Studies on Metal Ion Coordination in Solution

IV. The Complex Formation of Diphenylphosphino-benzene-m-sulphonate with Copper(I)

RAYMOND GEORGE and JANNIK BJERRUM

Chemistry Department I, Inorganic Chemistry, The H.C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

Zinc(II), cobalt(II), and nickel(II) salts in methanol do not form complexes with triphenylphosphine, but it was shown qualitatively by spectrophotometric measurements that they do with 1,2-bis(diphenylphosphine)ethane. Quantitatively, the complex formation between diphenylphosphinobenzene-m-sulphonate and the chlorocopper(I) complexes in aqueous 1 M LiCl was studied by measurements with a copper amalgam electrode. The data gave evidence for the formation of a tetraphosphine complex after a relatively large range of existence for the triphosphine complex, but, contrary to Ahrland and Chatt's findings [1] for silver(I), the copper(I) monophosphine complex had only a small range of existence (see Table 4). The data were programmed using a GIER computer and the following stepwise formation constants were found at 25°C: $K_1 = 10^{5.76}$, $K_2 = 10^{5.45}$, $K_3 = 10^{4.91}$, $K_4 = 10^{3.80}$ l·mole^{-1}. The data previously published for the mercury(II)-phosphine system [2] were treated in the same way, and the slightly revised stability constants are given in Table 3.

In some preliminary experiments the complex formation between unsubstituted triphenylphosphine and various metal ions was qualitatively examined in methanol by measuring the influence of added metal salts on the phosphine band in ultraviolet. It was found that Zn(II), Co(II), Ni(II), Pb(II), and Tl(I) in methanol solutions, 0.01 M in metal salt and ligand, had no influence on the phosphine band. However, addition of Ag(I) and Hg(II) salts caused a strong decrease of the absorbance at the foot of the band in the near ultraviolet. Gold(III) and Cu(II) were reduced by the ligand, but gave similar evidence of a strong tendency to complex formation in their lower oxidation states. Similar experiments were made with a new diphosphine,[3] *viz.* 1,2-bis(diphenylphosphine)ethane, and it was found that this chelate diphosphine showed a much greater tendency to complex formation than triphenylphosphine, and was able to form complexes also with zinc, cobalt(II), and nickel ions in methanol and other organic solvents. Some of the best results were obtained

in especially purified aqueous dioxane. However, the diphopshine was only slightly soluble, and extremely oxidizable especially in acid solutions. The spectrum of the oxidized ligand was similar to that of the complexes, and attempts to sulphonate the ligand gave no results. Owing to these difficulties no further experiments were made with the diphosphine, and in continuation of earlier investigations with silver (I)[1] and mercury(II),[2] a study was undertaken of the complex formation of diphenylphosphinobenzene-m-sulphonate with copper(I) in aqueous solution.

As uncomplexed copper(I) ions are unstable with regard to copper(II) ions in aqueous solution, it was chosen to make the measurements in a 1 M chloride solution where a simple calculation shows that the equilibrium concentration of copper(II) ions is negligible for $C_{Cu} < 10^{-2}$ M owing to the chloro complex formation of Cu(I). LiCl was preferred to NaCl and KCl in order to have a sufficiently high solubility of the ligand. Cells of the following type:

$$\text{Cu,Hg} \left| \begin{array}{c} C_{CuCl}, \ 1 \ \text{M LiCl} \\ C_L, \ 10^{-3} \ \text{M HCl} \end{array} \right| \begin{array}{c} 1 \ \text{M LiCl} \\ 10^{-3} \ \text{M HCl} \end{array} \left| \begin{array}{c} C_{CuCl}, \ 1 \ \text{M LiCl} \\ C_L = 0, \ 10^{-3} \ \text{M HCl} \end{array} \right| \text{Cu,Hg}$$

were measured for selected concentrations of copper(I) chloride and varying concentrations of the phosphine ligand in order to determine

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

E_M is defined [2,4] 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:

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

EXPERIMENTAL

Solutions and analysis. m-$(C_6H_5)_2PC_6H_4SO_3Na$, $2H_2O$ has been described previously.[1,2] The raw product was washed with hot benzene, crystallized twice from water, and finally from 85 % ethanol. It was dried at 110°C and kept over silica gel. As the ligand decomposes slowly in water, fresh solutions were always used for the experiments.

Stock solutions of copper(I) chloride in 1 M LiCl were prepared in the following way. Copper(I) chloride (Merck *pro analysi*) was washed with acidified 1 M LiCl solution until the solid was completely white. It was then transferred quickly into 1 M LiCl solution that had been thoroughly de-aerated with CO_2 and contained some copper amalgam. After bubbling about one day with oxygen-free CO_2, the last trace of copper(II) was completely reduced and the solution showed a constant titre for several days. The copper(I) analyses were made as outlined by Vogel.[5] Aliquots of the stock solution were pipetted directly into an excess of ferric ammonium sulphate and titrated back with ceric sulphate with ferroin as indicator.

Stock solutions of LiCl were made from the fused salt and analysed by chloride titration.

The copper amalgam (11 %) was prepared by electrolysis according to Cohen *et al.*[6] Before use it was diluted about 5 times with mercury and placed in a J-tube electrode as previously described.[7]

Procedure. One specially constructed electrode vessel of capacity 50 ml was used. It was filled with aliquots of ligand, LiCl-stock solution containing some hydrochloric acid, and the necessary volume of water in order to make the final solution 1 M in LiCl

and 10^{-3} M in HCl. The vessel was placed in the thermostat at 25°C and the solution de-aerated through the side tube with CO_2 for 10 min before the J-tube electrode was dipped into the solution. Then under continued CO_2-bubbling an aliquot of the CuCl-stock solution was added. After thorough mixing connection was established to a 1 M LiCl, 10^{-3} M HCl solution and the potential measured with a Cambridge Vernier potentiometer. The reference electrode was a 1 M KCl-calomel electrode.

MEASUREMENTS AND RESULTS

Measurements of E_M were made for three series of copper(I) chloride concentrations, viz. 0.155, 0.480, and 0.846 mM, and Table 1 gives the results for the two highest concentrations. In a preliminary treatment of the data using the Fronæus [4] combined method of corresponding solutions and integration, for determining $\bar{n}$ and [L], the stability constants were determined to be:[8]

$$K_1 = 10^{6.19} \text{ l·mole}^{-1}, \quad \beta_2 = 10^{11.61} \text{ l}^2\text{·mole}^{-2}, \quad \beta_3 = 10^{16.78} \text{ l}^3\text{·mole}^{-3}$$

A closer examination of the data gave some reason to believe that a tetraphosphine complex is also formed, and that the error due to inevitable air-oxidation was not negligible in the series with the lowest copper(I) concentration. Therefore, in order to get more exact and detailed information from the measurements an electronic data treatment was performed for each of the series.

From a chosen set of stability constants and the known value of C_{CuCl} it is possible for all the given values of C_L to calculate the corresponding E_M-values. Analogously from the constants and the observed values of E_M it is possible to calculate the corresponding C_L-values. Therefore, by minimizing either the expression:

$$\sum(E_M(\text{obs.}) - E_M(\text{calc.}))^2 \tag{1}$$

or

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

Table 1. Measurements of E_M, the potential relative to ligandfree half-cells with the same copper(I) chloride concentration. Concentrations are in mM and potentials in mV.

$C_{CuCl} = 0.480$		$C_{CuCl} = 0.846$	
C_L	E_M	C_L	E_M
0.250	10.4	0.500	13.7
0.500	28.9	1.00	33.6
0.750	48.3	1.25	47.1
1.00	91.4	1.50	63.0
1.25	129.8	2.00	110.9
1.40	164.7	2.25	140.1
1.50	204.4	2.50	183.6
1.75	246.2	2.75	220.0
1.80	278.4	3.00	278.5
2.00	352.2	3.30	354.9
2.25	398.5	3.50	406.6
2.50	428.8	4.00	463.5
2.75	464.7	4.40	498.3
3.00	484.2	5.00	527.8
3.50	510.8	5.50	544.5
		6.05	565.6

Table 2. Computed values for the stability constants of the copper(I) chloride-phosphine system in 1 M LiCl at 25°C.

$$\beta_n = K_1 K_2 \ldots K_n$$

Calc. by minimizing	$C_{CuCl} \times 10^3$	$\log K_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
(1)	0.846	5.85 ± 0.13	11.20 ± 0.10	16.24 ± 0.05	20.02 ± 0.07
(2)	0.846	5.78 ± 0.09	11.22 ± 0.12	16.28 ± 0.08	19.86 ± 0.09
(1)	0.480	5.73 ± 0.14	11.22 ± 0.07	15.98 ± 0.07	19.97 ± 0.07
(2)	0.480	5.67 ± 0.13	11.20 ± 0.10	16.00 ± 0.09	19.87 ± 0.06
Average	—	5.76	11.20	16.12	19.92

it is possible to obtain a set of constants which give the best fit of the data in question. The assumption which was put in the calculation was that the system was monomeric with a stepwise formation of complexes up to the tetraphosphine complex. The programming as well as the calculations at the GIER computer were all performed by Mr. Ole Mønsted. An estimate of the uncertainties of the computed set of constants was obtained using the method proposed by Sillén.[9] The results of the calculations of the data in Table 1 are given in Table 2.
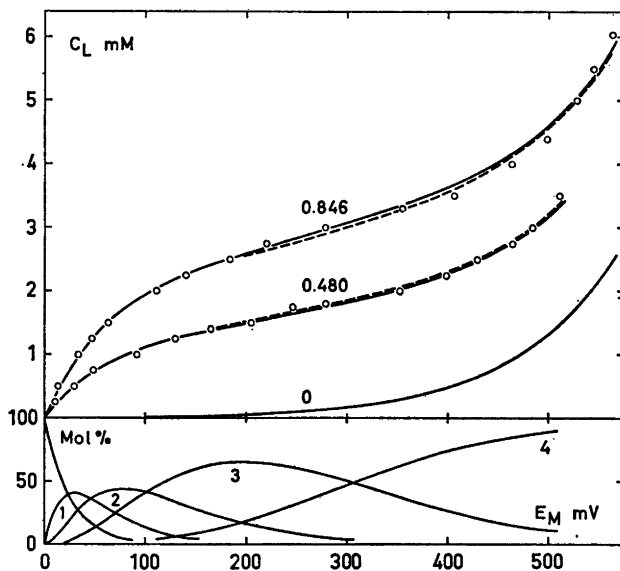

Fig. 1. Upper part. Curves for C_L *versus* E_M for the two copper(I) chloride concentrations given in Table 1. Experimental data are given as o-points. The dotted curves are calculated with the mean constants for the individual series, and the full-drawn curves including the curve for $C_{CuCl} = 0$ ($C_L = [L]$) with the average constants for the system given in Table 2.
Lower part. Graphic representation of the mole percentages of the four copper(I)-phosphine complexes as function of E_M calculated with the average constants given in Table 2.

Table 3. The mercury(II) diphenylphosphinobenzene-m-sulphonate system
(1 M KNO₃, 25°C).

		$\log K_1'$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
Salvesen and Bjerrum [2]	Fronæus treatment	14.3	24.6	29.7	33.0
O. Mønsted	Computer	14.46	24.72	29.76	32.4 [a]

[a] β_4 was only well-defined in the series with $C_{Hg(II)} = 0.19$ mM.

It will be seen that the two ways of calculation give nearly the same result, and further that the set of constants calculated from the two series with different copper(I) concentration are also in good agreement. Therefore, it can be said with a rather high certainty that our assumptions are fulfilled, and that the system is governed by a set of cumulative constants of the order of magnitude 10^6, 10^{11}, 10^{16}, and 10^{20}.

In Fig. 1 (upper part) C_L is plotted *versus* E_M. The curves are calculated from the computed stability constants, and the figure shows how well these curves fit the experimental data from Table 1 (plotted as o-points). The lower part of the figure shows the relatively large range of existence of the triphosphine complex.

In order to test the accuracy of the results on the mercury(II)-phosphine system,[2] the stability constants obtained by Salvesen and Bjerrum using the Fronæus treatment, have also been recalculated at the GIER computer by Ole Mønsted. His stability constants are compared in Table 3 with those of Salvesen and Bjerrum. It will be seen that the agreement is as good as could be expected.

DISCUSSION

Silver(I) and copper(I) have in case of σ-bonded ligands the characteristic coordination number two, but show in case of mainly π-bonded ligands such as phosphines and arsines a different behaviour. Ahrland, Chatt *et al.*[1] have studied the silver ion, diphenylphosphinobenzene-m-sulphonate system in aqueous solution and found that (1) the monophosphine complex has a relatively high range of existence and (2) that the highest complex seems to be the triphosphine complex. In the analogous copper(I) system studied here the complex formation has a temporary stop for $\bar{n} = 3$ before a tetra complex is formed at higher ligand concentration, but contrary to what is found in the

Table 4. Comparison of the silver(I) and copper(I)-phosphine systems (P = diphenyl-phosphino-m-sulphonate).

	$\log K_1/K_2$	$\log K_2/K_3$	$\log K_3/K_4$	$\log \beta_3$	$\log \beta_4$
Ag⁺, P	2.2	0.45	—	19.5	—
CuCl$_n^{1-n}$, P	0.31	0.54	1.11	16.1	19.9
Cu⁺, P				~22.0	~25.8

silver system, the mono complex has only a rather small range of existence (see Table 4). However, in this comparison it is not taken into consideration that the mono copper(I) complex is a mixed chloro-phosphine complex which very well could behave differently from an aqua-phosphine complex.

According to the stability constants for the aqua copper(I) chloride system, [10,11] $\beta_2 \sim 10^{5.5}$, $\beta_3 \sim 10^{5.7}$, a 1 M LiCl, CuCl-solution contains a mixture of the dichloro- and trichloro complexes, and the relative concentration of aqua copper(I) ion in such a solution is given by $1/(10^{5.5} + 10^{5.7}) = 10^{-5.9}$. Therefore, log β_4 in the aqua-phosphine copper(I) system can be assumed to be $19.9 + 5.9 = 25.8$, and log β_3 $16.1 + 5.9 = 22.0$ under the tacit assumption that not only the tetrakis- but also the tris(phosphine) complex does not contain complexly bound chloride ions.

Tetrakis(triphenylphosphine) complexes of copper(I) as well as of silver(I) perchlorate have recently [12] been prepared, and it is, therefore, reasonable to assume that also the silver ion can take up four phosphine ligands at a higher ligand concentration than that examined by Ahrland, Chatt et al.[1] However, in conclusion it is noteworthy that in both cases the tris complex has a relatively large range of existence, and further that the corrected stability of the copper(I) complexes, as also should be expected, is higher than for the silver(I) complexes (see Table 4).

REFERENCES

1. Ahrland, S., Chatt, J., Davies, N. R. and Williams, A. A. *J. Chem. Soc.* **1958** 276.
2. Salvesen, B. and Bjerrum, J. *Acta Chem. Scand.* **16** (1962) 735.
3. Chatt, J. and Hart, P. A. *J. Chem. Soc.* **1960** 1378.
4. Fronæus, S. *Komplexsystem hos koppar*, Thesis, Gleerupska Univ.-Bokhandeln, Lund 1948.
5. Vogel, A. D. *Quantitative inorganic analysis*, 3rd Ed., Longmans, London 1961, p. 323.
6. Cohen, E., Chattaway, F. D. and Tombrock, W. *Z. physik. Chem.* **60** (1907) 717.
7. Wright, G. and Bjerrum, J. *Acta Chem. Scand.* **16** (1962) 1262.
8. Bjerrum, J., George, R. S., Hawkins, C. J. and Olson, D. C. *Proceedings of the symposium on coordination chemistry*, Tihany 1964, Akadémiai Kiadó, Budapest 1965.
9. Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 159.
10. Bjerrum, J. *Metal ammine formation in aqueous solution*, Thesis, P. Haase and Son, Copenhagen 1941. Reprinted 1957.
11. Sillén, L. G. and Martell, A. E. *Stability constants of metal-ion complexes*, The Chemical Society, Special Publication No. 17, London 1964.
12. Cotton, F. A. and Goodgame, D. M. L. *J. Chem. Soc.* **1960** 5267.