The Structure of the Bis(triphenylphosphine)gold(I) Complex in Pyridine Solution

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The structure of the bis(triphenylphosphine)gold(I) complex in pyridine solution has been determined by means of the large angle X-ray scattering (LAXS) technique. The Au–P bond distances are 2.325(8) Å and the six shortest (three per triphenyl-phosphine) Au–C distances are 3.44(3) Å. These values agree with those found for the unsolvated linear bis(triphenylphosphine)gold(I) complex in solid compounds. No pyridine molecules are coordinated to gold(I) in its inner coordination sphere, and the complex most probably remains linear even in such a strongly solvating solvent as pyridine. This result is compared with those previously found for di-halogenocuprate(I) and mercury(II) halide complexes in solution.

In pyridine solutions containing no strongly coordinating ligands, gold(I) is solvated by four pyridine molecules, most probably in a tetrahedral fashion.[1] In the solid state, however, only two pyridines are coordinated.[2,3] Two stable complexes are formed consecutively with triphenylphosphine and tricyclohexylphosphine, and at least up to a free ligand concentration of 0.1 M no further ligands are coordinated.[4] The complexes are heavily enthalpy-stabilized, indicating the formation of strong Au–P bonds. The entropy changes are, on the other hand, unfavourable, as might be expected for ligands of this type, where the conformation entropies are large; this applies especially to the more bulky tricyclohexylphosphine. Although trialkyl- and tri-phenylphosphine complexes of gold(I) seem to be two-coordinated in pyridine solution, not only two- but also three- and four-coordinated gold(I) phosphine complexes exist in the solid state.[5] As expected, the two- and three-coordinated complexes have linear and trigonally planar structures, respectively. On the other hand, the four-coordinated complexes are never regularly tetrahedral. Even if the Au–P bond distances do not vary much, which they sometimes do,[6] the bond angles deviate considerably from tetrahedral symmetry.[7,8]

Both the 7,7,8,8-tetracyanoquindimethanide (TCNQ) and hexafluorophosphate salts of the linear bis(triphenyl-phosphine)gold(I) cation have been determined structurally.[5] For both compounds, much the same Au–P bond distance was found, viz. 2.286 and 2.312 Å, respectively.[5] The Au–P bond distances in linear bis(trialkylphosphine)-gold(I) complexes are found to be in the same range as in the bis(triphenylphosphine)gold(I) complexes, 2.306–2.325

Å.[9–11] This is somewhat unexpected, as the aliphatic phosphines should give stronger bonds, as is in fact indicated by their more exothermic complex formation reactions in solution.[4]

An important aim of the present study has been to determine whether the bis(triphenylphosphine)gold(I) complex formed in pyridine solution has the same structure as that formed in the solid state, or if a solvation takes place in the inner coordination sphere of gold(I). For the other d^{10} acceptors, both types of behaviour have been found. The dihalogenocuprate(I) complexes are not solvated in the inner coordination sphere of copper,[12] while the mercury (II) halide complexes are,[13–15] as will be discussed below. Consequently, the dihalogenocuprates(I) stay linear in solution, while the mercury(II) halides turn pseudotetrahedral, to an extent depending upon the solvating ability of the solvent.

Experimental

Preparation of solution. A solution of gold(I) perchlorate in pyridine was prepared as described elsewhere.[1] An excess of triphenylphosphine was then added to this solution, resulting in a dark-brown solution. The final composition of the solution studied is given in Table 1.

The measurements should be performed without delay as redox reactions tend to occur on prolonged standing. Thus, after about a year at room temperature, beautiful crystals had grown from the solution. These turned out to be the chloro(triphenylphosphine)gold(I) complex, $(C_6H_5)_3PAuCl$, with the structural parameters being identical with those previously found for this compound.[16] In the long term, chloride is evidently formed from the perchlorate ions by partial oxidation of the phosphine, at least in the presence of gold(I).

Table 1. Composition (in mol dm⁻³) and linear absorption coefficient, μ(MoKα) (in cm⁻¹) of the investigated solution.

Au	P(C₆H₅)₃	ClO₄⁻	Pyridine	μ
0.380	0.775	0.380	12.00	9.72

X-Ray scattering experiments. X-Ray scattering from a free surface of solution was measured in a large angle Θ–Θ diffractometer[17] of the Seifert GDS type at 25 ± 1 °C. The solution was enclosed in a cylindrical thin-walled glass container in order to avoid evaporation. The glass container was exactly half-filled, so that both in- and outgoing X-ray beams passed perpendicular to the glass walls at all angles. The absorption of the glass container and its angle dependence had been determined previously.[15] MoKα radiation (λ = 0.7107 Å) was used as an X-ray source. The scattered intensities were measured at discrete points in the region 4 < Θ < 65°, separated by 0.0335 in s, where $s = 4\pi \sin \Theta$ λ^{-1}, and the scattering angle is 2Θ. An extrapolation of the intensity data at Θ < 4° was necessary owing to the upward meniscus in the glass container. A statistical error of 0.35 % was achieved by measuring 4×10^4 counts twice at each sampling point. The fraction of incoherent scattering contributing to the intensity was estimated in the usual manner.[19]

Treatment of scattering data. The same data reduction and correction procedures as described before were applied.[18] The experimental intensities were normalized to a stoichiometric unit of volume containing one gold atom. The scattering factors, corrections for anomalous dispersion and values for incoherent scattering were the same as used before.[18] Correction for multiple scattering was performed. Spurious peaks below 1.4 Å in the experimental radial distribution function, which could not be related to interatomic distances within the pyridine molecule, the phenyl rings in the triphenylphosphine molecule or the
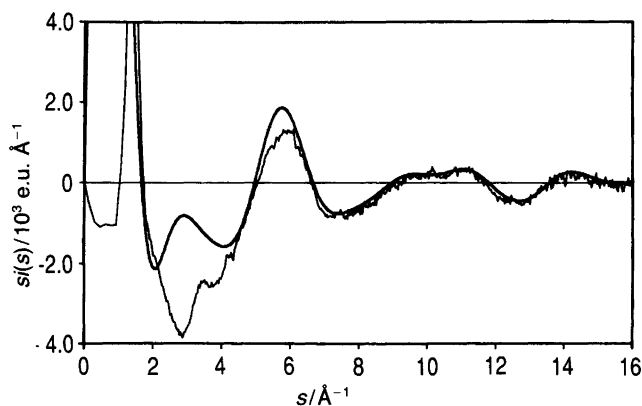

Fig. 1. Experimental (thin line) and calculated (thick line) reduced intensity curves $i(s)$ multiplied by s for the studied solution.
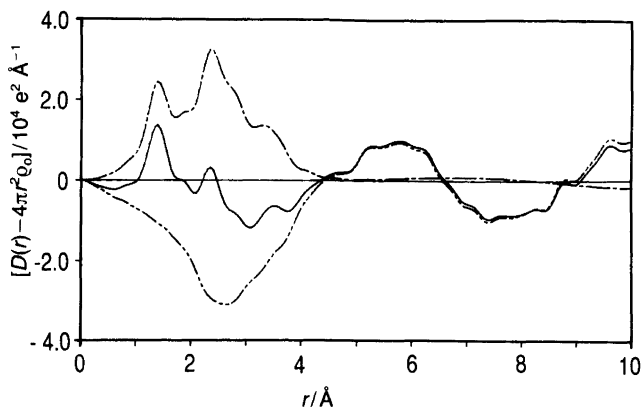

Fig. 2. The radial distribution function and the calculated peak shapes for the bis(triphenylphosphine)gold(I) complex in pyridine solution. Experimental function (solid line), theoretical function (single dashed line) and their difference (double dashed line) are given.

perchlorate ion, have been removed by a Fourier transformation procedure.[17] The reduced intensity function, $i(s)$, multiplied by the scattering variable s is shown in Fig. 1. The corresponding experimental radial distribution function, RDF, $D(r)-4\pi r^2 \varrho_0$, was obtained by a Fourier transformation of the reduced intensity function (Fig. 2). All calculations were carried out by means of the KURVLR[19] and STEPLR[20] programs.

Results and discussion

The radial distribution, $D(r)-4\pi r^2 \varrho_0$, shows peaks at 1.4, 2.4 and 3.4 Å (Fig. 2). The peak at 1.4 Å is due to the C–C and N–C bond distances within the pyridine molecules, to the C–C bonds in the phenyl groups of the triphenylphosphine and to the Cl–O bond distances within the perchlorate ion. The peak at 2.4 Å corresponds to the Au–P bond distance in the bis(triphenylphosphine)gold(I) complex; it also holds contributions from the intramolecular C–C and C–N distances in the pyridine and triphenylphosphine molecules, and from the O–O distances in the perchlorate ions. The peak at 3.4 Å in the RDF is assigned to the shortest Au–C distance in the bis(triphenylphosphine)gold(I) complex. The Au–P and Au–C distances have been refined to 2.325(8) and 3.44(3) Å, respectively. The Au–P bond distance is thus close to the values 2.286 and 2.312 Å found for the unsolvated bis(triphenylphosphine)gold(I) complex present in the solids quoted above.[5] A solvation in the inner coordination sphere would mean an increase of the coordination number and hence a marked lengthening of the Au–P bond distance; this is not the case. This conclusion is strengthened by the fact that no Au–N interaction can be discerned in the RDF function. If present, Au–N bond distances would be expected[1] in the range 2.2–2.3 Å, i.e. they would contribute to the peak at 2.4 Å. If the known intensities of the C–C, C–N and O–O interactions are subtracted, however, the remaining intensity corre-

Table 2. Interatomic distances, *d* (in Å), temperature factor coefficients, *b* (in Å²), and frequency of distances relative one gold atom, *n*. The refined parameters are those with e.s.d.s in parentheses.

Distance	*d*	*b*	*n*
Au–P	2.325(15)	0.004	2.0
Au–C	3.44(3)	0.009(3)	6.0

sponds very well to the expected number of two Au–P interactions. Furthermore, the six shortest Au–C distances in the solids are, on average,[21] 3.42 Å, in close agreement with the value found for the complex in solution. The intensity of the peak at 3.4 Å also corresponds to the expected six Au–C interactions. As the ligand does not contain any heavy scatterer, the angle P–Au–P of the complex in solution cannot be determined. The lack of solvation must imply, however, that the complex stays linear. Evidently, the bis(triphenylphosphine)gold(I) has virtually the same structure in pyridine solution as in the solid state. The parameters determined in solution are listed in Table 2.

The bis(triphenylphosphine)gold(I) complex thus behaves analogously to the manner found for dihalogenocuprate(I) in pyridine, and also in dimethyl sulfoxide and acetonitrile;[12] i.e. no solvent molecules enter the inner coordination sphere of the metal ion. This is in marked contrast to the behaviour of the mercury(II) halides which are easily distorted in solution.[13–15] In pyridine, the angles X–Hg–X are in fact in the range 142–145°. Simultaneously, the Hg–X bonds become weaker, and hence longer. In the solids they are 2.28, 2.41 and 2.62 Å, for chloride,[22] bromide[23] and iodide (yellow),[24] respectively; in pyridine solution[15] they are 2.38, 2.50 and 2.67 Å. Evidently, the preference for linear two-coordination is much more marked for the two-coordinated and charged complexes of the monovalent d^{10} states copper(I) and gold(I) than it is for neutral complexes of the divalent d^{10} state mercury(II).

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