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11. GOLD

W.E. SMITH

CONTENTS

INTRODUCTION

Gold has a varied chemistry, at least equivalent in complexity to that of copper, and yet many fewer studies are reported each year. As a consequence, the unique features of gold chemistry are only partially defined and many opportunities exist for further meaningful study. The problems of most current interest appear to be to understand the nature of the relatively facile redox processes, to define the ability of gold to coordinate with various complexing groups and to establish the major types of complex which can be formed by each gold oxidation state. During 1980, a number of studies have been reported which help to define and, in some cases, clarify these problems.

11.1 GOLD(III)

Gold(III) complexes are usually square planar, although five- and six- coordinate structures are known. However, spectroscopic data can be a very misleading indicator of coordination numbers higher than four. For example, the ligand *N,N*-dimethylethanamide forms a complex of empirical formula L_2AuCl_4 which was believed to be six-coordinate. In fact, the crystal structure reveals that, in the solid state, the 'ligand' is not bound to the gold, but forms a dimeric unit through a bridging proton: the compound should be formulated as $[(dma)_2H]^+[AuCl_4]^-$ [1]. The solution ^1H NMR spectrum has a proton signal at -14 ppm, which had previously been held to

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be indicative of ligand-metal coordination. It now seems more likely that it is assignable to bridge bonding between dma units. There is a related example described in Section 11.2 and, taken together, they suggest that in gold chemistry it would be prudent to exercise even more caution than usual in making predictions of higher coordination numbers from spectroscopic evidence. Continuing the theme of the predominance of four-coordination in gold(III) chemistry, a series of complexes of poly(pyrazolyl)borate has been reported [2]. These might have included a five coordinate structure, but it appears that a structure with one uncoordinated ligand group is more likely. Further, the compound $Au(SO_3F)_3$ is an excellent fluorophosphate ion acceptor forming the four-coordinate ion, $[Au(SO_3F)_4]^-$ readily [3]. This ion produces a range of salts with unusual cations, including $[Br_3]^+$, Br^+, $[BrSO_3F]^+$ and $[ISO_3F]^+$. There is also evidence of a $[Br_5]^+$ salt, but it has a low thermal stability [3].

Many complex halides such as $Cs_2AgAuCl_6$ also contain square planar $[AuCl_4]^-$ ions and it has been found possible, in the latter case, to substitute a considerable amount of the silver(I) with gold(III) to form crystals of formula $Cs_2Ag_{1-x}Au_{1+x/3}Cl_6$ with $0 \leq x \leq 0.64$ [4]. Thermal decomposition of these crystals produces mixed-valence crystals of formula $Cs_2Ag_{1-y}Au^{I}_{y}Au^{III}Cl_6$, with $0.23 < y < 1$. The gold(I) tends to form a {Cl-Au-Cl} unit, whereas the silver(I) does not, indicating a greater degree of covalency for gold(I) [5]. Thermal decomposition of $M[AuX_4]$ (M = K, Rb or NH_4; X = Cl or Br) produced a series of well-defined compounds of formula $M_3Au_3X_8$ in some cases: these are also intervalence compounds containing M^+, $[AuX_4]^-$ and $[AuX_2]^-$ ions [6].

Other examples of planar Au(III)-containing compounds for which crystal structures have been obtained include $[NH_4]AuCl_3$ [6], and a series of compounds of formula $ECl_4.AuCl_3$ (E = S, Se or Te) [7]. These latter compounds are tetragonal [7] rather than monoclinic and may, therefore, be of interest in spectroscopic studies: they dissociate in solution to give $[AuCl_4]^-$ [8]. However, selenium-gold binding is possible in solution and has been studied this year using the ligand 5-chloromethyl-4-selenohexahydropyrimidine-2-thione [9]. Finally, the gold(III) oxide and oxochloride system has been reviewed this year [10]: both compounds are planar and polymeric.

11.2 GOLD(I)

As would be expected, reports on gold(I) chemistry predominantly concern complexes with sulphur, phosphorus and nitrogen ligands. The nature of the bonding in these complexes, however, is not always as predictable. Soft nitrogen ligands are known to coordinate to gold(I) and a 2:1 imidazole complex with AuCl has been reported [11]. However, the crystal structure of the complex potassium dicyanoaurate(I)-

2,2'-bipyridine consists of discrete K^+, $[Au(CN)_2]^-$ and free bipyridine units, with the nitrogen of the bipyridine uncoordinated to the gold atom.[12]. Gold(III)-bipyridine complexes are well established, Is monodentate bipyridine a possibility in gold compounds?

Last year, on the basis of Mössbauer spectroscopy, it was proposed that in the compound $[(PPh_3)_4Au][ClO_4]$ the coordination of the phosphorus round the gold was tetrahedral [12] and, indeed, the absence of any quadrupole splitting in the spectra is quite unusual, suggesting a symmetrical environment. This year, however, three crystal modifications of the related complex $[(PPh_3)_4Au][BPh_4]$ have been submitted to structural analysis [13]. The crystal obtained from chloroform contains an essentially trigonal planar gold compound, with a long fourth phosphorus-gold distance (3.946 Å). The crystal obtained from ethanol has a disordered structure, with about 1:1 occupancy of tetrahedral and trigonal planar sites. The crystal obtained from ethanenitrile, and studied at -150 °C, favoured tetrahedral coordination, suggesting that the tetrahedral geometry may be the more stable of the two.

In the case of sulphur coordination, dithioethanoate produces a tetrameric gold(I) compound of empirical formula $Au(CH_3CSS)$, with bridging dithioethanoate ligands [3]. The gold-gold distance in this complex is 3.01 Å and, as such, it is comparable to that found between peripheral golds in gold cluster compounds [14]. Thus, as well as the common linear and trigonal coordination, many other modes of coordination to gold(I) are becoming apparent and it would appear that many more crystal structures will be required before all the structural types possible can be classified.

Much of the chemistry of gold(I), however. concerns solution studies of the characterisation of polymeric non-crystalline solids. In these cases, other techniques than X-ray structure determination are required, together with more well defined stoicheiometric compounds. An EXAFS study of disodium thiomalato-*S*-gold(I) and thioglucopyranosyl-*S*-gold(I), the compounds in the drugs Myocrysin and Solganol, has appeared [15]. The gold is bound linearly to two sulphur atoms in both cases, in a manner similar to that found in gold(I) thiosulphate, but the simplicity of the data, when contrasted with the above X-ray information, suggests that much remains to be discovered about the nature of gold bonding in compounds of this type. Gold(I) solutions with thiomalic acid (tmH_3) can contain polymeric species and it is, therefore, of interest that stoicheiometric complexes can be isolated, which include $Au(tmH_2)$, $Na_2[Au(tm)]$, $Ca[Au(tm)].2H_2O$ and $Ba[Au(tm)].2H_2O$, together with the mixed ligand complexes, bis(glutathionato)mono(thiomalato)gold(I) and (cysteinato)(thiomalato)digold(I) [16]. Compounds of formula $[AuL_2]X$ (L = thioethanamide of thiobenzamide: X = Cl, Br or I) and Au(L)X (L = dimethylthiomathanamide or dimethylthioethanamide; X = Cl, Br or I) have also been reported [17]. New opportunities for the synthesis of novel gold(I) compounds are provided

when the coordinating ability of phosphorus is altered by the productuon of phosphimide ligands. As well as phosphimide complexes, nitrogen and silicon-containing groups may be added to the ligands by bonding through the oxygen [18].

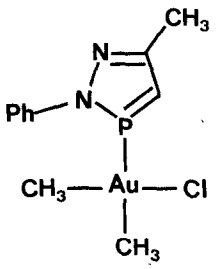
11.3 CLUSTER COMPOUNDS

$\{Au_9\}$ clusters usually consist of a centred *arachno* icosahedron with two vertices on either side containing no gold atoms. A theoretical study of the bonding in such complexes indicates that, on going from $\{Au_8\}$ to $\{Au_9\}$ clusters, the major change is a lowering of the energy of the 6s orbital on the central gold atom of the $\{Au_9\}$ cluster [19]. This is analogous to the known bonding of hydrogen in the centre of cages of other metal ions. In the gold case, both ^{31}P NMR [20] and XPES [21] studies also predict a strong influence of the central gold on peripheral gold and phosphorus atoms, with only weak interactions between peripheral gold atoms. XPES peaks are quite welldefined, both with respect to the 4f and 'valence band' 5d orbitals: they suggest that all gold atoms are best assigned as gold(I) [21]. The range of gold cluster compounds known has also been extended. A series of neutral $\{Au_{11}\}$ clusters of general formula $[Au_{11}L_7X_3]$ (L = P(aryl) ; X = I, SCN or CN) were prepared [22]. They are, again, based on a centred *arachno* icosahedron, but three vertices are not occupied on one side and one on the other side, making a structure of C_s symmetry. The reagent bis(toluene)titanium(0) is effective in producing cluster compounds by reaction with $(PPh_3)AuCl$ or $(PMePh_2)AuCl$ [19]. Compounds of $\{Au_8\}$, $\{Au_{11}\}$, $\{Au_{12}\}$ and $\{Au_{13}\}$ have all been prepared in this way. The $\{Au_{13}\}$ structure, $[Au_{13}(PPh_3)_{12}]^{5+}$, has the correct electronic requirements to form a stabilised centred icosahedron of gold atoms, and this may prove a common type of gold cluster. When the agent $Na[C_{10}H_8]$ was used in place of $[Ti(C_6H_5CH_3)_2]$, the complex $[(PPh_3)_2Au_2]$ was produced. This compound possesses an Au-Au bond and is analogous to $[Hg_2X_2]$ structures, except that the phosphines are at an angle to the Au-Au bond, producing a *trans* compound rather than a linear one [19]. The addition of triphenylphosphine to $[Au_9L_8]^{2+}$ clusters produces $[Au_8L_8]^{2+}$, an intermediate which can be effectively used to produce more $\{Au_{11}\}$ clusters [23].

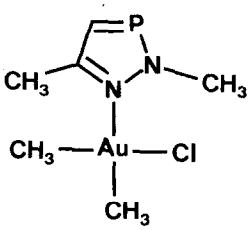
11.4 ORGANOMETALLIC COMPOUNDS

There is now quite an extensive organometallic chemistry of gold which is based on relatively simple organogold groups such as Me_2Au and PhAu and, as such, the chemistry is of as much interest to the inorganic chemist as to the organic chemist. For example, dithiocarbamate and arylxanthate complexes are known to contain partial double bonds between the C-O and C-N part of the ligands. Using the proton NMR signals from the methyl groups, it is possible to determine the energy barrier to

rotation in dimethylgold complexes of these ligands [24]. Complexes of dimethylgold(III) with β-diketonates [25] and arylphosphazoles [11] have been reported. Complexes of these latter ligands with the dimethylgold moiety contain the ligand coordinated to gold either through the phosphorus (1) or nitrogen (2) atoms,with the



(1)

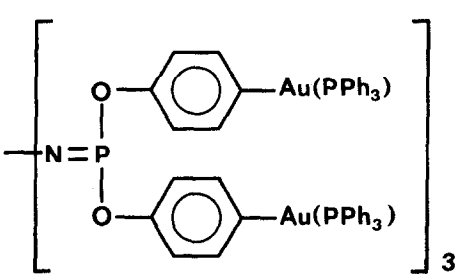


(2)

mode of coordination depending upon the ligand substituents. SO_2 may be inserted into methylgold bonds and, in contrast to main-group metal complexes, retention of the stereochemistry occurs [26].

The range of fluorophenyl complexes of both gold(I) and gold(III) has been extended this year [27-30]. A number of studies have used gold complexes of tetrahydrothiophen (tht), either to substitute or oxidise PhAu(tht) or to substitute (tht)AuCl . There is now a range of neutral gold(III) complexes of the form $Au(C_6H_5)X_2L$ (X = Cl, SCN; L = a group IVB, VB or VIB ligand) [29] ans ionic gold(I) and gold(III) complexes of the form $[AuRX]^-$, $[AuR_2]^-$, $[AuRR']^-$ and $[AuR_2X_2]^-$, $[AuRR'X_2]^-$, $[AuR_3X]^-$ and $[AuR_4]^-$ [27].

There are a number of other points of interest arising from the interaction of the organometallic and inorganic chemistry of gold. Side chains containing gold have been prepared for small-molecule cyclic polyazines [31]. These are analogues for the incorporation of gold into -P=N- polymers and the gold is linked as shown in (3).



(3)

The compound $(\eta^3\text{-}C_3H_5)Fe(CO)_3Au(PPh_3)$ appears to contain a π-intetaction between the gold and the carbonyl groups of the iron carbonyl. The carbonyl groups are in a semi-bridging position such that the Fe-Au distance is 2.519 Å, the Au-C distances are 2.59 and 2.67 Å, and the Au-O distances are 3.25 and 3.24 Å [32]. The authors prefer an explanation of the bonding in terms of a reverse-polarity effect rather than π-bonding. Ferrocene-gold complexes have been reported, with the gold attached to a carbon atom of the ferrocene ring [33,34].

More complex phosphorus-containing compounds that bond predominantly through carbon have been described. Trimethylphosphine converts α,ω-dibromopentane or -hexane into ω-bromoalkyltrimethylphosphonium bromides, which undergo cyclisation on treatment with $Na[NH_2]$ in thf to form phosphoranes such as $[Me_3P(CH_2)_6PMe_3]Br_2$ and the difunctional bis ylid, $CH_2=(CH_3)_2P(CH_2)_6P(CH_3)_2$. These react to form cyclic gold complexes, some of which are polymeric [35]. An arylgold phosphine complex has also been reported [36].

11.5 COMPLEXES IN UNUSUAL OXIDATION STATES

A simple gold(0) compound of ethene has been prepared by matrix isolation [37]. The compound has an intense charge-transfer band in the visible region which arises from a $^2A_1$ ground state: the d orbitals are largely non-bonding in nature. The Raman spectrum of the gold(V) complex $[NO][AuF_6]$ has been recorded. ν_1 and ν_2 bands can be identified but they lie close together, continuing a trend from iridium to gold in which the ν_1,ν_2 separation decreases towards gold [38]. The compound $KrF_2.AuF_5$ is, on the basis of Mössbauer and vibrational spectra, best formulated as $[KrF][AuF_6]$, with octahedral $[AuF_6]^-$ units. However, AuF_5 is polymeric, with bridging fluorides. [39].

11.6 REDOX PROCESSES AND OXIDATION STATE DETERMINATION

The relationship between the redox properties of gold and sulphur is quite complex, Thiols such as cysteine {capable, in the presence of oxygen, of oxidising gold(0) to gold(I)} and penicillamine can stabilise a gold(III) complex [40,41]. This year, the reduction of gold(III) to gold(0) by disulphides such as cystine and dipenicillamine [42] and a kinetic study of the reduction of gold(III) to gold(I) with thioethers have been reported [43]. The reaction in the latter case takes place in two stages. In the first step, a substitution reaction occurs which is fast compared to the reduction process and which is affected by steric facters (bulky ligands producing a slower reaction). In the second stage, the reduction process is accelerated by electronic rather than steric factors, such as increasing substitution on the gold and increasing basicity of the thioether. It is probably

an associative process, with the initial attack occurring on the bonded halide rather than gold, producing a chlorinated thioether which will react further and is not detected. The resulting lone pair of electrons on the gold leads to further rearrangement and the formation of gold(I). The problem condidered is one of long-standing, and the postulate that attack occurs at the halide rather than the metal may be a key factor in understanding these reactions. It remains to be seen whether further studies will substantiate this reaction sequence.

Two techniques are usually employed to differentiate between gold(III) and gold(I), namely, Mössbauer spectroscopy and XPES. Both techniques have been used in papers already discussed to estimate gold oxidation state but Mössbauer spectroscopy remains the preferred technique, since the combination of isomer shift and quadrupole splitting gives a reasonably unequivocal assignment of oxidation state. To date, however, efforts to relate this information to the nature of the bonding in the complexes examined have been less efficient. One reason for this failure has been that the radial terms required to calculate quadrupole splittings have been wrongly estimated: new values have become available this year [44].

The major disadvantages of Mössbauer spectroscopy lie in its cost, availability, the extreme sampling conditions used, and the time that can elapse between the preparation and analysis of compounds which may have a limited lifetime. Thus, a number of papers have appeared recently which attempt to develop XPES as an alternative method of oxidation-state determination, and as a probe of bonding [21,45,46]. The major difficulties with this technique are the effect of surface charging (with the consequence that considerable attention has to be paid to calibration) and decomposition of the sample in the beam. This latter problem also occurs in Mössbauer spectroscopy, but the removal of any need for liquid helium cooling means that XPES decompositions can more readily be studied over a longer period of time. This year, the decomposition of gold(III) dithiocarbamates [45] and tetraethylammoniumhalogold(III) salts [46] have been reported. In both cases the products are gold(I) compounds and the gold(III) and gold(I) signals are clearly identifiable, as they were in a study of cluster compounds discussed in Section 11.3 [21]. However, the effect of a change in ligand from sulphur to phosphorus, for example, causes a comparable shift in energy to that between gold(I) to gold(III) [45,46]. Consequently, where series of related complexes have been compared, the conclusion appears to be that, with care, oxidation states can be assigned among compounds with related ligands. XPES has the advantage that it also gives information on other atoms from the ligands and can be used to study peaks in the valence band region in favourable cases [21].

11.7 DISSOLUTION AND EXTRACTION OF GOLD

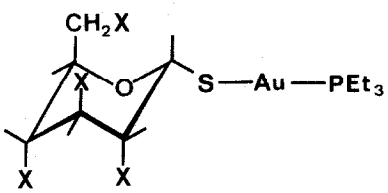
The anodic dissolution of gold, particularly in cyanide solution, has been

extensively studied [47-50]. There are three current peaks corresponding to the periods of maximum dissolution of gold in sweeps from -0.9 to +0.3 V, and they are all one-electron processes producing gold(I). However, the details of the reactions are not yet clearly understood and may, in some cases, involve dioxygen.

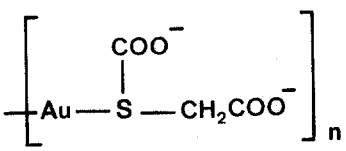
The extraction of gold remains of importance and this year it is reported that ketosulphides locate more electrons at sulphur than do sulphides and, hence, a more efficient extraction of gold(III) is obtained with them [51]. A more efficient extraction can also be obtained if anions are added to thiourea solutions in nitrobenzene [52].

11.8 MEDICAL APPLICATIONS OF GOLD

Finally, during 1980, the use of gold drugs in the treatment of rheumatoid arthritis has been reviewed, both from a chemical [14,15] and a pharmacological [53] standpoint. The clinical use of gold has, if anything, increased recently and this may well be given a further boost shortly, since the new drug Auranofin (4) is now



(4; X = O_2CMe)



(5)

under clinical trial in many centres in Europe. It is administered orally, whereas the standard compound Myocrisin (5) is given by intramuscular injection. Chemically, these compounds are quite different-(4) is a monomer, soluble in ethanol and insoluble in water, whereas (5) is a water soluble polymer which is insoluble in ethanol [53]. *In vivo*, sulphur ligands would be expected to substitute into both complexes, with the gold-sulphur bond of (4) being substituted before the gold-phosphorus bond and the likelihood is that complete substitution of the thiomalic acid in (5) may take some time. One major storage form of gold seems to be insoluble gold(I)-sulphur compounds and, to date, no extensive gold(0) deposits have been unequivocally established, although discolouration of the skin has been reported. The mechanism of action is still unknown, but the new drug has provided an opportunity to study the differences in *in vivo* actions between them. Neither the biochemical approach (which suggests that stabilisation of lysosomal membranes by gold produces the beneficial effect) nor a chemical one (which sought to find a specific, effective gold carrier) have, as yet, indicated any common action between the two compounds.

However, the differences in *in vivo* behaviour have made quite clear a point which is self evident to the chemist, namely, that different gold compounds must be treated as different chemicals and not simply regarded, as they usually are in medical literature, as 'gold'.

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