Database Analysis of Au ··· Au Interactions†

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The geometry of gold–gold interactions in a group of 693 gold-containing crystal structures has been examined using data from the Cambridge Structural Database. These contacts occur in the range 2.50–4.00 Å. Intermolecular Au ··· Au contacts are formed by compounds of the type AuXY (X, Y = any element) with the X-Au-Au-Y conformation being either staggered or eclipsed. Clusters of the type Au_nZ (where Z is any element including Au) are characterised by a large number of short gold–gold contacts reflecting an approach towards Au^0 in the interior of the cluster.

The existence of attractive gold–gold interactions has been repeatedly confirmed in many recent reports on gold chemistry.[1–3] The energy of the interaction has been estimated to be as high as 7–8 kcal mol^{-1}, comparable to hydrogen bonding. Such interactions have distinctive effects upon structure, properties and stereochemistry[4–8] and have been investigated by experimental and theoretical methods.[9–12] It is believed that correlation and relativistic effects are involved.[13–15] Of particular interest is the marked similarity in the behaviour of gold and the halogens,[16] the basis of this being that gold, with a $d^{10}s^1$ configuration, is one electron short of the closed configuration $d^{10}s^2$ just as the halogens, with a s^2p^5 configuration, are one electron short of the closed configuration s^2p^6. The halogen-like behaviour of gold is exemplified by high electronegativity (the highest of all metals and comparable with selenium), the ability to form compounds of the type CsAu and RbAu (isostructural with CsCl) with very electropositive elements, and the formation of stable Au_2 dimers (*ca.* 55 kcal mol^{-1}) in the gas phase. It is well known that the halogens Cl, Br and I form short, attractive contacts and that such intermolecular interactions control crystal packing.[17] Halogen-substitution in organic molecules is a well-accepted technique of crystal engineering, namely the specific design of crystal structures employing the directional properties of intermolecular interactions.[18] In this instance, the presence of one or more halogen atoms in the molecular periphery of a flat aromatic species, leads to the preferential adoption of an overlapped crystal structure with a stacking axis of *ca.* 4.00 Å. The analogy between gold and the halogens may therefore be extended to the ability to form attractive Au ··· Au or halogen ··· halogen contacts.

In this paper, we have investigated the geometrical properties of gold–gold interactions using information from the Cambridge Structural Database (CSD).[19] At present, there is a conveniently large number of gold-containing compounds in the CSD (693 entries out of a total of 82 129 in the 1990 version). Almost all of these are organometallic and cluster compounds, in which the metal centres can be considered as a link between the isolated Au_2 dimer in the vapour phase and the infinite structure of the solid element itself. Therefore a study of these structures is particularly relevant to the further understanding of Au ··· Au interactions. Use of the CSD has been established as one of the best methods of studying the directional properties of weak intermolecular interactions[18] and the large number of structures available ensures that reliable conclusions can be drawn. In all calculations only crystal structures with $R \leqslant 0.075$ were used and all duplicate entries eliminated. This study was initiated because no systematic analysis of the trends in gold–gold distances has been reported.[15]

Results and Discussion

A preliminary survey showed the presence of a large number of gold–gold distances in the range 2.50–4.00 Å. As a reference, the Au–Au distance in the metal is 2.89 Å, while the nominal Au ··· Au van der Waals distance is 3.60 Å. Some of the contacts (2.55–3.10 Å) were clearly assignable to Au–Au bonds within a cluster while slightly longer ones (2.90–3.30 Å) can represent Au ··· Au non-bonded interactions. Other distances, typically in the range 2.80–3.40 Å can be termed intermolecular Au ··· Au contacts between molecular species containing a single gold atom. It immediately became apparent that it would be difficult to define a gold–gold contact as bonded or non-bonded, or as intramolecular or intermolecular, solely on the basis of the gold–gold distance. Such a differentiation may not even be necessary in view of the unusual nature of the Au ··· Au interaction where there is much overlap between contact distances for these nominally different types of situations. Somewhat arbitrarily therefore (and because of the protocols required by the CSD-suite of programs), we have referred to all distances greater than 3.00 Å as non-bonded interactions.

The present study is divided according to two types of interactions. (*a*) Intermolecular gold–gold interactions, including (*i*) two-co-ordinated monogold compounds, AuXY (148 entries) and (*ii*) more than two-co-ordinated monogold compounds, AuX_3, AuX_2Y, AuX_2Y_2, AuX_4 *etc.* (234 entries; X, Y = any element); (*b*) intramolecular gold–gold interactions in compounds of the types Au_2Z (101 entries) and Au_nZ, where $n \geqslant 3$ (55 entries); Z is any element, including Au. Fig. 1 shows a schematic sketch of the four types of gold geometries discussed here. In Fig. 1(*a*) X^1 and X^2, Y^1 and Y^2 or Au^1 and Au^2 are equivalent and, in general, the assignment of these labels by the CSD programs is arbitrary. For such symmetrical structures, it has been shown that the data analysis should be carried out by expanding the original data set so that all symmetry variants are included.[20,21] In effect, the data set covers the whole of the relevant parameter space. It must be pointed out that while this method of symmetry expansion multiplies the number of data points, it does not add any new data. It merely highlights the implicit symmetry.

Intermolecular Gold–Gold Interactions.—Two-co-ordinated gold structures. The structures of the 148 AuXY entries were verified using the graphics version of the CSD and the values of the parameters *D*, θ, φ and the torsion angle τ (X^1–Au–Au–Y^2) were considered for the 17 hits (from 16 entries) where

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† *Non-SI unit employed:* cal ≈ 4.184 J.

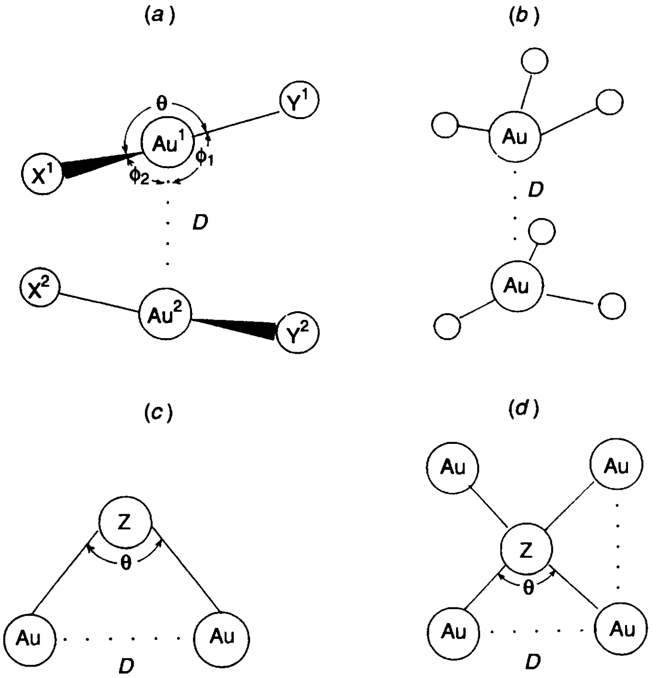


Fig. 1 Geometric fragments used in GSTAT[19] calculations: (*a*) two-co-ordinated monogold compounds, (*b*) more than two-co-ordinated monogold compounds (*c*) Au_2Z clusters (Z is any element) and (*d*) Au_nZ clusters ($n \geqslant 3$, Z is any element)

$3.00 \leqslant D \leqslant 4.00$ Å. For the most part, $\varphi \approx 90°$. According to our assumption, these structures contain non-bonded, intermolecular Au ··· Au contacts and the small number is indicative of steric hindrance caused by bulky X and Y groups, which prevent a close approach of neighbouring gold atoms. For example, in 58 entries, X = PPh_3 while in another 22, a gold-containing anion is sandwiched between layers of flat organic cations (organic superconductors) making a close Au ··· Au approach impossible. However, it is noteworthy that there are 17 short Au ··· Au contacts among this group of structures.

The scatterplots shown in Fig. 2 indicate that the angular geometries for these 17 Au ··· Au contacts are highly specific. Note that because of the symmetry expansion, 136 data points rather than 17 are plotted. Values of τ group around $\tau \approx 90°$ (staggered conformation; 48 data points) or $\tau \approx 0$ or $\pm 180°$ (eclipsed conformation; 80 data points). Fig. 2(*a*) shows that $\tau \approx \pm 90°$ is preferred for smaller *D* values while $\tau \approx 0$ or $\pm 180°$ is distinctly preferred for larger values. It also indicates that data for the structure $[Au(PEt_3)Cl]$[22] [$D = 3.57$ Å; $\tau \approx \pm 60, \pm 120°$; 8 data points in Fig. 2(*a*)] could represent an intermediate in the rotation around the Au^1–Au^2 axis, which converts the staggered to the eclipsed conformation or *vice versa*. Other than this structure there are no others with intermediate τ values. Even when gold–gold separations are greater than the nominal van der Waals distance, angular specificity is maintained. These results indicate that steric hindrance results in a preference for the staggered conformation and this has been stated explicitly in a previous theoretical study.[10] What is interesting is that the eclipsed conformation is found at all, contrary to earlier expectations; in fact it is more frequently observed than the staggered conformation in our limited set of structures and includes compounds like $[Au\{P(OPh)_3\}Cl]$[23] where steric hindrance could be a problem. This last observation suggests that factors other than steric hindrance may also be important in dictating the X–Au–Au–Y conformation, and π interactions have been suggested in this context.[10]

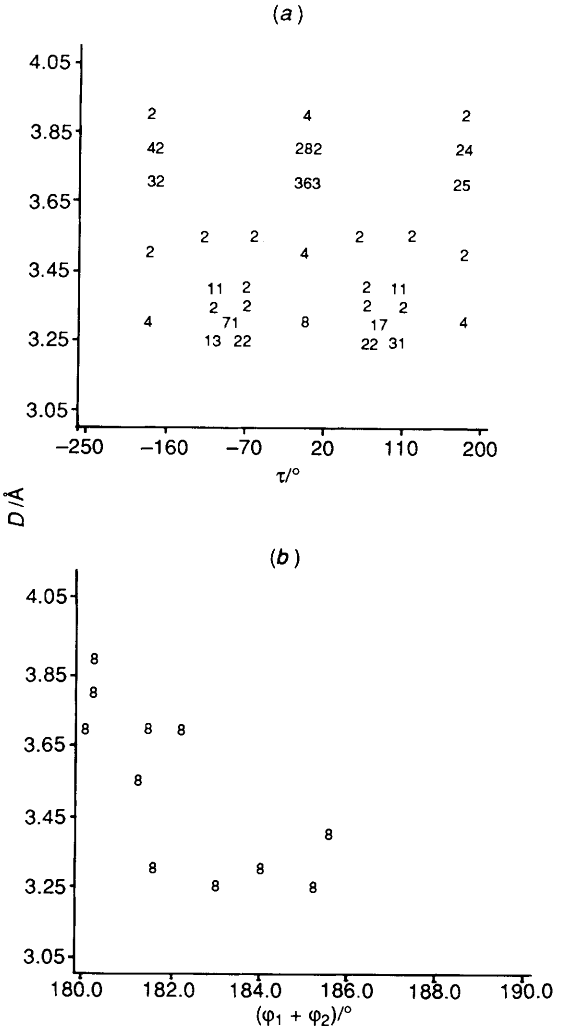
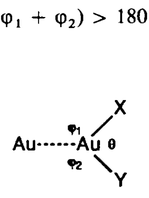
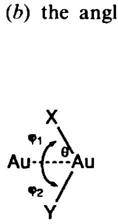


Fig. 2 Scatterplots for two-co-ordinated monogold compounds: gold–gold distance (*D*) *versus* (*a*) the torsion angle X–Au–Au–Y (τ) (the mean value of *D* is 3.527 Å) and (*b*) the angle ($\varphi_1 + \varphi_2$) for structures where ($\varphi_1 + \varphi_2$) > 180°

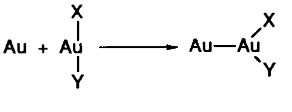


I



II

While studying the X–Au–Y angle, θ, two distinct situations may be considered. Since in both these cases θ < 180°, we examined specifically the quantity ($\varphi_1 + \varphi_2$). For ($\varphi_1 + \varphi_2$) > 180°, (structure **I**) there were 11 hits and 88 data points, and for ($\varphi_1 + \varphi_2$) < 180° (structure **II**) 6 hits were found. Fig. 2(*b*) shows a scatterplot for the 11 examples where ($\varphi_1 + \varphi_2$) > 180°. As *D* decreases, ($\varphi_1 + \varphi_2$) increases (within the range 180–186°) and the co-ordination around gold is distorted from a linear geometry towards a more trigonal geometry. This behaviour is paralleled by the changes in co-ordination geometry around the carbonyl carbon on the approach of a nucleophilic nitrogen atom (trigonal to tetrahedral), the Dunitz–Burgi principle of structure correlation.[24] Similarly the approach of a gold atom towards X–Au–Y can be compared with the early stages of the hypothetical reaction (1).



$$\mathrm{Au} + \overset{\mathrm{X}}{\underset{\mathrm{Y}}{\mathrm{Au}}} \longrightarrow \mathrm{Au{-}Au}\overset{\mathrm{X}}{\underset{\mathrm{Y}}{}} \qquad (1)$$

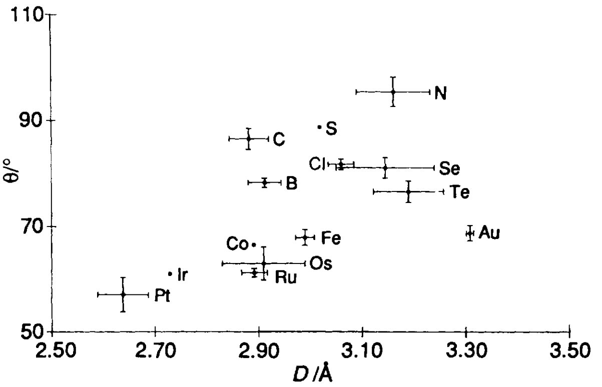
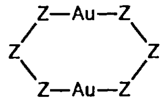


Fig. 3 Correlation between mean D and θ values for Au_2Z clusters, showing the individual elements Z

In conclusion, the angular approaches of the gold atoms are highly specific and these trends are reminiscent of the behaviour of intermolecular $Cl\cdots Cl$[25] and $S\cdots S$[26] contacts which also have very specific angular properties.

Another type of gold–gold contact is commonly observed in structures with eight-membered rings (**III**). This ring system is formally related to the AuXY compounds considered above. A search of the CSD indicated that there are 16 pertinent hits (from 24 entries) where $D < 3.40$ Å with a mean D value of 3.009(7) Å. However, in many of these cases $(\varphi_1 + \varphi_2) \approx 180°$ and so it might be argued that the transannular gold–gold approach does not distort the ring geometry significantly. Steric factors are undoubtedly important because all τ values for these compounds are around 180°. The ring size probably does not permit any other τ value. This type of gold–gold interaction is formally intramolecular but there is some similarity to the intermolecular $Au\cdots Au$ contacts in the AuXY compounds.



III

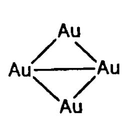
Z = C, P, N or Mn

More than two-co-ordinated gold compounds. Steric factors predominate here because the higher co-ordination of gold lessens the probability of its contact with another gold atom. Of the 234 entries, only 6 have short $Au\cdots Au$ distances within the range $3.00 \leqslant D \leqslant 4.00$ Å. These 6 entries provide 7 hits. There is a wide variation in φ with one at 65°, three at 80° and three at 105°. A similar situation prevails with the τ values, with one at 0°, another at 45° and the remainder at 90°. It is difficult to draw firm conclusions here because of the small number of hits.

Intramolecular Interactions.—Au_2Z *Clusters*. In the case of Au_2Z compounds, it was convenient to consider cases where $Z = Au$ and $Z \neq Au$ separately, as when $Z = Au$ symmetry expansion of the data was performed. The following number of structures were considered for a variety of elements Z: Pt, 2; Ir, 1; Fe, 3; Co, 1; Ru, 11; Os, 3; Te, 2; B, 2; C, 11; N, 2; S, 1; Cl, 1 and Au, 2. Two additional post 1990 structures, where Z = Se, were included in the plot.[27,28] The two gold atoms in the Au_2Z fragment were assumed to have an attractive interaction if $D \leqslant 3.40$ Å a value less than that chosen for the AuXY compounds (4.00 Å) as both gold atoms are bonded to a common central atom. Although 3.40 Å may seem to be a somewhat arbitrary cut-off, there are many instances where $Au\cdots Au$ distances < 3.40 Å have been shown to be of definite chemical significance.[1-8] Therefore, Fig. 3 is a plot of the gold–gold distance, D *versus* the Au–Z–Au angle, θ, with each point on the plot representing the average D and θ values for families of crystal structures incorporating the same element Z. There are three general regions in the plot: where Z = Pt, Ir, Ru, Os, Co, Fe, Te; where Z = B, C, S, Se, Cl, N and where Z = Au.

When Z is any metal other than Pt, Ir or Au, both D and θ values fall in narrow ranges, 2.85–3.05 Å and 61–68° respectively, indicating similar bonding and an icosahedral geometry. When Z = B, C, S, Se or Cl, the distance D is still within this narrow range and the necessary changes in the Au–Z distance are accommodated largely by changes in θ. This reflects the importance of the gold–gold interaction since this remains relatively insensitive to changes in Z. When Z = Pt or Ir, the gold–gold distance is shortened (≈ 2.70 Å) while θ remains invariant perhaps indicating the strength of Au–Pt or Au–Ir bonds compared with Au–Fe, Au–Os or Au–Ru. Conversely, when Z = Te, the gold–gold distance increases (3.19 Å) with θ invariant, perhaps due to a weak Te–Au bond which is polarised $Te^{\delta+}$–$Au^{\delta-}$.

When Z = Au, the situation is more complex since there are mutually attractive forces between three gold atoms at the vertices of a triangle. There are four hits from two crystal structures (DIVKOI and THACAU10), each structure containing an Au_4 tetramer **IV**. The mean of the shorter diagonal gold–gold distances is 3.30 Å (Fig. 3). Other gold–gold distances corresponding to sides of the Au_4 parallelogram are much shorter and may be considered as regular bonds.



IV

Au_nZ *clusters*. In these cases several gold atoms are attached to a common central atom Z. Again it is preferable to consider cases where $Z \neq Au$ and $Z = Au$ separately. The following number of structures were considered for various elements Z: Pt, 2; Ir, 2; Rh, 3; Re, 3; Mo, 1; Pd, 1; Ru, 3; Te, 1; Se, 1; Fe, 2; Co, 1; B, 2; C, 2; O, 1; S, 3 and Au, 30. In a cluster Au_nZ, where $Z \neq Au$, there are a number of possible sub-fragments $Au_2Z(m)$ where $D \leqslant 3.40$ Å. Fig. 4 shows a graph of the mean value of D *versus* the mean Au–Z–Au angle, θ, for various families of clusters Z_n^m (where n = number of Au atoms in the cluster). These results are very similar to those obtained for the Au_2Z clusters. The gold–gold distances in these clusters are nearly the same as that in the metallic element. However, tellurium and selenium clusters lie outside this range, as observed for the Au_2Z clusters. While the number of points is not large there is good evidence for an attractive gold–gold interaction. For example in the series S_3^1, S_3^2, S_3^3, mean D values become smaller with an increasing number of short gold–gold distances in the cluster confirming that as the structure tends towards Au^0, the stabilisation through gold–gold interactions becomes greater. Of course, we are only restating the well-known fact that in most chemical systems, elemental gold is distinctly favoured thermodynamically over its compounds.[29] For the C, O and B clusters, there do not seem to be a sufficient number of examples to make definitive conclusions.

When Z = Au, however, the symmetry expansion of the data does not permit an analysis in terms of Z_n^m. Here, it is more appropriate to plot histograms of the maximum and minimum gold–gold distances in the Au_3 fragments obtained. Fig. 5 shows that there is a tendency for the distances within the Au_3 triangular units to be unequal. This situation is comparable to that found in the Au_4 tetramers discussed above. In general, D values are even shorter than in the pure metal.

Conclusion

Gold–gold interactions, whether intra- or inter-molecular, occur within narrow distance ranges and the orientation of gold atoms in crystals are characterised by specific angular geometries.

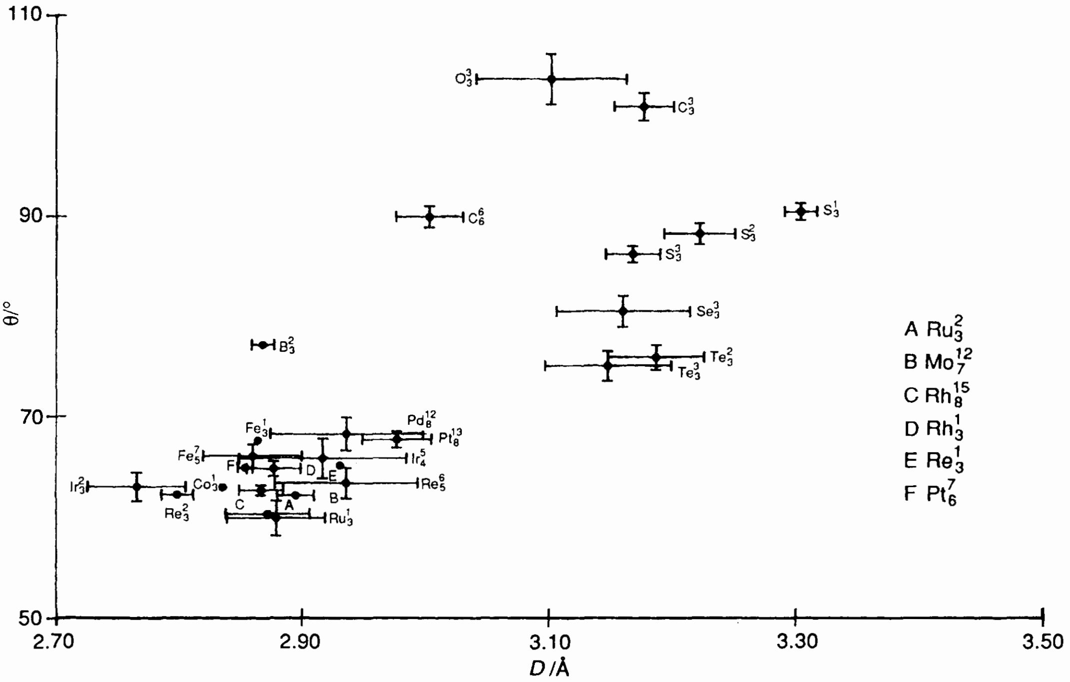


Fig. 4 Plot of D *versus* θ for Au_nZ, clusters where $n \geqslant 3$ and $Z \neq Au$. The different cluster types are defined by Z_n^m, where m = number of sub-fragments and n = number of Au atoms per cluster

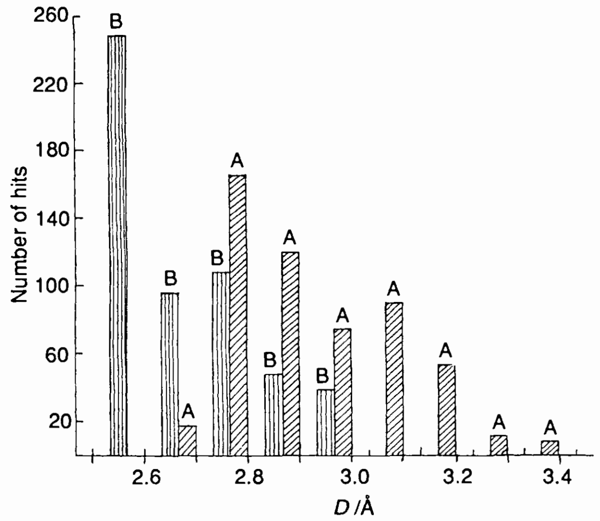


Fig. 5 Histogram of gold–gold distances in the triangular Au_3 fragment of Au_n clusters. A and B represent maximum and minimum values respectively for the three possible gold–gold distances

Mean gold–gold distances within clusters tend to decrease with an increasing number of gold atoms signifying an approach towards the thermodynamically most stable structure, namely the metallic element.

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