X-Ray Structural Investigations of Gold Compounds

A COMPILATION OF REFERENCE DATA. PART I

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Our knowledge of the structural chemistry of gold has been advanced in recent years by the use of X-ray techniques to the point where achievements in this field can be constructively discussed. In this article — Part II of which will appear in the next issue of Gold Bulletin *— the literature on the subject (intermetallic compounds of gold excepted) up to early 1980 is reviewed comprehensively and some selected, more recent examples are discussed.*

The use of X-ray crystallographic methods, both as an analytical tool and as a means of obtaining detailed structural information at the atomic level, is nowadays extremely widespread. This may be attributed to the development of fast, accurate and elegant diffractometers, computers and software at prices accessible to most large research establishments. The consequent volume of available X-ray structural data has rendered review articles of considerable usefulness. This review examines the structural chemistry of gold as revealed by X-ray studies.
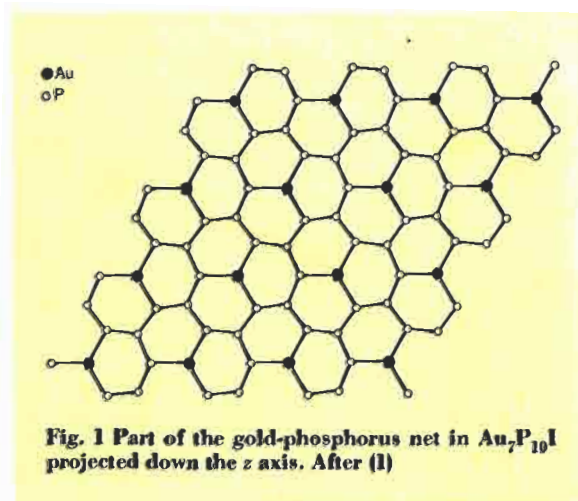
The problem of performing an exhaustive literature search is no small one. The author has made frequent use of the stored data and search programs of the Cambridge Crystallographic Data Centre, and would like to express gratitude to Dr. O. Kennard and co-workers for their assistance. The BIDICS series of publications (Dr. I. D. Brown and co-workers, McMaster University, Canada) has also been an essential source. It is hoped that the review is comprehensive up to Spring 1980, or, at least, that accidental omissions have been kept to a minimum. Where appropriate, some recently published results have also been included. Unpublished results have kindly been made available to me by the following colleagues: Prof. H. Schmidbaur, Prof. J. Strähle and Dr. P. R. Raithby.
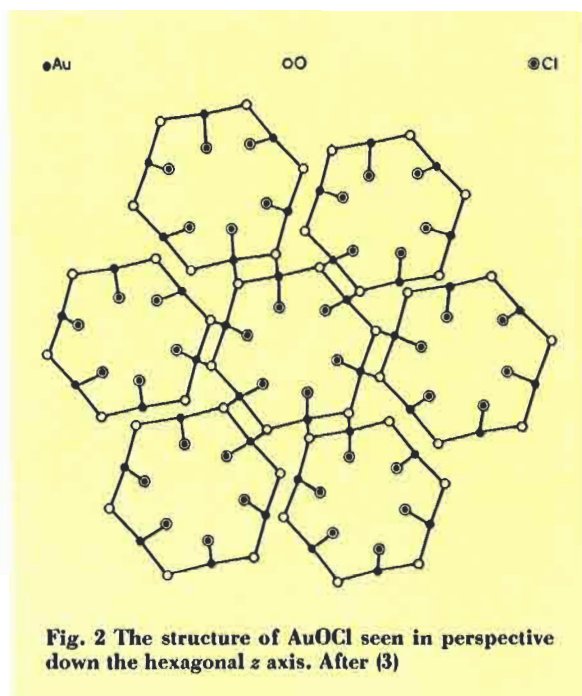
For reasons of space it is not possible to give here a description of crystallographic methods. Suffice it to say that the results of a structure determination consist quantitatively of lists of atomic coordinates and derived parameters such as bond lengths and angles, and qualitatively of a picture of the molecule. (The principle that one picture is worth a thousand words

is nowhere more applicable than in structural chemistry, and for this reason a representative sample of diagrams is given here.) The more interesting of these results form the bulk of this review; for further details of individual structures the reader must have recourse to the original articles. The practice of publishing crystal structures without lists of coordinates is strongly to be deprecated, although becoming less common with the introduction of deposition schemes for crystallographic data. References in which no coordinates are quoted are labelled 'nc'.

The (somewhat arbitrary) sections into which this article is divided are as follows:

    I. Simple Binary and Ternary Compounds
    II. Cluster Compounds
    III. Compounds with Gold-Transition Metal Bonds

Fig. 1 Part of the gold-phosphorus net in $Au_7P_{10}I$ projected down the z axis. After (1)

Fig. 2 The structure of AuOCl seen in perspective down the hexagonal z axis. After (3)

It is well-known (and implied in the section headings) that the archetypal coordination geometries for Au(I) and Au(III) are linear and square planar respectively. This will be assumed without further comment.

I. Simple Binary and Ternary Compounds

Group Vb Derivatives

No simple gold phosphides are known. Au_2P_3 (1) consists of P_6^{4-} rings linked both directly and through Au^I atoms (P-Au-P 180 and 171°). The related $Au_7P_{10}I$ (1), formally $Au_7^I(P_{10})^{6-}I^-$, possesses infinite sheets of P_{12} rings containing three-coordinate Au^I atoms (Figure 1). These sheets are joined by linear P-Au-P and (weaker) Au-I-Au bridges.

Na_2AuX (X = As or Sb) (1a) contains infinite zigzag chains of empirical formula AuX^{2-}, resembling the isoelectronic gold(I) halides (see below). Au-X distances are 250.1 and 264.9 pm for X = As and Sb, respectively. The angles at X are suprisingly acute (70.3 and 66.9°, respectively).

Group VIb Derivatives

Gold(III) oxide (Au_2O_3) (2) shows an interesting variation in Au-O bond lengths. One oxygen atom is coordinated to two Au atoms, and has the shortest Au-O bond (193 pm), the other to three Au atoms with appreciably longer bonds (201, 204 and 207 pm), the longest being *trans* to the 193 pm bond. The extended structure is polymeric and best seen as a stereoview (2).

Gold(III) oxychloride (AuOCl) (3) is a polymer consisting of linked hexameric rings (Figure 2). A *trans* influence — the lengthening of a metal-ligand bond by the ligand *trans* to it — is again observed, the Au-O bond *trans* to Cl being appreciably longer than the other two (207 against 199 and 201 pm).

AuSe (4) crystallizes in two forms, both containing linear and square coordinated Au atoms; the formulation $Au^IAu^{III}Se_2$ is thus appropriate (see section IX). Average Au^I-Se and Au^{III}-Se bond lengths are 243 and 248 pm in α-AuSe, and 243 and 250 pm in β-AuSe. In both cases the crystal quality was poor, but adequate for structure determination.

Gold(III) selenide bromide (AuSeBr) (5) displays a ribbon structure (Figure 3). There are two independent gold sites, one coordinated by two Se and two Br, the other by four Se. The Br atoms are terminal. There are considerable deviations from ideal square planar coordination at Au.

The compounds $AuTe_2X$ (X = Cl or I) (6) may be considered as $[Au^{III}(Te_2)_{4/4}]^+X^-$. (The 4/4 notation means that each gold atom is bonded to four Te_2 units and each Te_2 unit to four Au atoms.) Both structures contain corrugated two-dimensional nets of Au and Te atoms (Figure 4). Te_2 units bridge neighbouring Au^{III} centres, and the Au-Te distances are 267.4 and 268.8 pm for X = Cl and I respectively. Again, some deviation from ideal geometry at Au is observed. The

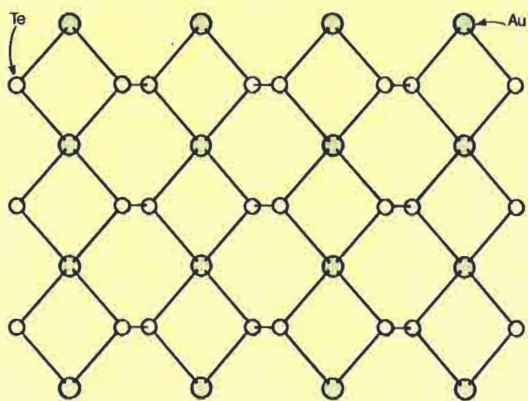**Fig. 3 Part of the ribbon structure of the compound AuSeBr. After (5)**
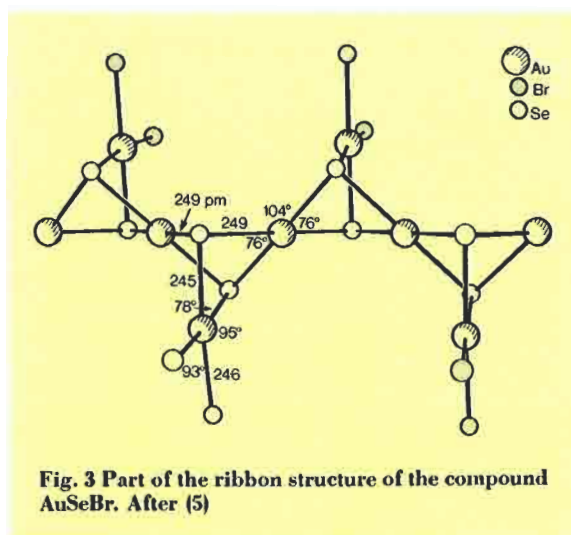
Fig. 4 Part of the gold-tellurium sheet in $AuTe_2Cl$ projected down the y axis. After (6)
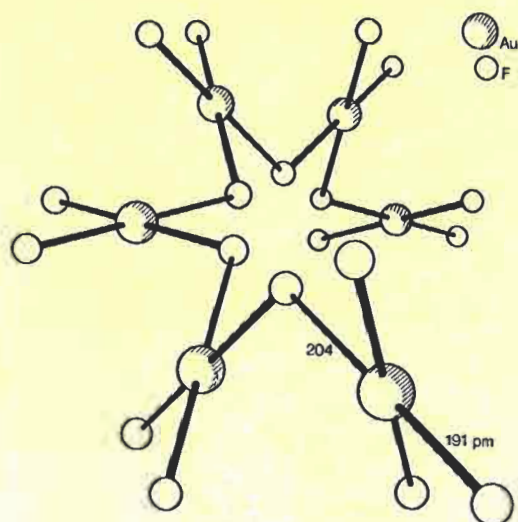

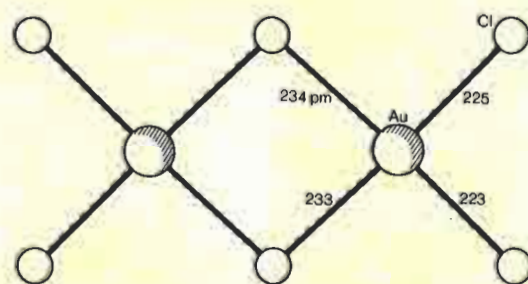Fig. 5 The helical structure of AuF_3 seen in exaggerated perspective down the z axis. After (9)

Fig. 6 The dimeric structure of gold(III) chloride. The structure of gold(III) bromide is analogous, but lacks the formal crystallographic centre of symmetry. After (10)
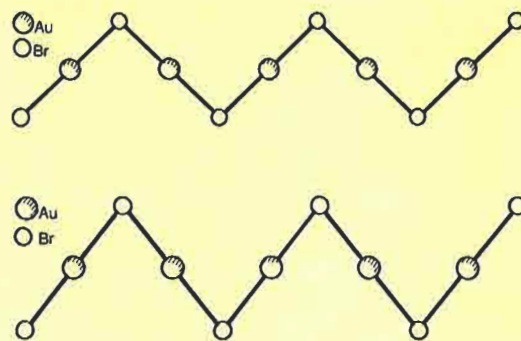

Fig. 7 Gold(I) halide chains, as typified by the two forms of AuBr.
Top: wide Au-X-Au angle form (isostructural with AuCl)
Bottom: narrow Au-X-Au angle form (isostructural with AuI)
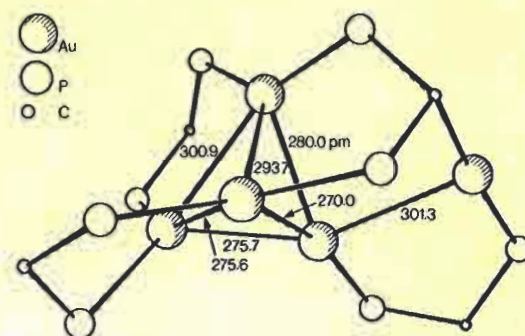Both are drawn to the same scale. After (15a)

Fig. 8 The Au_5 cluster. The phenyl rings are omitted for clarity. After (17)

It has been stated in various reviews that the minerals calaverite and krennerite, both $AuTe_2$, consist of isolated $AuTe_2$ molecules. This is, however, a considerable oversimplification; as was remarked in the original publications (7, 8) there are several short (<320 pm) Au-Te contacts for each gold atom.

(*Note added in proof:* The structure of AuTeI was accidentally omitted from this category. This structure was described by J. Fenner and D. Mootz, *J. Solid State Chem.*, 1978, **24**, 367-369.)

Halides and Pseudohalides

Gold(III) fluoride (9) is a helical fluorine-bridged polymer (Figure 5). The bridging Au-F bonds are, as expected, longer than the terminal ones. Weak cross-linking from chain to chain (Au...F = 269 pm) leads to a highly elongated octahedral geometry about the gold atom.

Gold(III) chloride (10) and bromide (11) are, on the other hand, dimeric molecules without unusually short Au...X contacts. Again, the bridging bonds are longer than the terminal bonds (Figure 6). The adoption of this structure by gold(III) fluoride would

halide ions are weakly associated with the gold atoms, with Au...Cl (terminal) = 293.7 pm and Au...I (bridging) = 333.0 pm. The structures do not explain the observed metallic conductivity.

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lead to a very short Au...Au distance; the bridging X-Au-X angles of the chloride and bromide (86°) may be effects of Au...Au repulsion.

Gold(I) halides have been investigated only by powder methods. These have the advantage that no single crystals need be prepared, but also the disadvantages of overlapping reflexions and difficulty in obtaining accurate intensities. The accuracy of the structure is thus often restricted. Gold(I) chloride (12, 13) is a case in point. Although single crystals were available, only powder investigations were carried out. The qualitative structure, a zigzag chain (Figure 7), was easily determined, but the Cl atoms were positioned by assuming an Au-Cl bond length. The Au-Cl-Au angles were then 92 and 94° in the two determinations. Gold(I) iodide possesses an analogous structure (14, 15), but with a much smaller Au-I-Au angle of 72°. Gold(I) bromide (15a) exists in two crystalline forms, isostructural with AuCl and AuI respectively.

The pseudohalide AuCN has a linear ...-Au-C-N-Au-... structure (16nc).

'Gold dichloride' is a mixed Au^I-Au^{III} derivative (see Section IX).

II. Cluster Compounds*

The study of transition metal clusters has been one of the most active areas of inorganic chemistry in recent years. X-ray crystallography usually provides the only unambiguous method of structure determination for such compounds; several gold clusters,

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*Some very recently published gold cluster structures will be included in a postscript to Part II of this article.
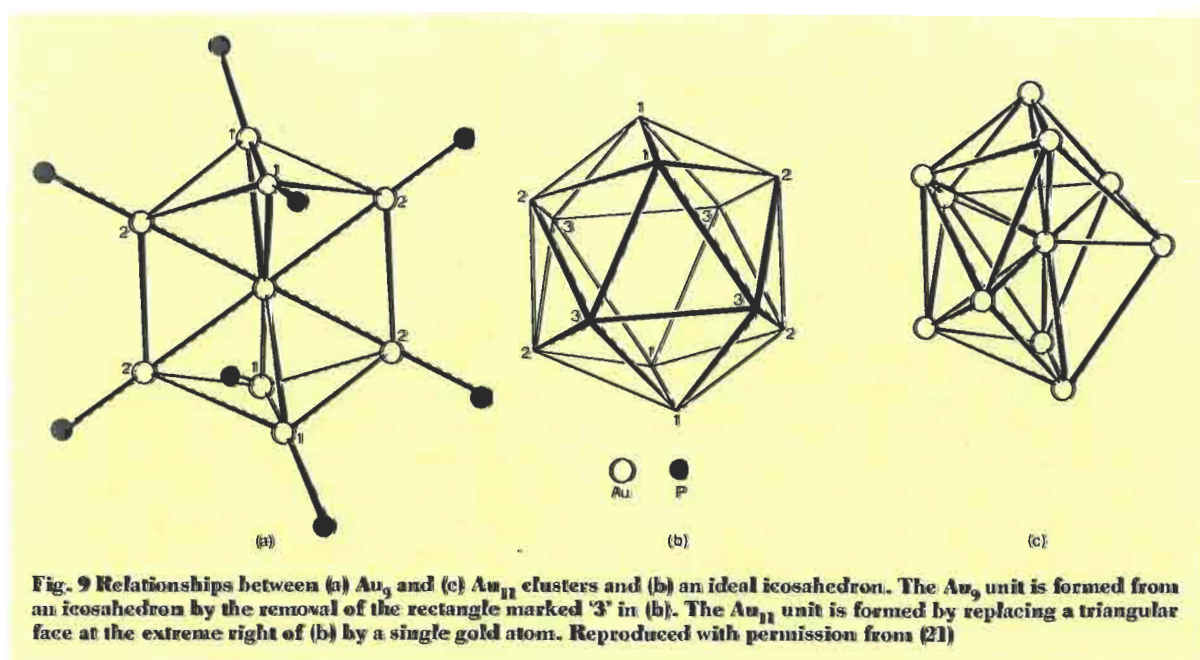
for example, have been falsely formulated on the basis of elemental analyses, molecular weight determinations and conductivity data. Gold clusters are given here in ascending order of number of metal atoms.

The Au_5 cluster in $[Au_5(Ph_2PCH_2PPh_2)_3$ $(Ph_2PCHPPh_2)]^{2+}$ (17) consists of an Au_4 tetrahedron, the fifth Au atom being bonded to one atom of this group (Figure 8). Au-Au distances range from 270 to 301 pm. One phosphine CH_2 group has been deprotonated, an Au-C bond resulting. An unusual feature of this cluster is that three Au atoms are each coordinated by two P atoms; other clusters show only one Au-P bond per metal atom.

In $[(Ar_3PAu)_6]^{2+}$, where Ar = p-tolyl (18), the Au_6 core is a somewhat distorted octahedron, with Au-Au ranging from 293.2 to 309.1 pm.

For the remaining cluster types (Au_8, Au_9, Au_{11}) the problem arises of describing the structures in terms of idealized geometry, and of making clear the relationships between them. In one case, independent workers described the same cluster in completely different ways. One unifying feature, which may usefully be mentioned at the outset, is the presence of a central Au atom (Au_c) bonded to all the others; these latter are then described as peripheral (Au_p) atoms. Au_c-Au_p bonds are appreciably shorter than Au_p-Au_p bonds.

In $[(Ph_3PAu)_8]^{2+}$ clusters (19, 20) each Au, including Au_c, is bonded to one ligand. Reported bond lengths (those from (20) are in brackets) are: Au_c-Au_p = 270.6 av. (263.5 to 272.3), Au_p-Au_p = 287.8 av. (282.6 to 296.0), Au_p-P = 230 av. (229 to 233) and Au_c-P = 238 (242) pm. The longer Au_c-P bond was

Fig. 9 Relationships between (a) Au_9 and (c) Au_{11} clusters and (b) an ideal icosahedron. The Au_9 unit is formed from an icosahedron by the removal of the rectangle marked '3' in (b). The Au_{11} unit is formed by replacing a triangular face at the extreme right of (b) by a single gold atom. Reproduced with permission from (21)

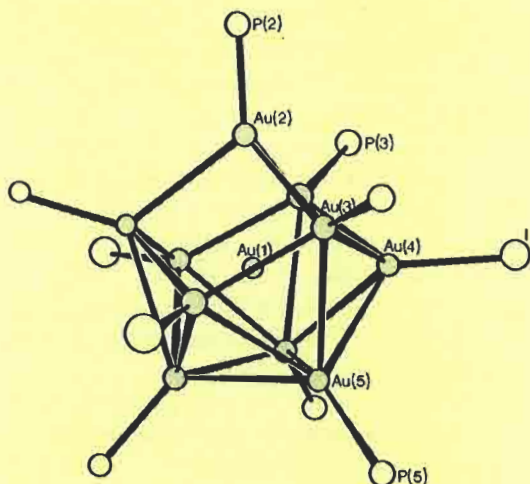**Fig. 10 Detailed structure of $Au_{11}(R_3P)_7I_3$. Bonds to the central Au atom are omitted for clarity. Reproduced with permission from (24)**
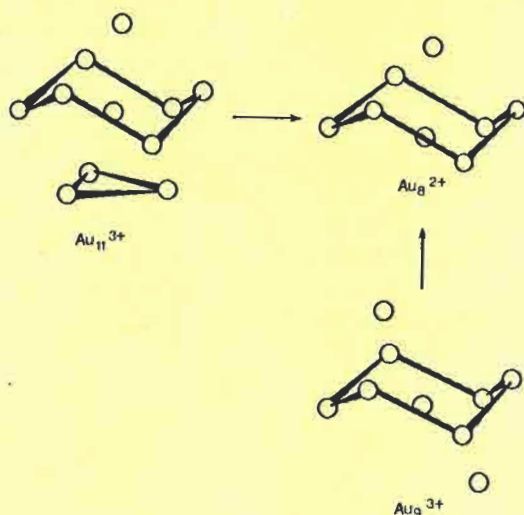

Fig. 11 The Au_6 'chair' common to Au_{11}, Au_9 and Au_8 clusters. Reproduced with permission from (19)

attributed to the lower availability of bonding orbitals on Au_c. The Au_8 geometry is best described as derived from either an Au_9 or Au_{11} unit (see below).

The central atom of the $[Au_9(Ar_3P)_8]^{3+}$ cluster (Ar = p-tolyl) (21nc) is bonded only to Au_p atoms, with bond lengths Au_c-Au_p = 268.9 to 272.9 and Au_p-Au_p = 275.2 to 286.8 pm. The cluster possesses crystallographic *222* symmetry; however it does not deviate significantly from *mmm* symmetry. The ligands are disordered. (For the non-crystallographer, disorder may loosely be defined as the phenomenon whereby an atom or group does not occupy the same position in each unit cell. This often leads to reduced accuracy in determining atomic positions.) The Au_9 core may be regarded as derived from a centered

icosahedron by removal of an equatorial rectangle (Figure 9).

Au_{11} clusters may also best be described as derived from a centered icosahedron, in this case by replacing one triangular face by a single Au atom (Figures 9 and 10). Three such clusters, of general formula $Au_{11}(R_3P)_7X_3$, have now been investigated with R = Ph and X = SCN (22nc), R = p-ClC$_6$H$_4$ and X = I (23nc), and R = p-FC$_6$H$_4$ and X = I (24). All possess the same Au_{11} core. Since disorder problems were encountered in determining the structures of the first two, only the third will be discussed further. The molecule possesses crystallographic *3* symmetry (Figure 10). The Au_c-Au_p distances average 268 pm and the Au_p-Au_p distances are in the range 284 to 319 (av. 298) pm. The iodide ions function as ligands, in contrast to the non-coordinating anions employed in the smaller clusters.

A useful alternative formal description of these clusters, and one which includes the Au_8 cluster, is based on a chair-form 6-membered ring. This structural unit is common to Au_8, Au_9 and Au_{11} clusters (19) (Figure 11).

III. Compounds with Gold-Transition Metal Bonds

Gold forms a wide range of compounds containing bonds between gold and transition metals. This occurs predominantly with gold(I) and with transition metal carbonyl derivatives. A number of compounds of general formula Ph_3PAuX (where X is the transition metal carbonyl moiety) has been crystallographically investigated, though none with great accuracy. Some distortions from linear coordination are observed (Table I).

The only M-Au-M system to have been studied, the $[Au\{Co(CO)_4\}_2]^-$ anion (29), is exactly linear as the gold atom lies on a centre of symmetry. The Au-Co bond length is 250.9 pm.

The Ph_3PAu moiety can also be incorporated into osmium clusters; structures of $Os_3(CO)_{10}(Ph_3PAu)X$ (X = Cl or Br) have been briefly reported (30nc) (Figure 12). The analogous X = SCN and X = H structures have also been determined (30a). Au-Os bond lengths are in the range 273 to 277 pm.

The complicated cation $[(\pi-(C_5H_5)Fe(\pi-(C_5H_4)Au_2(Ph_3P)_2]^+$ (31) is shown in Figure 13. One Au atom appears, most unexpectedly, to be bonded to the central iron atom, with Au-Fe = 281.8 pm, which is somewhat long for a bond from gold to a first row transition metal. In addition, there is an Au-Au contact distance of 276.8 pm. The C-Au-P angles are 169, 174°; although the concept of oxidation state has a purely formal significance in such compounds, this is consistent with formulating both gold atoms as Au^I. Thus, the effects of any Au-Fe and Au-Au bonding do

not distort the usual linear coordination at Au^I to any significant extent.

IV. Gold(I) Complexes with Short Au...Au Interactions

As was noted at the end of the previous Section, an Au-Au distance of 276.8 pm is observed in the gold-ferrocene derivative (31). So many examples of such short (270 to 340 pm) Au...Au contacts, both inter- and intramolecular, are now known that they merit a section of this article to themselves. A detailed list of such structures is given below, but a general discussion will initially be useful.

First, what is a 'short' Au...Au contact? Any contact distance of less than about 350 pm is unexpected for such large atoms, while 300 pm or less must rank as 'very short'. It is interesting to compare the following distances: Au...Au in gold metal is 288.4 pm (32), Au-Au in gold clusters (which must involve metal-metal bonding) is 260 to 310 pm and O...O in hydrogen bonds is mostly in the range 260 to 300 pm. If an O...O contact of less than 300 pm is regarded as unusually short, what of such an Au...Au contact?

Secondly, can short Au...Au contacts be further classified? A loose distinction may be drawn as follows: (a), compounds with bidentate ligands, or with two gold atoms bonded to a common atom, where the gold atoms are forced to be in close contact (but where one might have anticipated such a contact to prevent the binding of more than one of them) and (b), simple linear complexes in which the gold atoms are unexpectedly close to one another.

Thirdly, can an explanation be given for short Au...Au distances? Many authors have suggested that merely the ease of packing of linear molecules may be responsible, but it is difficult to reconcile this explanation with the wide range of known examples, particularly of class (a) above. It is reasonable to postulate some Au-Au bonding interaction for Au-Au distances as short as 270 pm since, otherwise, repulsive forces might be expected to predominate. A Raman study of the gold(I) diisobutyldithiocarbamate dimer (Au...Au = 276 pm, see below) has suggested an Au-Au bond order of about 1/4, caused by interaction of $6s$ orbitals into which charge is donated by the ligands (33). It is however difficult to extend this explanation to cover other, rather longer, Au...Au distances, since the strength of the bonding interactions would be expected to die off fairly rapidly with increasing distance. A satisfactory general explanation would also have to take into account that many such Au...Au interactions are almost perpendicular to the ligand-Au-ligand axis, and that they never substantially disturb the linear coordination at Au.

Compounds of class (b) above will be discussed first, since they are simpler and fewer. Molecules of

Table I

Crystallographic Data for Ph$_3$PAuX Compounds

X	Au-metal bond length, pm	P-Au-M angle, degrees	Reference
Mn(CO)$_5$	252(3)	168(1)	25nc*
Mn(CO)$_4${P(OPh)$_3$}	257(1)	165.5(.1)	26
W(CO)$_3$(C$_5$H$_5$)	269.8(.3)	173.8(.3)	27
Co(CO)$_4$	250(1)	177.5(.5)	28

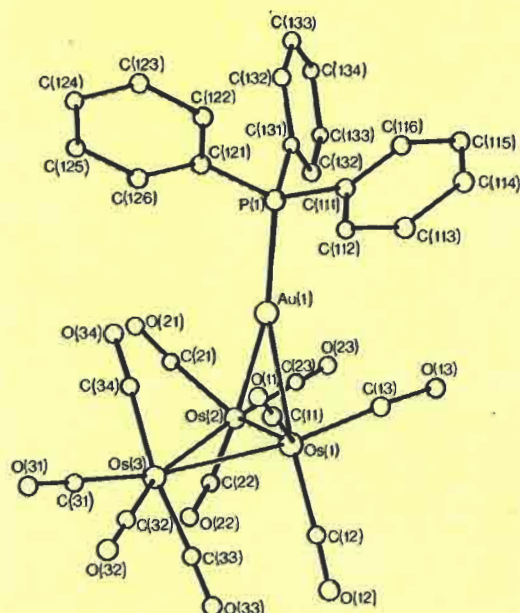*Problems in refinement of data because of pseudosymmetry.

Fig. 12 The structure of Os$_3$(CO)$_{10}$(Ph$_3$PAu)H. Note that this structure contains three-coordinate Au^I, although such mixed-metal clusters have been excluded from Section VI of this article. This diagram was kindly provided by Dr. P. R. Raithby
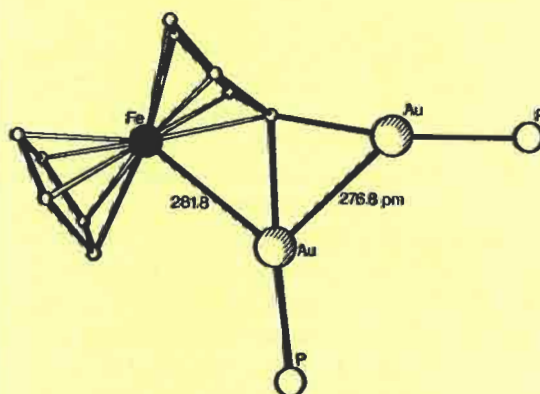

Fig. 13 The unusual cation [(π-C$_5$H$_5$)Fe(π-C$_5$H$_4$)Au$_2$(Ph$_3$P)$_2$]$^+$, which contains an Au-Fe bond. The phenyl rings are omitted for clarity. After (31)
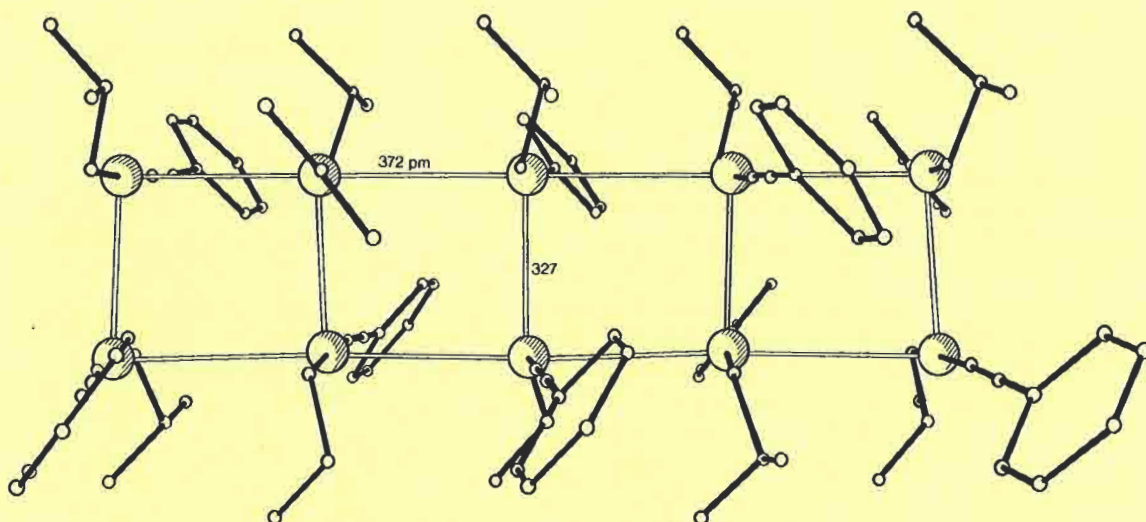
Fig. 14 Part of the Au...Au 'ladder' in (C₃H₇NH₂)Au(C≡CPh). After (35)

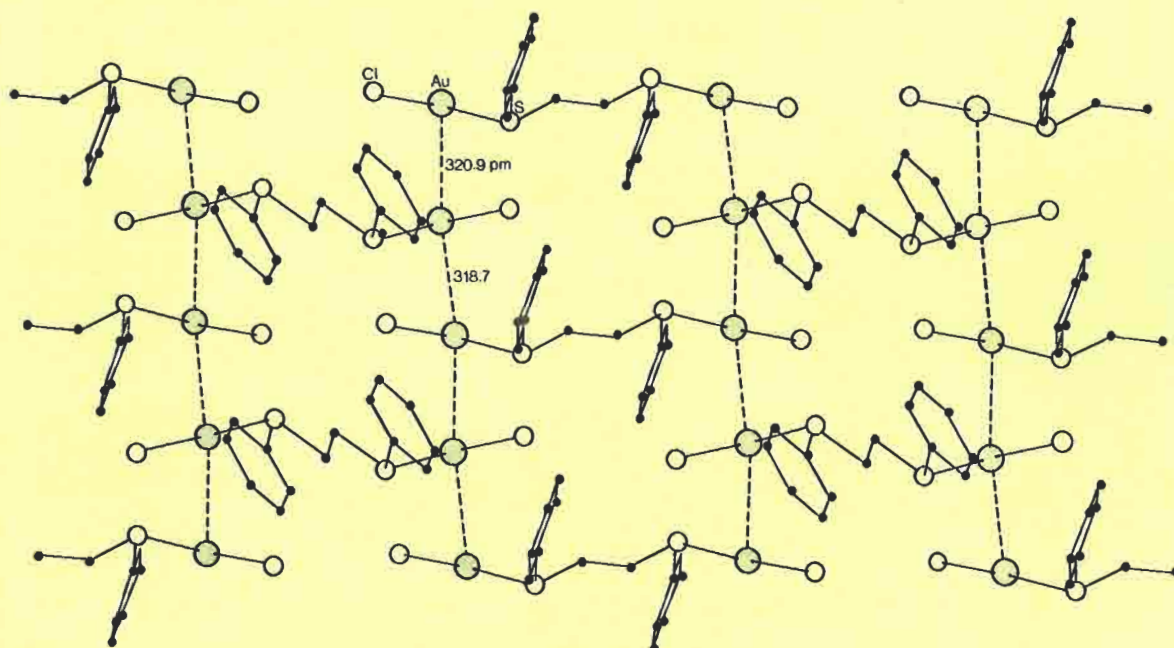**Fig. 15 Au...Au contacts in (C₇H₇SAuCl)₂ projected down the z axis. After (36)**

Cl₃PAuCl (34) pack so as to form zigzag chains of Au atoms, with Au...Au = 314 pm. (The Au-P and Au-Cl bond lengths given in (34) — 219 and 233 pm respectively — do not agree with those calculated from the atomic coordinates and cell constants — 218 and 229 pm.) In phenylethynyl(isopropylamine)gold(I), PhC≡CAuNH₂C₃H₇ (35), the molecules are associated in antiparallel pairs with Au...Au = 327.4 pm. There are further Au...Au contacts of 372.2 pm between adjacent pairs, forming an infinite twisted ladder of gold atoms (Figure 14). The compound

μ–[1,2-bis(phenylthio)ethane]-bis[chlorogold(I)], [PhS(AuCl)CH]₂ (36), possesses two crystallographically independent centrosymmetric molecules. These display no intramolecular Au...Au contacts. The packing is, however, such as to produce infinite, almost linear chains of Au atoms with alternating intermolecular Au...Au distances of 318.7 and 320.9 pm (Figure 15).

The gold atoms do not always form infinite chains; thus, in (piperidine)AuCl (37) the molecules form loose tetrameric clusters based on a square of gold
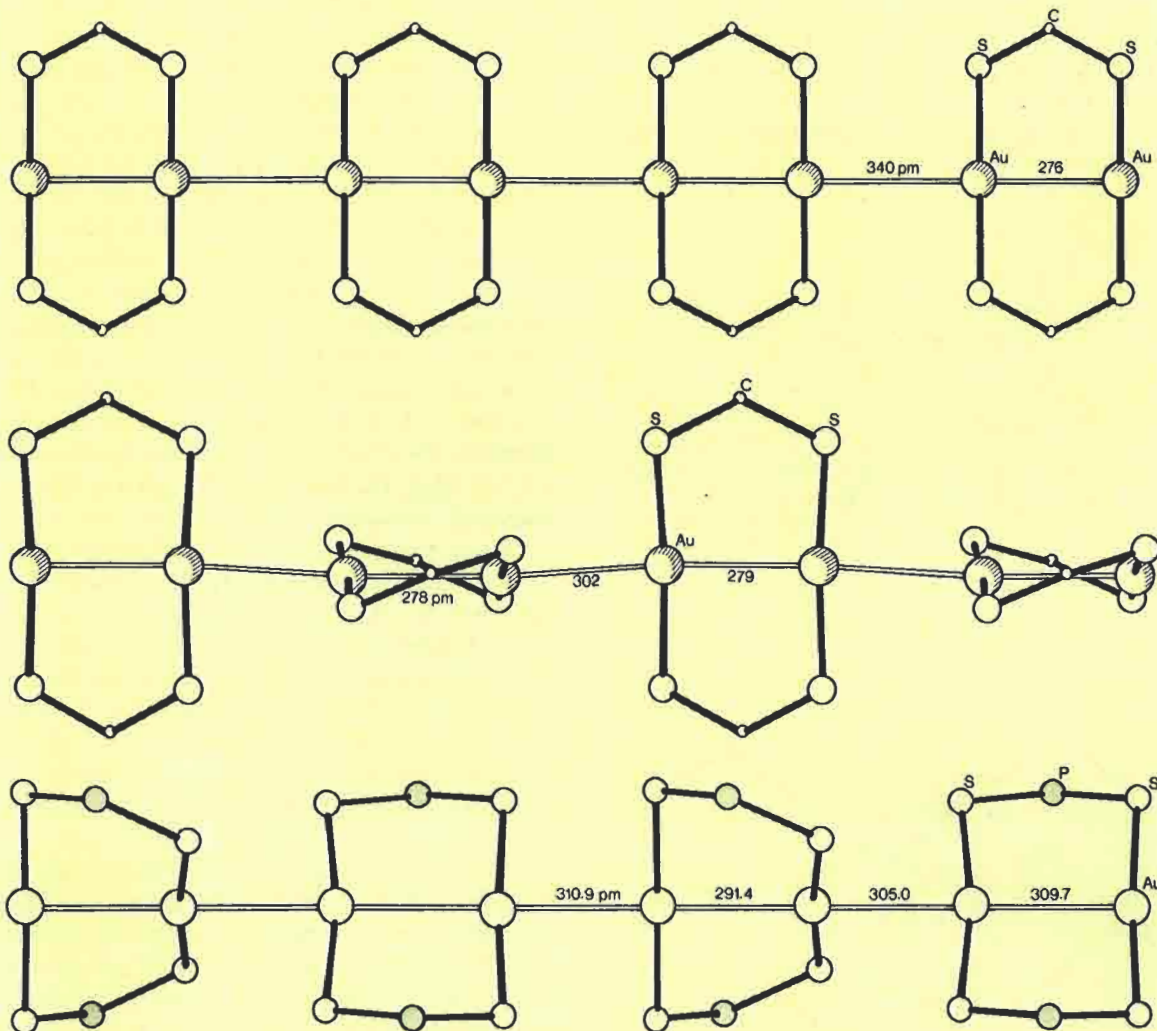
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Fig. 16 Au...Au chains in some sulphur complexes.
Top: R_2NCS_2Au, R = *n*-propyl. After (41)
Middle: same as (a), but R = *n*-butyl. After (43)
Bottom: $(RO)_2PS_2Au$, R = *i*-propyl. After (44)
These projections are perpendicular to the mean planes of the atoms shown and are all to the same scale. The peripheral groups are omitted for clarity. Note that a closer Au...Au approach between dimers, as in (b) and (c), necessitates a twisting apart of adjacent ligands to avoid S...S repulsions

atoms (Au...Au = 330.3 pm), and in the thiosulphate complex $Na_3[Au(S_2O_3)_2].H_2O$ (38, 39) the anions form centrosymmetrically related pairs with Au...Au = 330.2 pm. (Pyridine)chlorogold(I), long formulated simply as pyAuCl, but now shown to be $[py_2Au]^+[AuCl_2]^-$ (37a nc, 37b), displays pairs of cations linked centrosymmetrically with Au...Au = 341.6 pm, the N-Au-N groups being correspondingly bent (N-Au-N, 172.5°). The Au atom of each cation is further linked to an Au atom of $AuCl_2^-$ (Au...Au = 324.9 pm), thus forming zigzag Au_4 units.

Compounds of class (a), where two or more gold atoms are brought into close contact by being bonded to common atoms or groups, also comprise a number of types. In some cases such contacts might be regard-

ed as unsurprising and as involving insignificant bonding interaction, as is the case with the *cis*-ethylenic derivative $(Ph_3PAu)C(CF_3)_2$ (40nc), with a rather long Au...Au distance of 334 pm. There are however many more striking examples. The gold(I) dithiocarbamates R_2NCS_2Au (R = *n*-propyl (41) or *n*-butyl (42nc,43) form dimers with extremely short Au...Au distances (276 to 278 pm). These dimers are then further linked (Au...Au = 340 (41), 302 (43) pm) to form infinite Au...Au chains. An identical type of chain is seen in the dithiophosphate complex $(i-C_3H_7O)_2PS_2Au$ (44). These compounds are depicted in Figure 16. Gold(I) thioacetate, in contrast, forms tetramers with Au...Au = 301 pm on average (44a nc).

Bidentate phosphine ligands ('PP') can form compounds of the type PP(AuCl)₂ in which the -AuCl 'arms' might, on purely steric grounds, be expected to rotate away from each other. However, for PP = (Ph₂P)₂CH₂, which possesses crystallographic 2 symmetry, Au...Au is 335.1 pm (45) and for PP = cis-Ph₂PCHCHPPh₂ it is 305 pm (46).

In complexes with bridging mono-atomic anions, the bridged gold atoms are forced to be relatively near each other. They seem, however, to be unexpectedly close in the compound $[(Ph_3PAu)_2Cl]^+ClO_4^-$ (47). In the two independent cations, the Au...Au distances are 303.5 and 308.5 pm, and the Au-Cl-Au angles 80.7 and 82.7°, which is appreciably less than would be expected for p bonding. In the related sulphur derivative $[(Ph_3PAu)_3S]^+PF_6^-$ (48) there are again two independent cations, but the situation is more complicated. One cation shows low Au-S-Au angles (87.6, 86.4 and 83.4°) and correspondingly short Au...Au distances (323.4, 318.3 and 310.6 pm), the other only one low angle (82.8, 89.1 and 94.9°) and Au...Au contacts of 327.2, 307.0 and 340.8 pm. The cations are linked in pairs (Figure 17) by Au...Au contacts of 336.1 and 323.8 pm, forming an Au₆ ring with 'chair' conformation which is strikingly reminiscent of the Au₆ ring common to several clusters (see Section II).
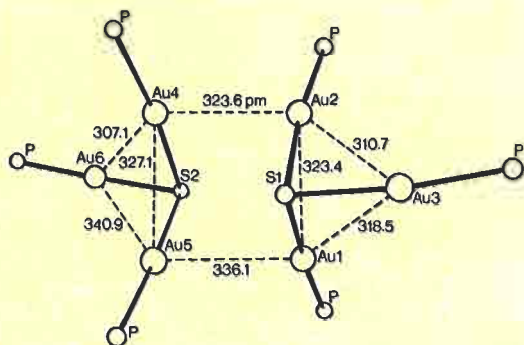
The zigzag chains of AuI (14, 15), the isostructural AuBr (15a) and the isoelectronic $AuSb^{2-}$ and $AuAs^{2-}$ (1a) furnish further examples of close Au...Au contacts between bridged gold atoms; zigzag angles of 67 to 77° are reflected in Au...Au distances of 288 to 308 pm.

Several cyclic complexes show transannular Au...Au contacts. Thus, the mixed Au^I-Au^{III} derivative 'AuCl₂' (49nc) (see Section IX) contains Au₄Cl₄ rings with Au^I...Au^I = 309.5 pm, and the trimer $[(ArN=COEt)Au]_3$ (Ar = p-tolyl) (50) (Figure 18) possesses 9-membered rings with Au...Au = 324.4, 328.8 and 329.9 pm. These latter distances are, perhaps not suprisingly, short for Au atoms constrained by ring geometry; however, the molecules are further linked in pairs (Au...Au = 324.4 pm),

Fig. 17 The Au₆P₆S₂ core of $[(Ph_3PAu)_3S]^+$, showing Au...Au contacts. After (48)
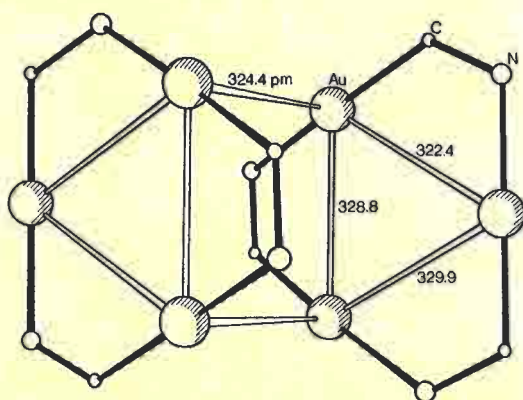
Fig. 18 The two linked 9-membered rings of $[(ArN=COEt)Au]_3$, showing Au...Au contacts. The Au₆ 'chair' is like that in Figure 17. After (50)

Table II
Bond Lengths in AuX₂⁻ Ions

X	Compound	Au-X bond length, pm	Comments	References
Cl	$py_2Au^+AuCl_2^-$	229.3(1.5), 226.0(1.4)	short Au...Au	37a nc, 37b
Cl	$Cs_2Au_2Cl_6$	228.1(.2)	4/mmm*	61
Cl	$Rb_3Au_3Cl_8$	228, 229(3)	short Au...Au	57
Br	$(dtc)_2Au^+AuBr_2^-$	234.9(.5)	at −150°C; $\bar{1}$*,**	62
Br	$Rb_2Au_2Br_6$	240.2(.8)	2/m*	57
I	$Rb_2AgAu_3I_8$	257.0(.9), 254.9(.9)	short Au...Au	58
I	$K_2Au_2I_6$	256.4(.3)	$\bar{1}$*	63
Br	$Cs_2Ag_xAu_{2-x}Br_6$	approx. 240	statistically disordered	63

* Au atom on special position with this symmetry.
** dtc = Bu_2NCS_2.

which implies some weak interaction over this distance. More examples are provided by the 8-membered rings shown in Figure 19 (51, 52, 52a, 53nc, 54nc, 55, 56). In (51) the S-Au-P angle of 173.5° is adduced as evidence for an Au...Au interaction, since the deviation from linearity is such as to bring the atoms closer. Unfortunately, in (53) the distortion (C-Au-C 166, 171°, in two independent molecules) causes the Au atoms to be farther apart than would otherwise be the case, so a generalization is again impossible. Sixfold disorder of Au atoms is described in (54), only four of the possible six S atoms being bridged in each disorder component. A rare example of three-coordinate Au^I (see Section VI) is reported in (55), in which the P-Au-P angle of 155.9° can perhaps better be attributed to the effect of a (rather long) Au-Cl bond than to any appreciable Au...Au interaction. In Au_2BaSnS_4 (56), chains of SnS_4^{4-} tetrahedra are linked by S-Au-S bridges.

The complicated gold phosphides already mentioned (1) display a number of (unclassifiable) short $Au^I...Au^I$ distances (293.2 to 313.6 pm). The metallic conductivity of the compounds has been attributed to these interactions.

Finally, some mixed-valence gold compounds (see Section IX) show short Au...Au distances. Thus, $Rb_3Au_3Cl_8$ (57) contains adjacent $AuCl_2^-$ ions with Au...Au = 323 pm, and $Rb_2AgAu_3I_8$ (58) contains AuI_2^- ions with Au...Au = 303.7 pm. The compound $[DMG_2Au]^+[AuCl_2]^-$ (59) (DMG = dimethylglyoxime; only Au atoms located) contains the only known example of a short Au^I-Au^{III} contact (326 pm).

V. Other Linear Gold(I) Complexes

Halides

An $AuCl_2^-$ derivative was studied in 1954, but only the Au atoms were located (59). The 3,3'-diethylcarbocyanin salt of the same anion has also been investigated with limited accuracy (60); the Au-Cl bond lengths were 229(2) and 231(1) pm. More accurate values for AuX_2^- ions were available, mainly from studies of mixed-valence compounds (see Table II and Section IX).

The appreciable difference in Au-Br bond lengths of the two $AuBr_2^-$ determinations reported in Table II is not easily explained.
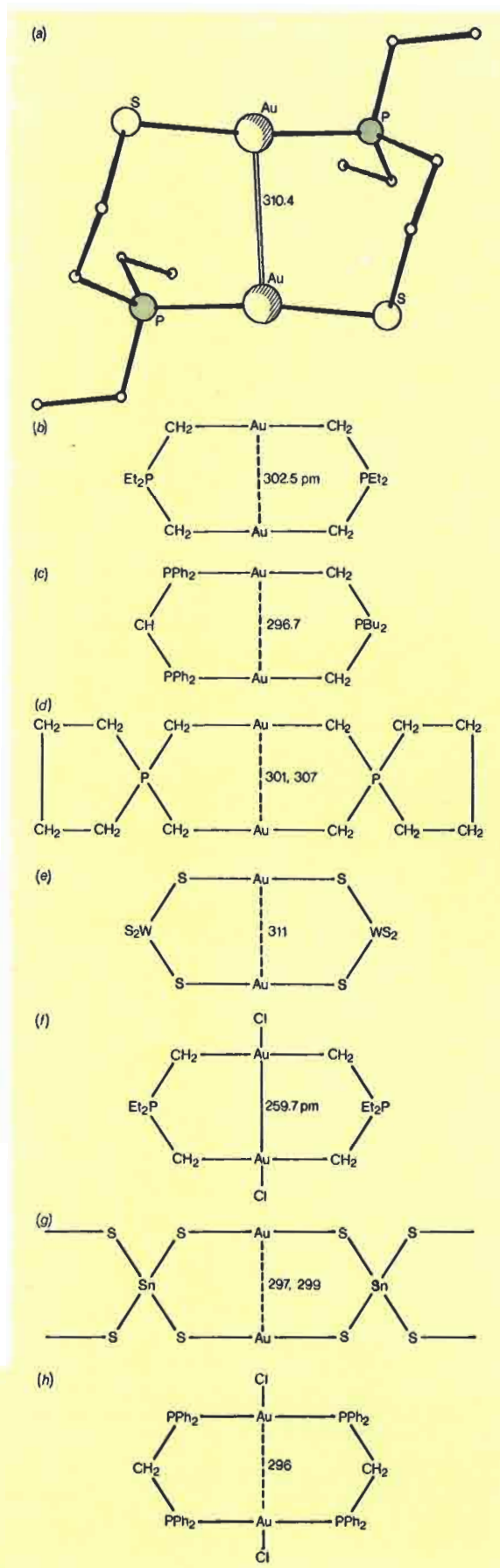

Fig. 19 Some examples of short Au...Au contacts across 8-membered rings.
(a) $[AuSCH_2CH_2PEt_2]_2$. After (51)
(b) to (h), line diagrams (not geometrically accurate) of similar structures established in (52), (52a), (53), (54), (163), (56) and (55) respectively. The compound studied in (163) is formally an Au^{II} derivative. See also Figures 21 and 29

Other halogen complexes (of the form LAuX) will be found under the appropriate L heading.

Oxides

Gold(I) forms very few compounds with Au-O bonds; only one crystallographic investigation has been carried out. Powder diagrams of the oxaurate CsAuO have shown (64) that it possesses an analogous structure to KAgO, and hence contains Au$_4$O$_4^{4-}$ units.

Compounds with Nitrogen Ligands

Being a typical class *b* metal, gold(I) shows a much greater tendency to form complexes with S and P than with O and N ligands. A correspondingly small number of N-donor complexes has been structurally investigated. Although the light atom positions (and hence Au-N bond lengths) are of limited accuracy in the presence of gold, the Au-N bond length seems not very sensitive to the nature of the ligands (Table III). An exception is the bis-hydantoin derivative (65) with short Au-N bonds (194 pm).

As mentioned in the previous Section, 'pyAuCl' has suprisingly been shown (37a nc, 37b) to consist of py$_2$Au$^+$ and AuCl$_2^-$ ions. It is the only LAuCl compound known to possess this structure and is an interesting contrast to (piperidine)AuCl (37).

Organogold(I) Derivatives

Gold(I) forms a variety of compounds containing Au-C bonds. Again, the problem of inaccurate light atom positions is encountered.

In cyanides and related complexes the Au-C bond length is fairly constant at around 200 pm (see Table IV). An exception is Ph$_3$PAuCN (66nc) which also shows some deviations from linearity (Au-C-N,

163(4)° and P-Au-C, 169(2)°). Exact linearity at Au is observed in $K^+[Au(CN)_2]^-$ (67). Its 1:1 addition product with 2,2'-bipyridyl was reported (68), from packing considerations imposed by a very short axis, to contain square-planar coordinated Au^I, a most unexpected geometry. It has now been shown (69) that a false space group had been assigned and that the structure consists of $Au(CN)_2^-$ ions and of bipyridyl coordinated only to K^+. (Methylisocyanide)cyanogold(I), an unexpected product of the reaction between MeI and $[Ph_4As]^+[Au(CN)_2]^-$, consists of linear molecules which pack parallel to each other, the gold atoms lying in two-dimensional layers with Au...Au = 352 to 372 pm (70). The dicyanatogold(I) anion — also called difulminatogold(I) — has been shown, by the linearity of the M-C-N moiety, to possess Au-C rather than Au-O bonds (71). C and O would otherwise be extremely difficult to distinguish using X-ray methods. The Au-spC bond in $C_3H_7NH_2AuC≡CPh$ (35) is rather short (193.5(15) pm).

Several examples of Au^I bonded to sp^2C are known; cis-$[Ph_3PAuCCF_3]_2$ (40nc) is a rare example of σ-bonding between an ethylenic moiety and a transition metal. A similar system, but with C=N bonds, is the trimer $[(ArN=COEt)Au]_3$ (50) (Figure 18). Two perfluorophenyl derivatives have been studied; in $Ph_3PAuC_6F_5$ (72) and $[(C_6F_5)_2Au]^-$ (73) the Au-C bond lengths are not significantly different.

For compounds in which gold is bonded to an sp or sp^2C atom, some $p\pi$-$d\pi$ bonding is theoretically possible. If extensive, this should be reflected in a shortening of the Au-C bond relative to Au-sp^3C (over and above the shortening of about 3 pm caused by change in hybridization of C). There are, however, few such sp^3C structures available for comparison. In the simple alkyl derivative Ph_3PAuMe (74) the Au-C bond length is 212.4(28) pm, in a phosphorus ylid complex (Figure 19b) it is 209, 210(3) pm (52). (An ylid is a sulphur or phosphorus compound with bonds to carbon representable either as X=C or X$^+$-C$^-$.) A further ylid has been studied (Figure 19d) (53nc), but no Au-C bond lengths were given. The mixed Au^I-Au^{III} compound cis-$[(Me_3PAuMe_2)(CF_3)C=C(CF_3)(AuPMe_3)]$ (74a nc) has Au^I-C = 210 pm. From Table IV it can be seen that a shortening of the Au-C bond is observed for potentially $p\pi$-$d\pi$ bonding systems, and therefore that this type of bonding probably occurs to an appreciable extent. This is however in conflict with conclusions from Mössbauer spectroscopy (74b).

Compounds with Sulphur Ligands

Several such complexes have already been mentioned in Section IV; in particular, complexes of bidentate sulphur ligands tend to possess short Au...Au distances. Where the only bonds to gold are from sulphur, their length is remarkably constant at about 228 pm (38, 39, 41, 43, 44); the exceptions occur when the gold atoms are disordered, leading to the wider ranges of 229.2 to 241.4 pm in $[Au_2(WS_4)_2]^{2-}$ (54nc) and 217 to 237 pm in Au_2BaSnS_4 (56). The Au atom in $[(etu)_2Au]^+Cl^-$ (75) (etu = ethylenethiourea) has been shown to be two-coordinate with uncoordinated chloride ion, underlining the tendency of Au^I to two-coordination. The molecule shows typical Au-S bond lengths, but is bent at Au (S-Au-S, 167.2°), probably to accommodate the water molecule which bridges the ligands by hydrogen bonding (Figure 20). The dithiocarbamate (dtc) complex $Ph_3PAu(S_2CNEt_2)$ (76) is also two-coordinate, despite the usually chelating dtc ligand; the Au-S bond length is 233.8 pm. The other S atom is too far from the Au atom to be involved in significant bonding interactions, as is reflected in the C-S distances (168 and 175 pm to the non-coordinated and coordinated S atoms respectively). There is however some deviation from linearity at Au (P-Au-S, 175.7°). It is interesting to compare this compound with the tetrathiosquarate described in Section VI. Au-S bond lengths $trans$ to P are somewhat longer than when $trans$ to S, as seen in the formally RS$^-$ and S^{2-} complexes $[Et_2PCH_2SAu]_2$ (51) and $[(Ph_3PAu)_3S]^+PF_6^-$ (48) (Au-S = 231 and 230.3 to 234.2 pm respectively). Au-S bond lengths $trans$ to Cl, on the other hand, are short; $[ClAuSCH_2Ph]_2$ (36) has Au-S = 226 pm on average. It is perhaps surprising that a wider range of S-Au complexes has not been studied.

Complexes with Phosphorus or Arsenic Ligands

Gold(I) forms a wide range of compounds with tertiary phosphine ligands, and a correspondingly large number of structures has been reported. This leads to the possibility that bond lengths in a series of related compounds could be correlated with assumed trends in electronic structure. Table Va shows bond lengths
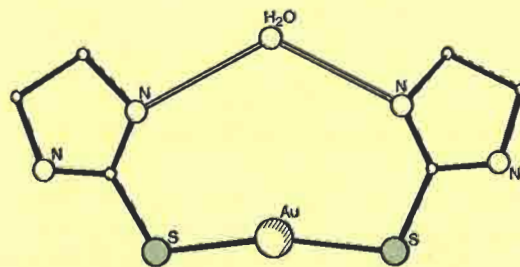

Fig. 20 The bis(ethylenethiourea) gold(I) cation, showing the distortion from linearity and the hydrogen bonding to the water of crystallization (open bonds). After (75)

Table V

(a) Bond Lengths in Some R_3PAuCl Species

Compound	Au-P bond length, pm	Au-Cl bond length, pm	Comments	Reference
Ph_3PAuCl	223.5(.3)	227.9(.3)		78
$(PhO)_3PAuCl$	219.2(.5)	227.3(.5)		77
Cl_3PAuCl	219	229	not refined	34
$[(Ph_3PAu)_2Cl]^+ClO_4$	223.0(.5), 223.9(.4)	232.8(.5), 234.0(.5)	two indep. cations	47

(b) Bond Lengths in Some Ph_3PAuX Species

Compound	Au-P bond length	Comments	Reference
Ph_3PAuCl	223.5(.3)		78
$Ph_3PAu(S_2CNEt_2)$	225.1(.3)	monodentate dtc	76
$[(Ph_3PAu)_3S]^+PF_6^-$	225.7 to 228.4; av. of six, 226.9	two indep. cations	48
Ph_3PAuMe	227.9(.8)		74
Ph_3PAuCN	227(1)		66nc
$[Ph_3PAuCCF_3]_2$	228 (av.)		40nc
$[(Ph_3P)_2Au]^+TCNQ^-$	228.6(.3)		79nc

in some R_3PAuCl species. Where R is an electronegative substituent, the Au-P bond length is shortened. This has been attributed (77) to contraction of the phosphorus lone pair rather than to increased $d\pi$-$d\pi$ back donation. The Au-Cl bond length is markedly affected only when the Cl ligand changes in nature from terminal to bridging.

Further compounds in which the observed trends are as expected are Ph_3PAuX (Table Vb). These compounds seem to conform to Bent's rule, that bonds with the most *s* character (the shortest bonds) are those to the least electronegative element. Thus, short Au-P bonds are observed *trans* to Cl and S. However, the changes observed are rather small. There is virtually no change in Au-P bond length for the series of organogold derivatives.

Complexes of some bidentate phosphine ligands have already been mentioned in Section IV.

The bis(phosphine) complex $[(Ph_2MeP)_2Au]^+PF_6^-$ was the first L_2Au^+ structure to be determined (80) and is exactly linear at Au. A similar compound $[(cy_3P)_2Au]^+SCN^-$ (cy = cyclohexyl) was investigated to ascertain whether the gold was two- or three-coordinate (81); the SCN^- ion is in fact not coordinated to the metal. The Ph_3P analogue has, however, been assigned a three-coordinate structure on the basis of its Mössbauer spectrum (82); steric effects may account for this difference.

The sole arsine complex to have been studied is $Ph_3AsAuBr$ (83); it is isostructural with Ph_3PAuCl, with bond lengths Au-As of 234.2(.5) pm and Au-Br of 237.7(.6) pm.

Fig. 21 Examples of irregular three-coordination of Au^I.
(a) $(Ph_3P)Au(S_2CNEt_2)$, best regarded as two-coordinate. After (76)
(b) $(Ph_3PAu)_2(C_4S_4)$ in which there are two identical Au environments per molecule. After (84)
(c) $[(Ph_3P)Au(bipy)]^+$. After (85)
(d) $(Me_2PhP)_2AuSnCl_3$. After (87)
(e) $[CH_2(PPh_2)_2AuCl]_2$. After (55)
All these are drawn to the same scale
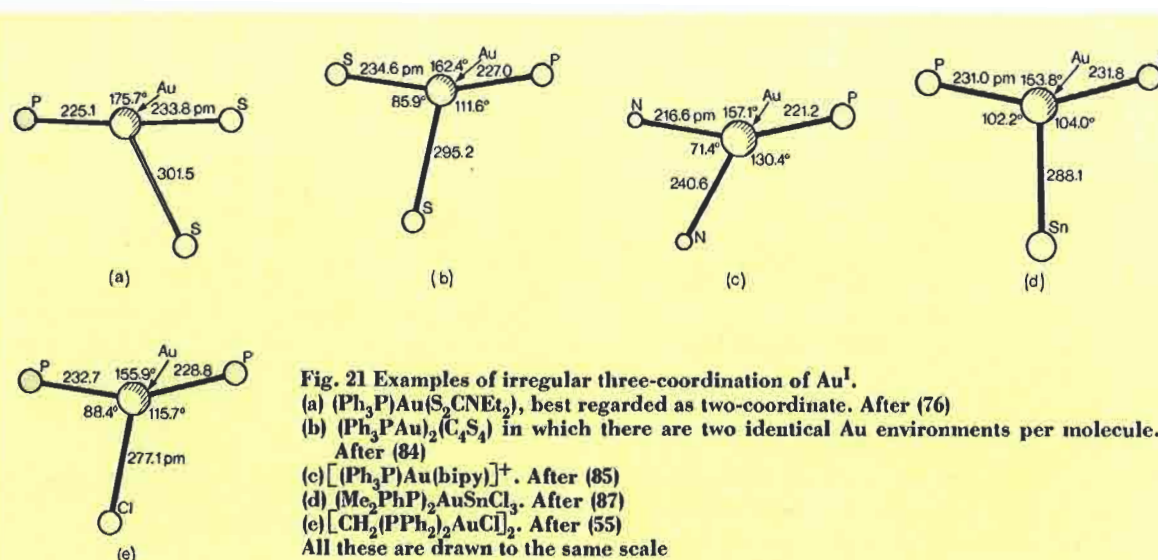
VI. Gold(I) Complexes with Higher

Coordination Number

Gold(I) complexes of the L$_2$AuX type (L = neutral ligand, X = anion which can also act as a ligand), [LAuL']$^+$ (L' = potentially chelating neutral ligand) or LAuX' (X' = potentially chelating anion) could, *a priori*, exhibit three-coordination. It is a tribute to the preponderant tendency to two-coordination that several species of these types fail to achieve the higher coordination number; thus, [(cy$_3$P)$_2$Au]$^+$SCN$^-$ (81) and [etu$_2$Au]$^+$Cl$^-$ (80) both contain non-coordinated anions, while the usually bidentate dtc ligand is monodentate in Ph$_3$PAu(S$_2$CNEt$_2$) (76). Nevertheless, several examples of three-coordination are known. These may be conveniently divided into two categories — distorted and regular three-coordination — for the purpose of discussion.

Distorted Three-Coordination

It is clear that, if a bidentate ligand is sufficiently rigid, the coordination of one donor atom to a metal ion must result in the other donor atom being fairly close to that ion. In the case of gold(I), its tendency to two-coordination often results in bonds of widely differing strength (and length) being formed to the two donor atoms. Suitable criteria as to whether the resulting complex may be reasonably described as three-coordinate are (a) the length of the bond to the more weakly bound donor atom and (b) the deviation from linearity of the other bonds at the gold atom. Thus, the dtc complex (see Section V) has been described as two-coordinate, with an S-Au-P angle of 175.7° and Au-S distances of 233.8 and 301.5 pm. The tetrathiosquarate complex [(Ph$_3$PAu)$_2$(C$_4$S$_4$)](84), on the other hand, shows a somewhat stronger interaction between gold and the farther S atom (Au-S = 236.4 and 295.2 pm) and a greater distortion of the larger S-Au-P angle (162.4°); it may thus be described as three-coordinate. A similar example is [Ph$_3$PAu(bipy)]$^+$PF$_6^-$ (85), with Au-N = 216.6 and 240.3 pm and a P-Au-N angle of 157.1°.

A different type of ligand-imposed geometry is seen in (PP)AuCl (86 nc), where PP is a bidentate phosphine ligand bridging *trans* coordination sites. The P-Au-P geometry is almost linear and the Au-Cl bond is long (281.8 pm).

A compound which achieves distorted three-coordination without the constraints of bidentate ligands is (Me$_2$PhP)$_2$AuSnCl$_3$ (87), with a P-Au-P angle of 153.8° and a rather long Au-Sn bond of 288.1 pm. A similar P-Au-P angle to this is observed in the dimer [(Ph$_2$P)$_2$CH$_2$AuCl]$_2$ (55), where the Au-Cl bond (277.1 pm) is shorter than in (PP)AuCl.

Geometries of distorted three-coordinate complexes are summarized in Figure 21.

Regular Three-Coordination

The dividing line between regular and distorted three-coordination is clearly a subjective one; the rule chosen here is that 'regular' three-coordination involves no angle greater than 135° at Au.

In [(Ph$_2$MePAu)$_2$(WS$_4$)] (88nc) each PAu- moiety is bonded symmetrically to two S atoms. The restricted 'bite' (distance between chelating donor atoms) of the WS$_2$ group inevitably leads to some deviation from ideal geometry at Au; the average S-Au-S and P-Au-S angles are 98 and 131° respectively. It is interesting that the almost equal bite of the tetrathiosquarate ligand leads instead to distorted three-coordination (see above). The Au-S bonds are rather long (average 243 pm), but the Au-P bonds (average 227 pm) are of similar length to those in two-coordinate species.

The compounds (Ph$_3$P)$_2$AuX (X = Cl (89) or I (90)) both show P-Au-P angles somewhat wider than 120° (132 and 131° respectively) and P-Au bond lengths (average 233 and 234 pm respectively) rather longer than in two-coordinate species. The latter is a normal trend with increase in coordination number. In addition, the Cl derivative shows a long (250.0 pm) Au-Cl bond consistent with the principle that the widest angle in trigonal species is opposite the weakest bond. The corresponding Au-I distance is 276.6 pm; no other Au-I bonds are available for comparison.

The most regular three-coordination is, not suprisingly, observed in compounds where all three ligands are identical, such as the ternary compounds Au$_7$P$_{10}$I (1) (trigonal AuP$_3$ moieties with Au-P = 233.9 pm and P-Au-P 118.5°, site symmetry *3m*) and Tl$_6$Au$_2$I$_{10}$ (91) (two AuI$_3$ units with Au-I = 274 and 281 pm — calculation from published coordinates and cell constants give 272, 283 pm — all angles 120°, site symmetries *32* and *6* respectively). The latter structure is however complicated by disorder. The only structures of non-polymeric materials with three identical ligands are those of [(Ph$_3$P)$_3$Au]$^+$ salts. Despite the cations being formally identical, significant differences are observed in structures of the B$_9$H$_{19}$S$^-$ (92) and BPh$_4^-$ (93) salts. The thiadecaborate salt shows less regular geometry, the Au atom lying 30 pm out of the P$_3$ plane.

Figure 22 summarizes the geometries of regular three-coordinate complexes.

Mention should also be made of the tetracyanoethylene complex (Ph$_3$P)$_2$Au(TCNE) (94nc), which may be regarded as three-coordinate, containing two Au-P and one Au-olefin bond; the P-Au-P angle is 133.7°.

Four-Coordinate Complexes

Four-coordinate gold(I) complexes have often been mentioned in the literature, but for many years only

Fig. 22 Examples of regular three-coordination of Au^I.
(a) $(Ph_3P)_2AuCl$. After (89)
(b) $(Ph_3P)_2AuI$. After (90)
(c) $[(Ph_3P)_3Au]^+$. After (92)
(d) $[(Ph_3P)_3Au]^+$. After (93)
(e) two AuI_3 moieties in $Tl_6Au_2I_{10}$. After (91)
All these examples are drawn to the same scale (see Figures 1 and 12 for further examples). The structural principle that the weakest bond is opposite the largest angle, is generally well obeyed in the examples of Figures 21 and 22

one structure was known; that of $L_2Au^+I^-$, where L is the bidentate arsenic ligand o-$C_6H_4(AsR_2)$, R = Et. In this early work, only Au, As and I atoms were located (95). A recent study of the analogous cation $[(diars)_2Au]^+$ (R = Me) (29) confirms its four-coordinate nature. The symmetry is approximately D_{2d} (Figure 23), the bite of the ligand being too small to allow ideal tetrahedral coordination. Further exactly analogous structures have been observed for derivatives of cis-bis(diphenylphosphino)ethylene (96).

Four-coordinate complexes with monodentate ligands have only recently been studied crystallographically (97). The compound $L_4Au^+BPh_4^-$ (L = Ph_3P) has long been known in powder form. Recrystallization leads to a variety of solvates, none of which shows the expected simple tetrahedral geometry. The chloroform solvate contains an $L_3Au...L$ unit, with trigonal planar L_3Au (Au-P = 240 pm average) and a very long Au...L contact (395 pm). The ethanol solvate possesses two alternative,
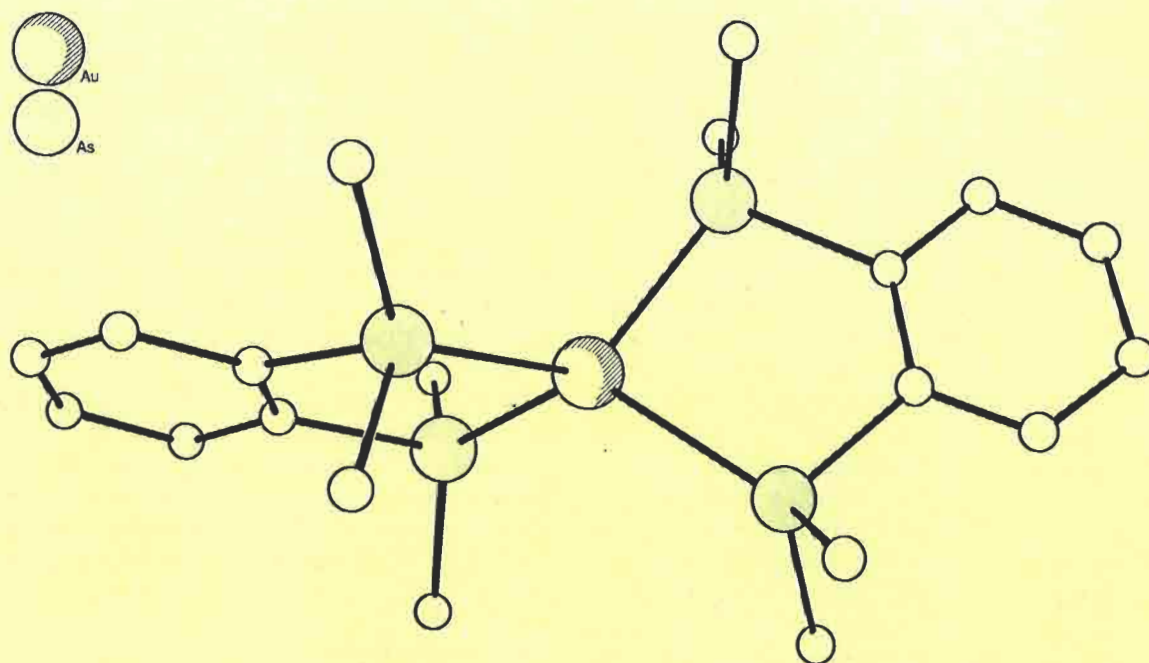

Fig. 23 The $[(diars)_2Au]^+$ cation, an example of four-coordinate Au^I with chelating ligands. After (73)

equally populated Au sites within an L_4 'cage'. One site is tetrahedrally coordinated (site symmetry 2) with very long Au-P bonds (260, 261 pm), the other is trigonal with Au-P = 245 pm on average. Finally, the isomorphous acetonitrile solvate was examined at −150°C in an attempt to 'freeze out' the disorder into one component. The disorder remains, but with a 7:1 ratio of tetrahedral to trigonal sites. The question whether gold(I) can show simple tetrahedral geometry without these disorder components remains unanswered.

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Gold in Bubble Memories

Bubble memories are microelectronic serial-access information devices in which data from a storage film of garnet are carried as microscopic domains of magnetic polarization in a separate drive layer of garnet grown epitaxially on the storage layer. These domains appear as bubble-like discs when viewed with polarized light. A new type of device, which is currently being developed, utilizes gold films in the movement of information bubbles.

Existing information storage devices, in which magnetic bubbles are carried by travelling potential wells in Permalloy chevron-elements, presently offer a storage density of about 1 million bits (Mb) per square centimetre with a possibility of achieving 1.5 Mb/cm². This, however, would strain the capabilities of the photo-lithographic technology used in the manufacture of the devices, due to the very high resolution required to produce parts of the circuit pattern which should have dimensions of a fraction of the bubble diameter — for example, sub-micrometre dimensions in the case of a 1 μm bubble.

A recent article (*IEEE Spectrum*, 1981, **18**, (2), 30-34) by S. Lin and I. L. Saunders, of IBM San Jose Research Laboratory, discusses the possible replacement of the current technology with a new generation of contiguous-element magnetic bubble devices in which the elements are undulating gold deposits. Devices in development at present have a storage density of 4 Mb/cm², and 16 Mb/cm² appears within reach with standard production methods.

In the proposed contiguous-disc bubble circuitry, Permalloy propagation patterns are not involved and the bubbles are moved not under the circuit pattern, but alongside it. Thus, lithographic features greater than the bubble diameter are permitted, yielding possible storage densities of 4 Mb/cm² for 1 μm bubbles and 16 Mb/cm² for 0.5 μm bubbles.

In these contiguous-disc devices, the gold circuit pattern acts primarily as a mask for ion implantation to alter the magnetic characteristics of the surface garnet layer. The gold patterns may also carry the currents that provide the magnetic fields for such functions as bubble generation and switching. The flow of magnetization within the garnet, resulting from an applied magnetic field which is forced into the plane of the drive layer as a result of ion implantation of the structure, bends around the gold discs — more accurately diamonds or triangles — like the flow of a river around islands, forming diverging and converging charged walls which attract the memory bubbles and carry them along as the walls rotate with the in-plane magnetic field. This behaviour was depicted by Lin and Saunders in the diagram shown below.   C.L.