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8. GOLD

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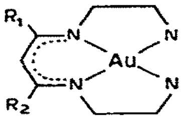
INTRODUCTION

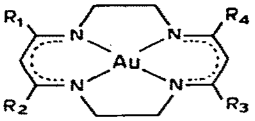
By comparison with other related transition elements, the chemistry of gold has, until recently, been rather neglected. Part of the reason for this is probably the complexity of the chemistry and problems associated with the identification of the valence and geometry of gold compounds. However, with modern techniques, the picture is changing and last year there were a number of developments.

8.1 GOLD(III)

Amines coordinated to gold(III) are potentially nucleophilic, with pK_a's ranging from 6.5 to 2.2. β-diketones react with $[Au(en)_2]Cl_3$ to give the complex (1), which converts within a few hours to (2), a gold(III) macrocyclic complex. The ease of oxidation is decreased as R becomes more bulky [1]. This is a relatively facile route to the synthesis of this macrocycle and, since the gold can be replaced by Zn(II), it may be used as a route to the synthesis of other transition-metal complexes of the ligand by metal ion replacement reactions. Azo groups are often postulated as complexing agents, but they are not usually particularly strong and normally form complexes as part of chelates or macrocycles. However, in the crystal structure of [(4,4′-azotolu-



(1)



(2)

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ene)$AuCl_3$], coordination is by a single gold—nitrogen bond; the geometry about the gold is the normal square—planar arrangement [2].

The formation of deep-red species which are often transient and which can be difficult to isolate is a standard feature of the reactions of gold(III) with sulphur-containing ligands. Therefore, the structure of the deep-red compound produced by the reaction of chloroauric acid with thianthrene (L) is of some interest. It is an approximately planar $AuCl_3L$ structure, with the thianthrene bonded through one sulphur [3]. Also this year, there have been a number of studies of related complexes of gold(III). These include the preparation of complexes of dialkyldithiocarbamategold(III) cations, with TCNQ radicals, which are semiconductors [4], CD studies of gold(III)—nucleic acid complexes [5], the preparations of complexes of hydrazone derivatives in which the bonding is thought to be through the keto and azomethine groups [6], and reports of square—planar complexes of dithiols containing the quinoxaline ring [7], a polymeric *pseudo*-crown ether complex of $[AuCl_4]^-$ [8], and a series of dithiocarbamatotriphenylphosphinegold(III) complexes [9].

The system HSO_3F—$Au(SO_3F)_3$ has been used to prepare a range of complexes of the type $M[Au(SO_3F)_4]$ (M = NO, ClO_2, Li and Cs) [10]. The gold system is not very strongly acidic but has a noted lack of oxidising power and, hence, allows oxidisable cations to be stabilised and studied. A solid-state proton NMR study of $HAuCl_4 \cdot 4\,H_2O$ suggests that the proton exists in dynamic equilibrium in an $H_3O^+ \cdot H_2O$ entity [11].

From a kinetic study, the substitution with Br^- of $[Au(NH_3)_4]^{3+}$ goes through a *trans*-intermediate, $[Au(NH_3)_2(Br)_2]^+$, which was isolated [12]. Other kinetic studies include the substitution of azide in a gold(III) complex [13], a study of the rate of disproportionation of gold(I) to gold(III) and gold(0) [14], and the reduction of tetrachloroaurate(III) by thiourea [15]. In other physical measurements, the NQR spectra of tetrachloroaurate(III) and tetrabromoaurate(III) have consistent average values of M—X, but the splittings are compound-dependent [16], whereas the electronic spectra of a range of $LAuX_3$ compounds (where L is a nitrogen donor) suggest that band intensity can be a more sensitive indicator of substitution differences than transition energy [17]. X-ray structure determinations of Au_2O_3 [18] and AuOCl [19] indicate a square—planar arrangement around the gold, and there is evidence of a *trans* influence in the bond lengths. There is an 18-membered ring containing gold in the latter structure.

8.2 GOLD(I)

In the chemistry of gold(I), the tendency for phosphorus ligands to produce compounds with higher coordination than the more usual linear arrangement has been further characterised. The compounds $[Au(PPh_3)_n]$-$[ClO_4]$ (n = 2, 3 or 4) have Mössbauer spectra which are consistent with linear, trigonal or tetrahedral geometries. There are large differences in isomer shift and, with $n = 4$, there is no quadrupole splitting, indicating a symmetric (tetrahedral) environment [20]. The addition of triethylphosphine to dichloromethane solution of $[Au(PEt_3)_2][PF_6]$ or $[Au(PEt_3)Cl]$ produced gold ions of the type $[Au(PEt_3)_n]^+$ (where $n = 3$ or 4), with no evidence of free PEt_3 unless it was present in more than a four-fold excess. The mixed complexes $[Au(PEt_3)_n\{P(OEt)_3\}_{4-n}]^+$ were also characterised [21]. The coordination number in gold(I)—phosphine complexes has been shown to depend on both steric and electronic factors. $P(C_6H_{11})_3$ gave a maximum coordination of $[AuL_2]^+$, whereas PBu_3 gave $[AuL_3]^+$, and the softer ligands PMe_2Ph and $PMePh_2$ gave $[AuL_4]^+$ compounds. There was extensive exchange, in the latter cases at the higher coordination numbers, between the complexes and free ligand, and this was studied by ^{31}P NMR spectroscopy [22].

There were many indications that much remains to be clarified before the nature of gold(I)—phosphorus coordination is properly understood. A 1 : 1 mixture of $[Au(PPh_3)Cl]$ and $[Au(PPh_3)X]$ ($X = ClO_4$ or PF_6) produced the single-bridged complex $[(PPh_3)AuClAu(PPh_3)]X$ [23]. The already extensive series of gold clusters was further extended by the preparation of $[Au_9L_8X_3]$ ($L = PPh_3$) and, in solution, by the formation of the ions $[Au_{11}L_8X_2]^+$ and $[Au_9L_{10}]^{3+}$ ($L = PPh_3$) [24]. Gold can also be used to stabilise the usually rather unstable phosphinic anhydrides; completion of the reaction leads to formation of a trimer $[Au(Me_3C)_2P{=}O]_3$, with linear P—Au—O bonds [25]. Complexes of organophosphine halides [26] and of new phosphines with other functional groups (CN and CO_2Et) [27] were reported and the structure of the known compound $[AuSCH_2CH_2PEt_2]_2$ was shown to contain a ten-membered ring with linear P—Au—S bonds [28].

By contrast, there has been little incisive work this year on the structure of gold(I)—sulphur systems. However, an increase in understanding of the coordination of gold(I) to other complexing groups has occurred. Sodium bis(*N*-methylhydantoinato)gold(I) tetrahydrate is the first example of a stable gold(I) species coordinated to two soft nitrogen ligands; the coordination is linear [29]. A range of pyrazolato (pzl) complexes in which the ion can act in a monodentate or bidentate (bridging) fashion have been reported; $[Au_3(pzl)_3]$ has a triangular ring arrangement, with each gold bonded to two nitrogens. Addition of iodine leads to the complex $[Au_3(pzl)_3I_2]$ with the iodine bonded to a single gold atom to give a mixed-valence compound [30]. A range of methyl isocyanide complexes [31] and a triphenylphosphine pentaborane complex [32] have also been characterised.

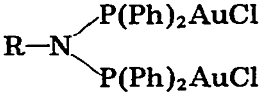
One organometallic study of inorganic interest is the reaction of a dimethylgold(III) moiety with amino acids (L) to form compounds of general formula $[(CH_3)_2AuL]$. Amino acids with H, CH_3 or $CH(CH_3)_2$ side chains coordinate to the gold as chelates through the amino and carboxylato groups. A similar complex bonded through sulphur and oxygen is obtained with cystine, but with histidine, polymeric imidazole bonding is suggested at certain pH's [33].

8.3 UNUSUAL AND MIXED VALENCE STATES

The ease of oxidation and reduction of gold and the determination of the oxidation state of the complexes are recurrent themes in gold research. A number of unusual oxidation states and intermediates have been suggested. The crystal structure of Au_2P_3 reveals that it is a polyphosphide and the gold is probably best described as gold(I), not gold(III) [34]. The Raman spectrum of a mixture of $[NO][AuF_6]$ with excess fluorine and NOF is consistent with the formation of an Au^{IV} entity, $[NO]_2[AuF_6]$ [35] and in the XPES spectra of the entities AuBr and AuCs, the $4f_{7/2}$ level is at a lower energy than that in gold metal, suggesting a -1 oxidation state for the gold [36]. $Cs_2[Au_2Cl_6]$ [37] and $K_2[Au_2I_6]$ [38] both contain linked chains of —Au—X—Au— with alternate gold(I) and gold(III) sites. The gold(I) sites are compressed octahedral (linear) and the gold(III) elongated octahedra (planar). The chloride structure was studied at high pressure where a cubic arrangement was formed, posing a problem with regard to the gold oxidation state. $Tl_6Au_2I_{10}$ consists of Tl_6I_6 units with the gold held in channels between them. One form of the gold is linear and complexed not only to I^- but to $[I_3]^-$ — a result which may have significance in explaining some of the well-known non-stoicheiometric gold—iodide complexes [39].

2,3-dimercaptopropanol forms a range of polymeric complexes with gold, some of which contain both gold(I) and gold(III) [40] and the reaction of AuRL (R = Me, L = PMe_3 or PMe_2Ph) with hexafluorobut-2-ene also gave mixed-valence-state complexes [41].

Some unusual intermediates have also been suggested. The reaction of bis-(diphenylphosphino)amine with $H[AuCl_4]$ or [ClAu(CO)] produces a gold(I) compound (**3**), which appears to cyclise. Oxidation produces a compound (**4**) which, from its Mössbauer spectrum, contains one gold species, presumably $[Au_2]^{4+}$. Further oxidation produces (**5**) [42].



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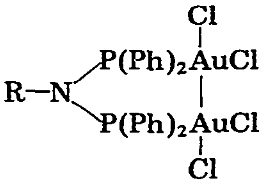

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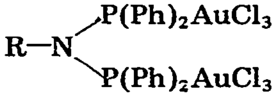

(**5**)

A stopped-flow investigation, at -50° C, of the oxidation of bis(μ-dibutyldithiocarbamate-*SS'*)digold(I) by I_2, IBr or Br_2 to form $[Au^{III}(S_2CNBu_2)_2][Au^IX_2]$ indicated that the decomposition of an intermediate $[Au(S_2CNBu_2)_2]X_2$ was the rate-determining step [43].

8.4 APPLICATIONS

Gold continues to be a subject of considerable interest in the applied sciences, with a number of papers appearing in the areas of catalysis, electroplating, and solid-state devices. In catalysis, some of the more fundamental studies indicate that ion implantation of gold in inorganic substrates such as SiO_2 produces gold entities closer to gas-phase atoms than to gold metal [44], and AuGe entities have been identified above the surface of a gold—germanium alloy [45]. One notable development was the publication of a supplement to the Journal of Rheumatology [46] concerning the new gold drug auranofin, which is suggested for use in rheumatoid arthritis. This is an oral drug for which chemical trials to date appear promising. It contains a phosphorus—gold—sulphur entity. Its biochemical and pharmacological profile is significantly different from the more standard drug myocrisin, which is given intramuscularly. It is interesting that, in spite of toxicity problems, myocrisin sales continue to increase — an indication that gold therapy is still a valued therapeutic approach. A review of the chemical aspects of gold therapy has appeared [47].

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