, the cone angle (θ) of each ligand has also been calculated. Cone angles were devised by Tolman[44,45] to investigate the relative steric effects of phosphine ligands in catalysis; however, their use can be extended to a broad range of ligands. Figure 8 shows a diagram of the parameters required to calculate the cone angle of ligand Y in [BrAuS(CH$_2$Ph)$_2$][46] (CIBLUU).

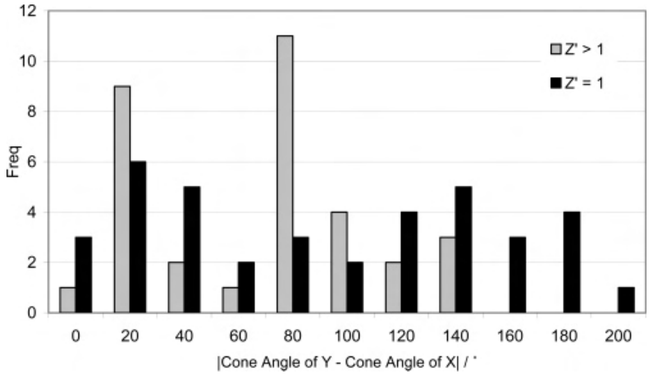


Figure 9. Difference in cone angles for X and Y.

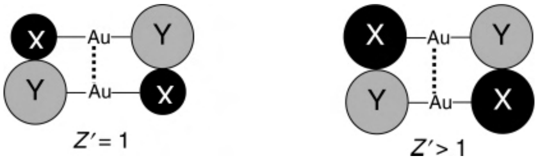


Figure 10. Schematic of the proposed $Z' = 1$ and $Z' > 1$ eclipsed systems.

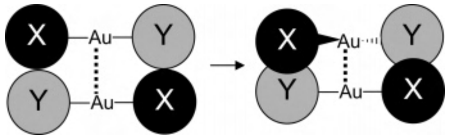


Figure 11. Diagram showing the reduced Au···Au distance invoked by a “twist”.

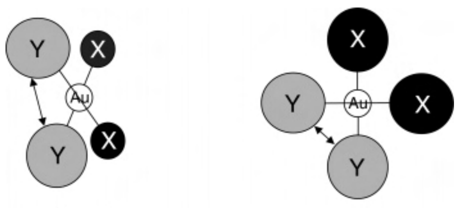


Figure 12. Schematic of possible staggered arrangements for gold···gold systems, showing the enhanced flexibility of $Z' = 1$ systems. View is down the gold−gold axis.

For each atom involved in the calculation, a parameter ϕ_i is calculated (eq 1) which relates the Au−atom distance d_i and the Au−contact-atom angle a_i as well as a correction

---

(44) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.
(45) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.
(46) Strahle, J.; Hiller, W.; Conzelmann, W. *Z. Naturforsch., B: Chem. Sci.* **1984**, *39*, 538.

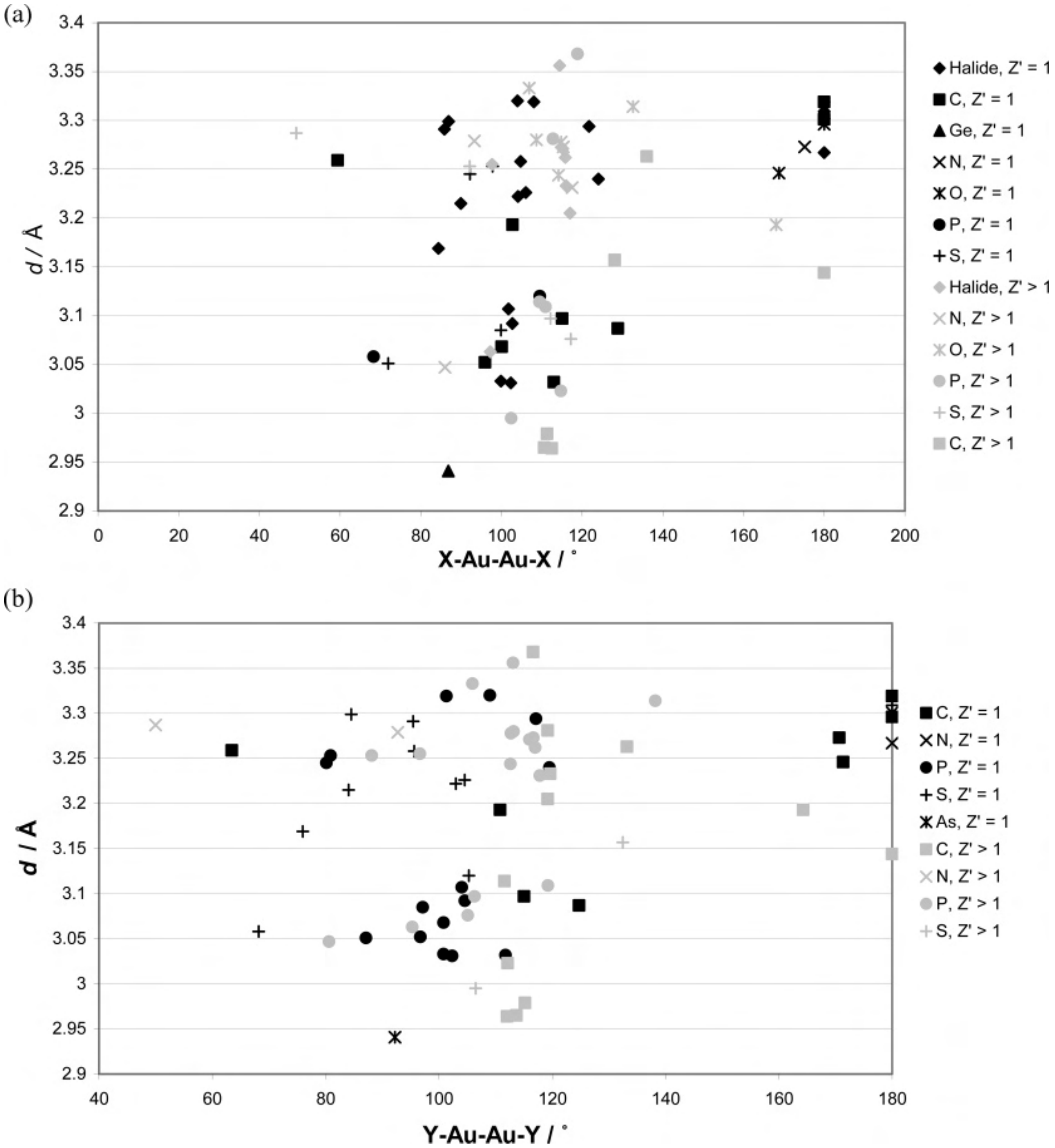


Figure 13. Scatterplot of values of (a) X−Au−Au−X angle vs *d* and (b) Y−Au−Au−Y angle vs *d*.

factor for the van der Waals radius (in Å) of the atom in question (hydrogen in the example shown in Figure 8). The overall cone angle is then calculated using the formula shown in eq 2, where *n* is the number of atoms used in the calculation. The cone angles for all the ligands in this study can be determined using five or fewer atoms (eq 2).

$$\phi_i = \sin^{-1}\left(\frac{r_{\text{vdw}}(A)}{d_i}\right) + a_i \quad \text{for each atom} \qquad (1)$$

$$\text{Then } \theta = \frac{2}{n}\sum_{i=1,n}\phi_i \quad (n = 2-5) \qquad (2)$$

Figure 9 shows the distribution of the difference in cone angles for X and Y.

This distribution follows the pattern observed in the molecular volume study, namely, that the $Z' > 1$ structures show a smaller difference in cone angles than the $Z' = 1$ structures. The average values also support this (81.2° for $Z' = 1$ and 58.9° for $Z' > 1$). Figure 10 shows simple schematics for the two cases.

In the $Z' = 1$ case, where the ligands are different sizes, the gold atoms can maximize their proximity with greater ease even in the eclipsed conformation. For the case where the two ligands are of similar sizes, an approach in the eclipsed conformation leads to longer Au···Au distances; therefore, to increase the strength (and therefore increase the stability) of the interaction, the molecules are forced to twist away from each other to minimize steric repulsion (Figure 11).

In this “twisted” core, there are only a few values of the X−Au−Au−X and Y−Au−Au−Y torsion angles where the molecules can be related by crystallographic symmetry elements; therefore, the structure is forced to have $Z' > 1$ to account for this necessary twisting behavior.

This argument can also be extended to structures forming a staggered arrangement, which has been shown to be a more stable arrangement than the eclipsed form for some species.[47]

Complexes which have ligands of different sizes have more flexibility and, hence, have more opportunity to arrange the ligands into symmetry-related forms, as Figure 12 shows.

We have shown above that steric considerations can have a big effect on the geometry and Z' behavior of linear gold species; however, this is obviously not the only consideration and the electronic characteristics of the ligand may also be important. To investigate this further, the data used above was also categorized according to the electronic nature of the ligand bonded to Au. As before, the ligand X was chosen to always be smaller (i.e., have a lower molecular volume) than Y. Figure 13 shows a graph of the X−Au−Au−X and Y−Au−Au−Y torsion angles vs the Au···Au distance for $Z' = 1$ and $Z' > 1$ structures where the data has also been subdivided according to the nature of the contact atom of X and Y.

The graphs show a wide variation in *d* and torsion angle values; however, some trends in the contact atom can be observed. For example, Figure 13a shows that ligands with O and N as the contact atom tend to form with longer Au···Au distances, whereas ligands with C as the contact atom tend to form shorter Au···Au contacts. This observation suggests that electronegativities could be important, as the electronegativities of O (3.45) and N (2.98) are greater than that of C (2.55); however, the atoms attached to the contact atom as well as their bonding modes have a large effect on the electronegativity of the contact atom. For example, −C≡CPh has a group electronegativity of 2.527 compared with 2.161 for $-CH_2Ph$;[48] therefore, knowing the exact composition of the ligand is vital when considering the electronegativity. Previous theoretical studies[47] have also shown that in certain systems the molecular orbitals on the ligands themselves may interact and affect the gold···gold interaction. It is clear from this that the ligand can exert a wide variety of influences on the Au···Au interaction and that in any designed system, the exact choice of ligand is key.

Conclusions

Since the original study in 1993,[23] over 300 new structures with short Au···Au interactions have been published. These structures provide a much larger spread of values between staggered and eclipsed conformations and are useful when considering rotation around the gold−gold axis and the transformation between these conformations.

Compounds with gold···gold interactions have also been shown to have a tendency to form structures with more than one molecule in the asymmetric unit ($Z' > 1$). This behavior is believed to be related to the size differential of the two substituents. Molecular volume calculations have shown that if the two ligands have a disparity in size, then $Z' = 1$ is favored, whereas the ligands of equivalent size have a tendency toward forming structures with $Z' > 1$ as a non-crystallographic twist is needed to minimize the length and, hence, maximize the strength of the Au···Au interaction. The type of packing arrangement also differs in Z' behavior, with $Z' > 1$ structures showing a preference for discrete motifs over infinite chains as well as having discrete units containing more than two gold centers. $Z' = 1$ structures are somewhat evenly distributed between the two arrangements and do not show any larger motifs than dimers.

Finally, we have shown that to design and engineer complexes with Au···Au interactions, the electronic characteristics of the ligand also need to be carefully considered.

Acknowledgment. This work was supported by EPSRC Grant EP/D040329/1.

IC700466Y

---

(47) Jiang, Y.; Alvarez, S.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 749−757.
(48) Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1007−1010.