

Studies on Metal Ion Coordination in Solution

V. The Complex Formation of Diphenylphosphinobenzene-*m*-sulphonate with Gold(I)

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The complex formation between diphenylphosphinobenzene-*m*-sulphonate and the di-thiocyanatogold(I) complex in aqueous thiocyanate solutions was studied potentiometrically with a gold electrode. The data gave evidence for the formation of a tri-phosphine complex after a relatively large range of existence for the mono-phosphine complex. The stability constants in 0.1 M NaSCN at 25°C were determined to have the following values

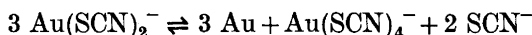
$$\beta_1 = 10^{7.5}, \beta_2 = 10^{12.4}, \beta_3 = 10^{16.5}$$

The value of the standard electrode potential of the aqua gold(I), gold couple is discussed, and evidence given for this potential having a value close to +2.12 V. With the knowledge of this potential, stability constants referring to the aqua-gold(I) ions are estimated (see Table 4).

The most suitable method to obtain the stability constants of strong Class (b) metal phosphine complexes is based on measurements of the free metal ion concentration with an electrode of the metal. This method can be applied to most of the Class (b) metals, and is especially convenient to use when the solutions in equilibrium with the metal contain the metal ions in one valence state only as in case of the studies made of the complex formation of diphenylphosphinobenzene-*m*-sulphonate with silver,¹ cadmium,² and bismuth.³ However, the method is more complicated to use when the solutions contain analytical concentrations of the metal ions in more than one valence state. Such difficulties were encountered in the studies of the phosphine complex formation of mercury(II)⁴ and copper(I).⁵ Studies with gold complexes as performed in this paper have the further complication that solutions containing aqua ions of gold cannot be prepared. In the copper(I) phosphine system the influence of copper(II) ions was overcome by referring the stability constants to the copper(I) chloride system in 1 M LiCl instead of to the aqua

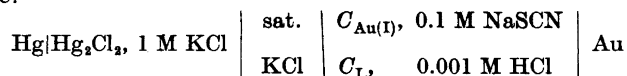
ions. For metallic gold in equilibrium with the chlorogold complexes a high chloride concentration is not sufficient to stabilize gold(I) towards disproportionation to gold(III) and metallic gold.⁶ However, this is obtainable in thiocyanate solution.

Because of the insolubility of some of the gold(I) phosphine species in 1 M thiocyanate, the medium was limited to 0.1 M NaSCN, and in one series of measurements also 0.1 M NaSCN + 0.9 M LiCl was used. For this thiocyanate concentration according to the equilibrium constant, $K = 33$ for the reaction⁷



the percentage of the trivalent species does not exceed 0.3 for solutions where $[\text{Au(SCN)}_2^-] \leq 10^{-3}$ M.

Gold electrode potentials are not very well defined,^{6,7} but it was hoped that reproducible potentials could be obtained by stirring the solutions with gold powder to establish complete equilibrium in the system. Cells of the following type:



were measured for selected concentrations of Au(SCN)_2^- , $C_{\text{Au(I)}} \leq 10^{-3}$ M, and varying concentrations of the phosphine ligand (C_L) in order to obtain measurements of

$$E_M = \frac{RT}{F} \ln X$$

E_M is defined^{4,8} as the potential difference between the complex solution in question and a ligand-free solution with the same total metal concentration. In case of a mononuclear complex system the following relationship is valid:

$$X = \sum_0^N \beta_n [\text{L}]^n$$

where β_n is the cumulative stability constant for the complex ML_n and $[\text{L}]$ the free ligand concentration.

EXPERIMENTAL

Solutions and materials. The complex gold solutions were made from KAu(SCN)_4 and $m\text{-(C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{SO}_3\text{Na}$, $2\text{H}_2\text{O}$. These solids were weighed into measuring flasks, and the other chemicals pipetted from stock solutions. Redistilled water was used. The gold salt was prepared according to the method of Bjerrum and Kirschner,⁷ purified by recrystallization from ethanol and dried *in vacuo*. (Found: Au 55.34; C 6.9; N 7.9; S 17.9. Calc. for KAu(SCN)_4 (352.3): Au 55.9; C 6.8; N 7.95; S 18.2). The ligand $m\text{-(C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{SO}_3\text{Na}$, $2\text{H}_2\text{O}$ has been described previously.^{1,4,5} The gold powder used to equilibrate the solutions was prepared by reduction of KAuCl_4 with $\text{Na}_2\text{S}_2\text{O}_5$. All other reagents were of Analytical Reagent quality and were used without further purification.

Electrodes. The gold electrodes were prepared by plating gold onto platinum plates (4×4 mm) from a KAu(CN)_2 solution with a current density of 2 mA cm^{-2} . Two gold electrodes were used for each measurement. Before use the electrodes were cleaned in concentrated nitric acid to which had been added one drop of concentrated hydrochloric

acid and washed thoroughly with water. The electrode vessels (with a volume of about 50 ml) were equipped with an inlet and outlet for nitrogen as well as a syphon type bridge with a stopcock. Traces of oxygen were removed from the nitrogen by passing the gas through a Meyer-Ronge apparatus. A 1 M KCl-calomel electrode was used as reference electrode. It was prepared in the usual way in an electrode vessel of the Lewis, Brighton, and Sebastian type.⁹ The emf measurements, carried out with a Cambridge Vernier potentiometer and a Kipp spot galvanometer, were made in a water thermostat at 25.0°C.

Potential adjustment. The solutions to be measured were shaken with freshly prepared gold powder. In the experiments on 0.1 M NaSCN performed by Hawkins, the solutions were shaken overnight in a nitrogen atmosphere before they were placed in the electrode vessel. In the experiments in 0.1 M NaSCN + 0.9 LiCl made by Mønsted, the shaking with gold powder was made directly in the electrode vessel by means of magnetic stirring. The potential adjustments were slow. But after hours to days reproducible potentials to within a few millivolts could be obtained. Nernst's law was found to be fulfilled for solutions without added phosphine ligand as seen from Fig. 1.

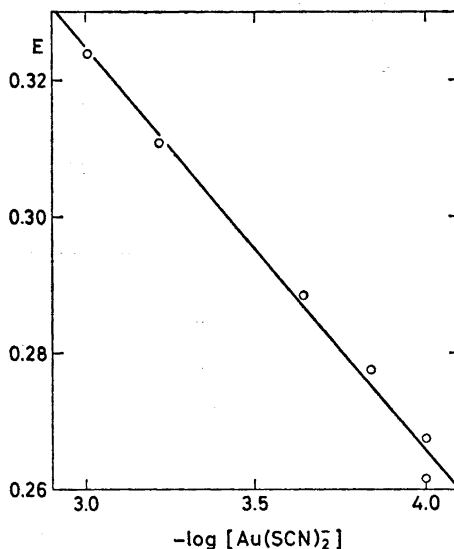


Fig. 1. Experimental test of Nernst's law for the AuX_2^- -Au half-cell. Solutions of $\text{KAu}(\text{SCN})_2$ in 0.1 M NaSCN. The line has the theoretical slope, 0.0591 for 25°C.

In solutions with added phosphine ligand, the higher the phosphine concentration the more sluggish was the potential adjustment. In the beginning the potential drops and after a shorter or longer time comes to a standstill, and then shows a tendency to increase again. The lowest potential was taken as the equilibrium potential, and the tendency of the potential to increase again is probably due to a slow oxidation of the ligand to the phosphine oxide.^{3,4}

It is not likely that the slow irreversible decomposition of the free dicyanogen in equilibrium with the small concentration of $\text{Au}(\text{SCN})_4^-$ present in the solution⁷ is connected with the drift of the potential, and it can also be mentioned that some preliminary measurements carried out with AuBr_2^- -phosphine solutions showed still more sluggishness in the potential adjustment than that found for the thiocyanate system.

For the solution marked with an asterisk in Table 1, the potentials in mV of the two gold electrodes towards the calomel electrode were as follows: after 1 day -32, -43, 2 days -58, -63, 3 days -63, -63, 5 days -61, -59, and after 6 days -57, -58. In accordance with this the potential was chosen as -63 mV. When this value is subtracted from the potential found for the phosphine-free solution with the same gold concentration +335 mV, one gets the value for E_M given in the table.

Table 1. Measurements of E_M , the potential relative to ligandfree half-cells with the same gold(I) concentration. The series $E_M(1)$ were measured by Hawkins in 0.1 M NaSCN, and the series $E_M(2)$ by Mønsted in 0.1 M NaSCN + 0.9 M LiCl. Gold(I) and the phosphine ligand concentrations are given in mM and the potentials in mV.

$C_{Au(I)}=0.20$		$C_{Au(I)}=0.50$		$C_{Au(I)}=0.50$		$C_{Au(I)}=1.00$	
C_L	$E_M(1)$	C_L	$E_M(1)$	C_L	$E_M(2)$	C_L	$E_M(1)$
0.101	8	0.352	25.5	0.246	16	0.757	29
0.152	30	0.426	43	0.493	102	1.010	71.5
0.196	93	0.460	75	0.742	155	1.249	135
0.307	154	0.510	101	1.075	225	1.504	167
0.398	179	0.611	131	1.300	265	2.008	197
0.511	267	0.792	163	1.452	295	2.291	230
0.600	336	0.974	201	1.549	309	2.498	279
0.794	366	1.099	245	1.568	327	2.772	332
1.004	378	1.105	218	*1.815	398	2.991	365
		1.211	266	2.072	412	3.502	379
		1.299	293				
		1.488	355				
		1.751	372				
		2.004	383				

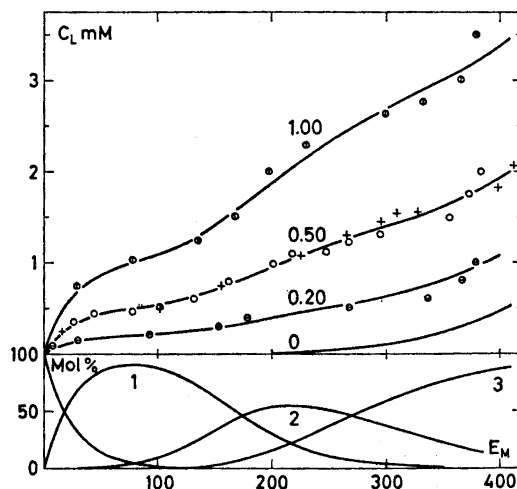


Fig. 2. Upper part. Curves for the total phosphine concentration C_L versus E_M . Hawkins' data in 0.1 M NaSCN are plotted as \odot points for the series with $C_{Au(I)}=1.00$ mM, as \circ points for the series with $C_{Au(I)}=0.50$ mM, and as \ominus points for the series with $C_{Au(I)}=0.20$ mM. Mønsted's data in 0.1 M NaSCN + 0.9 M LiCl for the series with $C_{Au(I)}=0.50$ mM are plotted as $+$ points. The full-drawn curves including the curve for $C_{Au(I)}=0$ ($C_L=[L]$) are calculated with the stability constants given in Table 2.

Lower part. Graphic representation of the mole percentages of the complexes with one, two, and three moles of phosphine ligands per gold atom in 0.1 M NaSCN as function of E_M (calculated with the stability constants given in Table 2).

RESULTS AND DISCUSSION

The experimental material is given in Table 1, and in Fig. 2 (upper part) the total phosphine concentration C_L is plotted against the measured values for E_M . The results of a preliminary treatment of the data (in 0.1 M NaSCN) using the Fronæus' graphical method⁸ of corresponding solutions and integration for determining \bar{n} and $[L]$, are given in Ref. 10. A finer treatment of the data was performed with the GIER computer of the Ørsted Institute. For this purpose the expression

$$\sum(C_L(\text{obs.}) - C_L(\text{calc.}))^2$$

was minimized using the method outlined by Sillén.^{11,12} It was assumed that one had a consecutive formation of four mononuclear complexes. As initial values for β_1 , β_2 , β_3 , the graphically determined values¹⁰ were used, and K_4 was tentatively taken to be 10^3 . The concentration of free ligand was approximated by means of Newton-Raphson's method, *i.e.* obtaining from an initial value $[L]'$ a better value $[L]''$ using the expressions

$$f([L]) = [M] \sum_0^4 \beta_n [L]^n - C_M$$

$$[L]'' = [L]' - f([L]') / \left(\frac{\partial f([L])}{\partial [L]} \right)_{[L]=[L]'}$$

and continuing the iteration until $|f([L])/C_M| < 10^{-5}$. The program written in Gier Algol 4 was constructed from that of Ingri and Sillén.¹³

In Table 2 the result of the calculation is given. The computed values for the constants (with uncertainties, σ , defined according to Sillén^{11,12})

Table 2. Calculated stability constants of the gold(I)-phosphine system in 0.1 M NaSCN at 25°C.

	$\log K_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
Graphical	7.54	12.47	16.60	—
Computer	7.47 ± 0.08	12.44 ± 0.09	16.50 ± 0.19	(18.9 ± 0.4)

are seen to be practically identical with the graphically determined values. This fact is not too surprising considering that the rather high uncertainties on the individual measurements may give rise to many relative minima on the surface on which the minimum is sought. The minimum found may not be the absolute minimum, and therefore not too much confidence should be placed on the estimated uncertainties on the constants. A gold(I) complex with four bound phosphine ligands may exist, but the value given for β_4 is not defined according to the measurements. This is evident from the fact

that the calculated values for C_L (the fulldrawn curves in Fig. 2) only increases 1–2 % for $E_M > 300$ mV, when β_4 is taken into consideration.

From Fig. 2 it will be seen that Mønsted's measurements in 0.1 M NaSCN + 0.9 M LiCl (+ points) closely merge with Hawkins' measurements in 0.1 M NaSCN (○ points). This shows that the stability constants in the two different media can only be slightly different. The uncertainties on the individual measurements are high in both cases, but it will be seen that the later measurements in 0.1 M NaSCN + 0.9 M LiCl follow the calculated curve with lesser individual variation than the older measurements.

In Fig. 2 (lower part) the mole percentages of the gold(I) complexes with 1, 2, and 3 phosphine are plotted versus E_M . This graphic picture of the distribution of the phosphine complexes is valid in 0.1 M NaSCN, but dependent on the thiocyanate concentration if the phosphine ligands taken up displace the thiocyanate ions from the dithiocyanatoaurate(I) complex. This probably happens, and a paper of Malatesta and coworkers¹⁴ gives some information on this point. The authors have prepared and studied the properties (mole weight and conductivity in organic solvents) of several triphenylphosphinegold(I) complexes. They find that it is possible from a solution of $[\text{Ph}_3\text{PAuCl}]$ in methylene chloride containing an excess of triphenylphosphine to isolate salts of the types $[\text{Au}(\text{Ph}_3\text{P})_n]\text{X}$ with $n = 2, 3$, and 4, and anions such as ClO_4^- or NO_3^- . The preparation of these complexes supports the idea that the tri-phosphine complex at sufficiently high ligand concentrations is followed by a tetra-phosphine complex. In the copper(I) chloride-phosphine system the existence of the tetra complex could be directly proved,⁵ and a tetra complex most probably also exists in the silver phosphine system.⁵

The consecutive formation constants in 0.1 M NaSCN are according to Table 2 (with slightly rounded-off values):

$$K_1 = 10^{7.5}, K_2 = 10^{4.9}, K_3 = 10^{4.1}$$

Now assuming that the two phosphine ligands first taken up displace both of the thiocyanate ions, the following equilibrium constants are defined ($\text{L}^- = \text{Ph}_2\text{PC}_6\text{H}_4\text{SO}_3^-$, $\text{X}^- = \text{SCN}^-$):

$$K_1^* = \frac{[\text{AuXL}^-][\text{X}^-]}{[\text{AuX}_2^-][\text{L}^-]} = K_1[\text{X}^-] = 10^{6.5}$$

$$K_2^* = \frac{[\text{AuL}_2^-][\text{X}^-]}{[\text{AuXL}^-][\text{L}^-]} = K_2[\text{X}^-] = 10^{3.9}$$

$$K_3^* = \frac{[\text{AuL}_3^{2-}]}{[\text{AuL}_2^-][\text{L}^-]} = K_3 = 10^{4.1}$$

The normal coordination number for gold(I) is two, but the values of the constants K_n^* show in a very pronounced manner that in the gold(I) phosphine system as also found in the silver system, it is the mono- and tri-complexes which have the relatively highest stability.

For the gold(I) systems, apart from the phosphine complexes reported here, data in the literature are limited to the ratio of stability constants $\beta_2(\text{X}^-)/\beta_2(\text{Cl}^-)$ for some 1:2 complexes, *e.g.* for $\text{X}^- = \text{CN}^-$, SCN^- , *etc.* The constant

$$\beta_2(\text{Cl}^-) = [\text{AuCl}_2^-] / [\text{Au}(\text{H}_2\text{O})_2^+][\text{Cl}^-]^2$$

cannot be directly determined. However, the order of magnitude of $\beta_2(\text{Cl}^-)$ can be estimated using trends in the Periodic Table. From data in the litera-

Table 3.

	Cu(I)	Ag(I)	Au(I)	Hg(II)	Tl(III)
N	2	2	2	2	4
Q	0.51	0.63		0.83	1.03

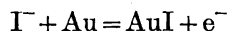
ture,¹⁵ one of the authors^{10,16} has in Table 3 for Cu(I), Ag(I), Hg(II), and Tl(III) calculated the quantity

$$Q = \left(\frac{1}{N} \log \beta_N(\text{Cl}^-) + \log 55 \right) / \left(\frac{1}{N} \log \beta_N(\text{CN}^-) - \frac{1}{N} \log \beta_N(\text{Cl}^-) \right)$$

In this expression the numerator is a measure of the mean affinity between the chloride ion and the aqua metal ion as defined in Ref. 16, and the denominator the difference between the corresponding mean affinities for cyanide and chloride ions. Interpolation in Table 3 gives for Au(I) $Q \sim 0.7$, and $\log \beta_2(\text{Cl}^-) \sim 17$. This value is hardly too high considering that $\log \beta_2$ for HgCl_2 is 14, and that the complexity of the chloro complexes increases when going from Zn(II) to Cu(I) as well as from Cd(II) to Ag(I).

The standard electrode potential for the $\text{Au}(\text{H}_2\text{O})_2^+, \text{Au}$ couple

Combining the estimated value for $\log \beta_2(\text{Cl}^-)$ with the standard electrode potential for the couple $\text{AuCl}_2^-, \text{Au}$ determined by N. Bjerrum⁶ to be 1.119 V at 20°C, one gets for the $\text{Au}(\text{H}_2\text{O})_2^+, \text{Au}$ couple $E^\circ = +2.12$ V. For the same potential Latimer in his well-known book¹⁷ has estimated the value +1.68 V. Latimer takes as his starting point the standard electrode potential for the reaction.



which, using data in the literature, he estimated to be +0.50 V. In order to calculate the standard electrode potential for the couple $\text{Au}(\text{H}_2\text{O})_2^+, \text{Au}$ from this potential, one must know the solubility product of gold(I) iodide. Knowing that the solubility products of CuI and AgI are about 10^{-12} and 10^{-16} , respectively, Latimer extrapolates the solubility product of AuI to be 10^{-20} . However, this is a hazardous extrapolation since the jump between AgI and AuI according to the usual trend in the Periodic System must be assumed to be larger than between CuI and AgI. Using the value assumed

Table 4. Estimated stability constants for some gold(I) complexes.

$$\beta_n = [\text{AuX}_n^{1-n}] / [\text{Au}(\text{H}_2\text{O})_2^+][\text{X}^-]^n$$

X ⁻	Cl ⁻	Br ⁻	SCN ⁻	CN ⁻	Ph ₂ PC ₂ H ₄ SO ₃ ⁻
log β ₁	17	20	25	47	35.4
log β ₃	—	—	—	—	39.5

here for the aqua-gold(I),gold couple 2.12 V, the solubility product of AuI is calculated to be 10⁻²⁷.

When the value +2.12 V is accepted as standard potential for the Au(H₂O)₂⁺,Au couple, it is possible to estimate the real stability constants for gold(I) complexes from the known values of the standard electrode potentials for the AuX₂⁻,Au couples. The values given for X⁻=SCN⁻ and CN⁻ by one of the authors in the Stability Constant Tables¹⁵ are estimated in this way. A collection of such stability constants is given in Table 4. The values of β₂ and β₃ for the phosphine complexes are calculated from the K_n^{*} constants by means of the estimated β₂-value for the Au(SCN)₂⁻ complex, i.e. β₂=K₁^{*}·K₂^{*}×10²⁵, β₃=K₁^{*}·K₂^{*}·K₃^{*}×10²⁵ under the assumption that the di- and tri-phosphine complexes do not contain complex-bound thiocyanate.

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