The Structural Chemistry of Gold(I) Quinoline-2-thiolate and Iodide Complexes of Polytertiary Phosphines

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Gold(I) Complexes, Thiolate Complexes, Aurophilicity, Hydrogen Bonding, Polytertiary Phosphine Complexes

The treatment of (chloro)gold(I) complexes of di- and tetra-tertiary phosphines with equivalent quantities of sodium quinoline-2-thiolate in methanol/dichloromethane affords the corresponding (phosphine)gold(I) quinoline-2-thiolates in high yields. The di- and tetranuclear complexes, respectively, of \( \alpha,\alpha'-\text{bis(diphenylphosphino)-propane} \) (1), -butane (2) and -pentane (3) and of tris(2-diphenylphosphino-ethyl)phosphine (4) have been obtained as crystalline solids, and the structures of 2 and 4 have been determined by single crystal X-ray diffraction studies. Unexpectedly, the molecules of 2 are loosely aggregated into strings via weak intermolecular gold-gold interactions, not via Au-Au interactions. Compound 4 is a monomeric tetranuclear cluster in the solid state with two intramolecular gold-gold bonds. Bis(2-diphenylphosphino-ethyl)phenylphosphine (PPP) forms trinuclear complexes with gold(I) chloride, bromide and iodide (5a-c). The iodide complex features a chain structure through intermolecular Au-Au contacts between the two terminal P-Au-I units. The closest contacts between the chains are determined by Au-I and I-I interactions of the central P-Au-I unit.

Introduction

The design of functional materials with interesting photo-physical properties is currently an important and challenging research topic [1]. Our approach to this end is to take advantage of aurophilic interactions of two-coordinate gold(I) compounds in the solid state. Materials based on units connected via Au-Au contacts are known to be, i. a., strongly photo-luminescent [2].

Aurophilic interactions [3] represent a new type of bonding for the construction of supramolecular aggregates [3e]. The individual bonding is generally comparable to a standard hydrogen bond regarding both the geometrical flexibility and the distance (2.5 - 3.5 Å) as well as the energy of the interaction (6 - 12 kcal/mole) [4]. As soon as the relevance of aurophilicity was recognized, the phenomenon has been the subject of extensive experimental studies and theoretical calculations [5 - 11]. Recent quantum-chemical calculations including relativistic and correlation effects have indicated that the bond energy is a function of the nature of the substituents at the gold atom, and that thiolate and iodide ligands are predicted to yield optimum bond strength [12].

This conclusion has not been fully supported by subsequent experimental investigations, where Au-S interactions were found to be competing favourably with Au-Au interactions [13]. The evaluation of a specific structure is generally not straightforward since weak forces such as those arising from aurophilicity are easily overruled by steric crowding in the aggregates and by complicated packing features of the individual crystal.

In the present investigation of the structural chemistry of some new compounds of the type L-Au-X we employed an aryl thiolate as the anionic ligand L and di-, tri- and tetra-tertiary phosphines as the neutral ligands L. Di-, tri- and tetrafunctional phosphines were chosen because previous work on the corresponding (halo)gold(I) complexes has already shown that this pattern is favouring multidimensional structures [14]. The thiolate anions were expected to shed new light on the relative importance of various facets of secondary bonding at gold(I) centers. The quinoline heterocycle may offer extra stabilization to a lattice through stacking.
of dipolar arenes. Bis(2-diphenylphosphino-ethyl)phenylphosphine (PPP) was introduced as a ligand for Au(I), because these components offer various opportunities for intra- and intermolecular Au⋯Au and/or Au⋯I and I⋯I contacts giving rise to an efficient supramolecular assembly and crystal packing.

Quinoline-2-thiolate has previously been introduced into a gold(I) complex of bis(diphenylphosphino)methane (dppm) to give a pentanuclear cluster \([\text{Au}_5(dppm)_2(QNS)_3]^{2+}\) [15], and into a hexanuclear copper(I) cluster \([\text{Cu}_6(QNS)_6]\) [16]. Both compounds show intriguing structural and spectroscopic properties which also prompted the present investigation.

**Preparation and Properties of the Complexes**

The title quinoline-2-thiolate complexes have been prepared by treating the (phosphine)gold(I) chlorides, which are known compounds, with equivalent quantities of sodium quinoline-2-thiolate generated \textit{in situ} from the thiol and sodium methoxide in methanol/dichloromethane (Scheme 1). The products were isolated as air-stable, pale yellow solids by crystallization from \(\text{CH}_2\text{Cl}_2/\text{MeOH}\) in yields between 73 and 82%. The complex 5a was generated from the ligand (PPP) and three equivalents of (dimethylsulfide)gold(I) chloride. The trinuclear (PPP)gold(I) bromides and iodides were obtained from the chloro complex employing aqueous solutions of KBr and KI, respectively. All products were identified by their NMR and mass spectra as well as by elemental analysis (Experimental Section). Single crystals of 2 and 4 were obtained from diethylether/dimethylformamide and dichloromethane/\(n\)-hexane, respectively.

\[
\begin{align*}
[\text{PP}(\text{AuCl})_2] + 2 \text{NaQNS} & \rightarrow [\text{PP}(\text{Au}(\text{QNS}))_2] + 2 \text{NaCl} \\
& \text{(PP = dppp); } 2 \quad (\text{dppb}); 3 \quad (\text{dpppn})
\end{align*}
\]

\[
\begin{align*}
[\text{PP}_3(\text{AuCl})_4] + 4 \text{NaQNS} & \rightarrow [\text{PP}_3(\text{Au}(\text{QNS}))_4] + 4 \text{NaCl} \\
& \text{PPP + 3 (Me}_2\text{S)AuCl} \rightarrow [\text{PPP}(\text{AuCl})_3] + 2 \text{Me}_2\text{S}
\end{align*}
\]

Scheme 1.

**Structural Studies**

Crystals of \([1,4\text{-bis(diphenylphosphino)butane}]\text{-digold(I) bis(quinoline-2-thiolate)} (2) (from diethyl ether/dimethylformamide), are monoclinic, space group \(P2_1/c\), with 2 formula units in the unit cell. The structure of the individual molecules obeys the symmetry of a center of inversion located in the middle of the central bond of the unfolded, extended butane chain (C2-C2', Fig. 1). The conformation and bond lengths and angles of the Au(dppb)Au unit are as expected and fall in the ranges established for this phosphine in other gold(I) complexes. The quinoline-2-thiolate anions are S-bonded to the metal atoms with angles P-Au-S = 175.38(4) and Au-S-C131 = 103.2(3)°. There is no structural indication of any donor interaction of the pyridine nitrogen atoms and the gold atoms in the same or a neighbouring molecule.

The molecules are aggregated into meandering strings through an intimate approach of the terminal Au-S groups to form \(\text{Au}_2\text{S}_2\) parallelograms with edges Au-S = 2.2979(14) and Au⋯S 3.634 Å and with a transannular Au⋯Au contact of 3.907 Å (Fig. 2). It is clear from this geometry that the Au⋯S contact represents the dominating secondary interaction. There is precedent for this type of aggregation from recent studies in this laboratory and elsewhere [13].

It thus appears that the aggregation of P-Au-S units is following this pattern more often than not.
against expectations based on theoretical calculations which favour Au...Au bonding. It should be noted that only a minor slippage of the two P-Au-S units against each other is required to allow for Au...S instead of Au-Au interactions. This slippage is probably associated with a very shallow energy profile which moreover is easily affected by other contributions, e.g. from packing forces.

Diagrams of the unit cell show that there are several realms with significant arene (phenyl and quinoline) stacking which are expected to contribute to the organization of the molecules in the unit cell. A minor loss of lattice energy through P-Au-S slippage (above) may therefore be easily compensated by this stacking or related effects.

Crystals of [tris(2-diphenylphosphino-ethyl)phosphine]trigold tri(quinoline-2-thiolate) (4) are orthorhombic, space group Pna21, with 4 molecules in the unit cell. The lattice contains isolated molecules, with no sub-van-der-Waals contacts to neighbouring complexes (Fig. 3). A gold thiolate unit is attached to each phosphorus center solely via its sulfur atom. The resulting four quasi-linear P-Au-S units are arranged in two pairs with short intramolecular Au...Au contacts: Au1-Au2 3.058(2), Au3-Au4 3.430(2) Å. The dihedral angles S-Au...Au-S are close to orthogonal indicating a “sword-crossing” of the respective units which has been observed previously in related compounds [13].

In the lattice, there is a disorder of quinoline rings which makes the positioning of these substituents only tentative. This affects the overall quality of the structure determination, but the relevant ordering of the core of the molecules is not in doubt. This core structure is different from that of the corresponding tetranuclear AuCl complex of the same ligand, [ClAuP(CH2CH2PPh2AuCl)3] [14b], where intermolecular Au...Au contacts are preferred over intramolecular interactions of the same type. This difference probably arises from the shielding of molecule 4 by the bulky quinoline groups which prevent intimate intermolecular contacts.

Crystals of [bis(2-diphenylphosphino-ethyl)phenylphosphine]trigold triiodide (5c) (from CH2Cl2 / Et2O) are orthorhombic, space group Abn21, with 4
molecules in the unit cell. The symmetry of the individual molecules obeys a mirror plane through the central phosphorus atom (P1), its AuI unit (AuIII) and the ipso carbon atom of its phenyl group (C111) (Fig. 4). The ligand has a standard geometry and conformation, and the geometrical parameters of the three P-Au-I groups follow the usual pattern \([\text{Au1-P1 2.258(5)}, \text{Au2-P2 2.253(3)}, \text{Au1-I1 2.561(2)}, \text{Au2-I2 2.5742(9) Å}; \text{P1-Au1-I1 176.01(12)}, \text{P2-Au2-I2 170.83(7)°}]\).

In the lattice, the molecules are linked to each other via short Au...Au contacts \([\text{Au2...Au2'} 3.052(1) Å]\) between terminal P2-Au2-I2 units to give strings along the y axis (Fig. 5). Clearly, these triatomic units are crossed like swords [dihedral angle \(\text{II-Au1...Au2-I2 70.6°}\)] and bent very significantly [deviation from linearity \(\text{ca. 9.2°}\)] in order to allow a close approach.

The central triatomic unit P1-Au1-I1 is not engaged in aurophilic bonding. Its closest contacts are between iodine and gold atoms and between iodine and iodine atoms of neighbouring chains \([\text{Au1...I2' 4.269, I1...I2' 4.716 Å}]\) with distances close to or even beyond the sum of the van der Waals radii. In the lattice this leads to layers populated only by the heavy gold and iodine atoms and separated by the tritertiary phosphine ligands (Fig. 6).

**Conclusions**

The results of the present study have shown that aurophilicity is a dependable intra- and/or inter-molecular bonding principle which gives rise to specific alignments of subunits of molecules (4) or of molecules in a lattice (5c) whenever the mutual approach of the components is not impeded by steric effects. A sword-crossing pattern is typical for the interacting triatomic units (P-Au-X).

Soft anionic ligands \((I^-, SR^-)\) may be advantageous for aurophilic interactions as recently predicted by quantum-chemical calculations \([12]\), but such ligands may also lead to structural variations: With sulfur ligands in particular, Au...S interactions are able to overrule Au...Au interactions and lead to multi-center side-on contacts instead (2). This arrangement appears to be associated with similar bond energies as compared to standard two-center aurophilic bonding.

**Experimental Part**

General: The experiments were carried out routinely under an atmosphere of dry and pure nitrogen. Glassware and solvents were dried and filled/saturated with nitrogen. NMR: Jeol GX 400 spectrometer; deuterated solvents with the usual standards. MS: Varian MAT 311A instrument (FAB, p-nitrobenzyl alcohol). Quinoline-2-thiol (HQNS) and bis(2-diphenylphosphino-ethyl)phenylphosphine (PPP) are commercially available. \([\text{PP(AuCl)}_2]; \text{PP} = \text{bis(diphenylphosphino)propane, dppp; bis(diphenylphosphino)butane, dppb; bis(diphenylphosphino)pentane, dpppn]}\) and \([\text{PP} (\text{AuCl})_3]\)
[PP₃ = tris(2-diphenylphosphinoethyl)phosphine] were prepared following the literature procedures [14].

\[PP(Au(QNS))₂\] (1 - 3)

The reaction of NaQNS [92 mg (0.5 mmol), obtained from HQNS (81 mg, 0.5 mmol) and NaOMe (30 mg, 0.55 mmol) in MeOH (25 ml)] with [PP(AuCl)] (0.25 mmol) in CH₂Cl₂/MeOH (1:1, 50 ml) at r.t. for 4 h gave pale-yellow solutions. The solutions were concentrated in a vacuum to give pale-yellow crystalline solids which were recrystallized by slow evaporation of CH₂Cl₂/MeOH solutions. The resulting solids of [PP(Au(QNS))₂] (PP = dppp 1; dppb 2; dpppn 3) were obtained in 78, 82, and 73% yield, respectively. Single crystals of 2 were grown from an Et₂O/DMF solution.

\[\text{1: M. p. } 141 \degree \text{C (decomp.)}, \text{MS (FAB): } [\text{dppp-Au(QNS)}]_2, \text{m/e } = 994, 100\%; [\text{dppb-Au(QNS)}]_2, \text{m/e } = 966, 74\%. \{^1 \text{H}\} 31\text{P NMR (CDCl}_3, 20 \degree \text{C}) : \delta 32.18 [s], \text{H} \text{NMR (CDCl}_3, 20 \degree \text{C}) : \delta 1.99 [m, 2H, -CH₂-], 2.92 [dd, (J PH ) = 9.5 Hz, 7(HH) = 7.0 Hz, 4H, -PCH₂-], 7.19 - 7.69 [m, 32H, QNS + PPh₂].

\[\text{2: M. p. } 165 \degree \text{C (decomp.)}, \text{MS (FAB): } [\text{dppb-Au(QNS)}]_2, \text{m/e } = 980, 100\%. \{^1 \text{H}\} 31\text{P NMR (CDCl}_3, 20 \degree \text{C}) : \delta 35.55 [s], \text{H NMR (CDCl}_3, 20 \degree \text{C}) : \delta 1.90 [br, 4H, -CH₂-], 2.44 [br, 4H, -PCH₂-], 7.41 - 7.73 [m, 32H, QNS + PPh₂].

\[\text{3: M. p. } 141 \degree \text{C (decomp.)}, \text{MS (FAB): } [\text{dppp-Au(QNS)}]_2, \text{m/e } = 1193.7, 8.5\%; [\text{dppb-Au(QNS)}]_2, \text{m/e } = 961.9, 6.5\%. \{^1 \text{H}\} 31\text{P NMR (CDMSO-d₆, 20 \degree \text{C}) : } \delta 31.3 [d, J(PP)=51.8 Hz, 1P, -PPh], 33.8 [t, 2P, -PPh₂]. \text{H NMR (CDMSO-d₆, 20 \degree \text{C}) : } \delta 2.42 [m, 8H, C₆H₄], 7.47 - 7.80 [m, 25H, Ph].

\[\text{AuC}_{76}\text{H}_{68}\text{N}_{24}\text{P}_{3}\text{S}_4\]

Calcd C 44.59 H 3.14 N 2.67 Au 37.54%, Found C 44.45 H 3.31 N 2.45 Au 37.27%.

\[PP(AuCl)] (5a)

The reaction of a suspension of (Me₂S)AuCl (330 mg, 0.57 mmol) in dichloromethane (10 ml) with [PPP] (500 mg, 1.7 mmol) at r.t. for 1 h gave a colourless solution. The solution was concentrated in a vacuum and gave a colourless solid after addition of hexane (30 ml). The product (620 mg, 88%) is only soluble in dimethylsulfoxide and dimethylformamide. M. p. 204 °C (decomp.). MS (Cl): [PPP(AuCl)]_₂, m/e = 1193.7, 8.5%; [PPP(AuBr)]_₂, m/e = 1285.8, 2.1%. \{^1 \text{H}\} 31\text{P NMR (CDMSO-d₆, 20 \degree \text{C}) : } \delta 32.3 [t, J(PP)=48.1 Hz, 1P, -PPh], 34.7 [t, 2P, -PPh₂]. \text{H NMR (CDMSO-d₆, 20 \degree \text{C}) : } \delta 2.42 [m, 8H, C₆H₄], 7.42 - 7.80 [m, 25H, Ph].

\[PPP(AuBr₃)] (5b)

Compound 5a (250 mg, 0.2 mmol) was suspended in dichloromethane (20 ml) and the mixture layered with an aqueous solution of KBr (710 mg, 6 mmol; 20 ml). The solid components rapidly dissolved upon vigorous stirring. The organic phase was separated and dried over MgSO₄. The product 5b was precipitated by addition of pentane and filtered off. The colourless solid (200 mg, 73%) is soluble in dimethylsulfoxide and dichloromethane. M. p. 196 °C (decomp.). MS (Cl): [PPP(AuBr₃)]_₂, m/e = 1257.5, 100%; [PPP(AuBr)]_₃, m/e = 1053.9, 21%. \{^1 \text{H}\} 31\text{P NMR (CDCl}_3, 20 \degree \text{C}) : \delta 31.57 [q, J(PP) = 92.0 Hz, 1P, P(-CH₃)]].

\[PPP(AuI)] (5c)

The iodide 5c was obtained similarly from 5a (700 mg, 0.56 mmol) and KI (2.79 g, 16.8 mmol) in CH₂Cl₂/H₂O [20/25]. The product was precipitated from the dried organic layer by addition of diethyl ether as a colourless solid (580 mg, 69%). M. p. 174 °C (decomp.). MS (Cl): [PPP(AuI)]_₂, m/e = 1377.5, 100%; [PPP(Au)]_₃, m/e = 1053.9, 42%. \{^1 \text{H}\} 31\text{P NMR (CDCl}_3, 20 \degree \text{C}) : \delta 2.47 [m, 6H, PCH₂-], 2.98 [m, 6H, -CH₂PPh₂], 7.24 - 7.73 [m, 54H, QNS + PPh₂].
Table I. Experimental data for 2, 4, and 5c.

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\[a\] \(R = \Sigma (lF_{o}-lF_{c})/\Sigma lF_{o}; \quad [b\] \(wR2 = \{[\Sigma w(F_{o}^2 - F_{c}^2)^2]/\Sigma [w(F_{o}^2)]\}^{1/2}; \quad w = 1/\{\sigma^2(F_{o}^2)+ (ap)^2 + bp\}; \quad p = (F_{o}^2 + 2 F_{c}^2)/3; \quad a = 0.0443 (2), 0.1642 (4), 0.0672 (5c); b = 2.38 (2), 0.00 (4), 50.97 (5c);\]

\(\delta\) 34.9 [t, 1P, (PP)=48.6 Hz, -PPh], 35.8 [d, 2P, -PPh_2].

\(^1H\) NMR (CDCl_3, 20 °C): \(\delta\) 2.39 [m, 8H, C_2H_4], 7.44 - 7.72 [m, 25H, Ph].

Au_3C_{44}H_{33}I_3P_3

Calcd C 26.42 H 2.22 1 23.93%,

Found C 26.71 H 1.79 1 24.07%.  

Crystal Structure Determinations

Specimens of suitable quality and size of compounds 2, 4, and 5c were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo Kα radiation, \(\lambda\)(Mo-Kα) = 0.71073 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Lp correction was applied and intensity data of 2 and 5c were corrected for absorption effects (Psi-scans). The structures were solved by direct methods (SHELXS-86) and completed by full-matrix-least squares techniques against \(F^2\) (SHELXL-93). The thermal motion of all non-hydrogen atoms of compound 2 was treated anisotropically. The phenyl group at P1 in compound 5c was slightly disordered around the mirror plane and was refined with isotropic thermal parameters. The Au, P, and S atoms of 4 were refined with anisotropic thermal parameters. However, the structure of 4 suffers from heavy disorder of all phenyl rings and of the quinoline ligands. These atoms were included as rigid groups with fixed coordinates and isotropic contributions into the refinement. All hydrogen atoms were placed in idealized calculated positions. Further information on
crystal data, data collection and structure refinement are summarized in Table I. Important interatomic distances and angles are shown in the corresponding Figure Captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. The data are available on request on quoting CCDC No. 118472 (2) and 118473 (5c).

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