

## Stability of some Mercury(II) Phosphine Complexes in Pyridine

FELIX HULTÉN

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

and INGMAR PERSSON

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

(Received December 10, 1986)

Only a few studies of stabilities of mercury(II) phosphine complexes have been reported so far [1–3]. On the other hand, the thermodynamics for the complex formation between silver(I) and ligands donating through P, As and Sb atoms have been studied extensively in water [1, 2], DMSO [4, 5] and pyridine [6, 7]. The stabilities of silver(I) phosphine complexes are proportional to some physical parameters of the phosphines [7], which are a measure of the electron density on phosphorous. These parameters are dipole moment, and an electronic parameter  $\nu$  determined from the  $\text{Ni}(\text{CO})_3\text{PR}_3$  complex in dichloromethane [8, 9], and basicity in aqueous solution. The stability of a certain silver(I) phosphine complex is furthermore inversely proportional to the heat of solvation of the silver(I) phosphine it is formed from [7, 10]. This shows that the silver(I)–phosphine bonds are of mainly  $\sigma$ -character and that there most probably is no  $\pi$ -bonding or back-bonding present in these bonds. This is probably due to the low tendency of silver(I) to form  $\pi$ -bonds. These relationships between stability of silver(I) complexes and physical parameters of the phosphines, and the solvation of the silver(I) complexes allow prediction of the stability of silver(I) phosphine and probably also phosphite complexes in a number of solvents with high accuracy.

The purpose of this work is to study if mercury(II) forms complexes with phosphines in the same regular pattern as silver(I) and to obtain information on the character of the mercury(II)–phosphine bonds. The mercury(II) triphenylphosphine, tri-*n*-butylphosphine and tricyclohexylphosphine systems have been studied in pyridine for comparison with similar complexes in aqueous and DMSO solution.

## Experimental

### Chemicals

Bis(pyridine)mercury(II) perchlorate,  $\text{Hg}(\text{C}_5\text{H}_5\text{N})_2(\text{ClO}_4)_2$ , has been prepared and analyzed as described

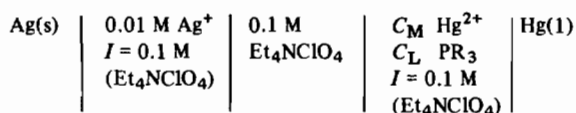
previously [11, 12]. Tetraethylammonium perchlorate and pyridine (all Fluka) were of analytical grade. The tetraethylammonium perchlorate was dried at 80 °C under vacuum and stored over silica gel. The pyridine was stored in dark bottles over 3 Å molecular sieves. Triphenylphosphine, arsine and stibine (all Fluka) and tricyclohexylphosphine (Strem) were used without further purification and stored at room temperature over silica gel under vacuum. Tri-*n*-butylphosphine and stibine (all Strem) were used without further purification and stored in sealed ampoules over  $\text{N}_2$  and Ar.

### Solutions

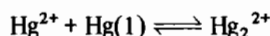
The solutions were prepared by weighing out the salts or ligands prior to dissolving them in pyridine. The tetraethylammonium concentration was set to 0.1 M in all solutions by the perchlorate salt. Because of the low stability of the ligand solutions, they were freshly prepared every day. No decomposition of the ligands could however be noticed during a titration.

### Potentiometric Measurements

The measurements were performed by an automated potentiometric titration system described elsewhere [10]. Mercury pool electrodes have been used for the determination of the concentration of free mercury(II). The measurements were performed at  $25.0 \pm 0.1$  °C. The emf of the following cell was measured:



In the absence of stabilizing ligands, solutions of mercury(II) perchlorate in pyridine are partly reduced by metallic mercury according to



In the present medium, the reproporationation constant is reported to be  $K_r = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}] = 0.171 \pm 0.005$  [12]. The titrations were therefore conducted from higher to lower values of  $\bar{n}$  and stopped when the reproporationation became perceptible; the initial solution thus contained an excess of ligand as described previously [3]. The potential of a standard mercury half-cell 1 M  $\text{Hg}^{2+}/\text{Hg(l)}$  relative to the reference cell used here is 306.1 mV under present conditions [13].

The least-squares computer program EMKBAK was used to calculate the stability constants from the potentiometric measurements [12].

TABLE I. The Stability Constants,  $K_j$  ( $M^{-1}$ ), for the Complex Formation of some Mercury(II) Phosphine Complexes in Pyridine Solution at 25 °C. Medium 0.1 M  $Et_4NClO_4$ <sup>a</sup>

Stability constants	Ligand		
	$P(C_6H_5)_3$	$P(C_4H_9)_3$	$P(C_6H_{11})_3$
$\log K_1$	$(4.14 \pm 0.22) \times 10^4$	$(2.87 \pm 0.21) \times 10^{11}$	$(5.89 \pm 0.41) \times 10^{11}$
$\log K_2$	$(39.1 \pm 3.4)$	$(1.03 \pm 0.11) \times 10^8$	$(1.08 \pm 0.18) \times 10^7$
$\log K_3$		$(150 \pm 16)$	$(48 \pm 19)$
NP <sup>b</sup>	172	241	337

<sup>a</sup>The limits of error refer to three standard deviations. <sup>b</sup>NP denotes the number of observations (emfs measured) for each system.

TABLE II. The Overall Stability Constants,  $\beta_j$  ( $M^{-j}$ ), and the Changes in Free Energy,  $\Delta G^\circ_{\beta_j}$  ( $kJ mol^{-1}$ ), of some Mercury(II) Phosphine and Arsine Complexes in Water, DMSO and Pyridine at 25 °C

	Ligand/Solvent						
	Dop/ $H_2O^a$	Dpm/ $H_2O^b$	$P(C_6H_5)_3$ / DMSO <sup>c</sup>	$As(C_6H_5)_3$ / DMSO <sup>c</sup>	$P(C_6H_5)_3$ / pyridine <sup>d</sup>	$P(C_4H_9)_3$ / pyridine <sup>d</sup>	$P(C_6H_{11})_3$ / pyridine <sup>d</sup>
$\log \beta_1$		14.3	11.1	6.8	4.62	11.5	11.8
$\log \beta_2$	37.3	24.6	17.6	9.0	6.21	19.5	18.0
$\log \beta_3$	42.5	29.7				21.7	20.5
$-\Delta G^\circ_{\beta_1}$		81.5	63.3	38.8	26.4	65.6	67.3
$-\Delta G^\circ_{\beta_2}$	212.7	140.3	100.4	51.3	35.4	111.2	107.2
$-\Delta G^\circ_{\beta_3}$	242.3	169.4				123.7	116.9

<sup>a</sup>Ref. 1: Dop =  $(C_2H_5)_2PCH_2CH_2OH$ ;  $I = 1$  M ( $KNO_3$ ), 22 °C.

<sup>c</sup>Ref. 3:  $I = 0.1$  M ( $NH_4ClO_4$ ).

<sup>d</sup>This work.

<sup>b</sup>Ref. 3: Dpm =  $(C_6H_5)_2PC_6H_4SO_3^-$  (m-);  $I = 1$  M ( $KNO_3$ ).

## Results

Mercury(II) forms two mononuclear complexes with triphenylphosphine and tricyclohexylphosphine and three mononuclear complexes with tri-*n*-butylphosphine in pyridine solution. The stepwise stability constants are given in Table I. The stabilities decrease in the order  $K_1 > K_2 \gg K_3$ , which means that every complex has a certain range of free ligand concentration where it predominates; the range of the second complex is very wide. The complex formation functions are given in Fig. 1. The overall stabilities of

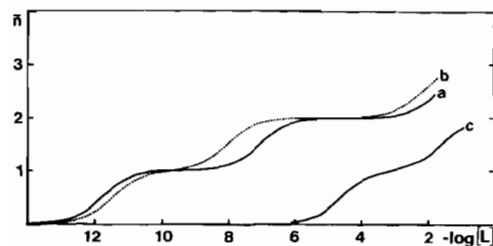


Fig. 1. The complex formation curves of the mercury(II)  $PR_3$  systems in pyridine,  $PR_3 = P(C_6H_{11})_3$  (a);  $P(C_4H_9)_3$  (b);  $P(C_6H_5)_3$  (c). Ionic medium 0.1 M  $Et_4NClO_4$ .

some mercury(II) phosphine complexes in water, DMSO and pyridine are given in Table II. The complex formation between mercury(II) and triphenylarsine and stibine and tri-*n*-butylstibine is too weak to be measured with a mercury pool electrode according to the reproporationation reaction;  $K_1$  is certainly less than 100.

## Discussion

The stabilities of the mercury(II) phosphine complexes are proportional to the corresponding silver(I) complexes independent of the solvent, Fig. 2. This Figure shows that the mercury(II) phosphine complexes are markedly more stable than the corresponding silver(I) complexes. The linear relationship between the stability constants of silver(I) and mercury(II) phosphine complexes means that (1) the mercury(II)–phosphine bonds are of mainly  $\sigma$ -character, and the contribution from  $\pi$ - or back-bonding is negligible as in the silver–phosphine bonds; (2) the stability constants of mercury(II) phosphine complexes can be predicted for a number of phosphine and solvents from dipole moment,  $\nu$  parameter, and/or basicity in aqueous solution, of the

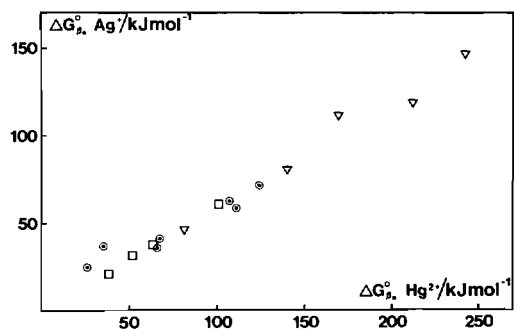


Fig. 2. The free energy relationship of the complex formation of silver(I) and mercury(II) with different phosphines, in pyridine (circles with dot) [6, 7], DMSO (open squares) [4, 5] and aqueous solution (open triangles) [1–3].

phosphine, and the heat of solvation of the mercury(II) ion or from the stability of the corresponding silver(I) system in the same solvent. Mercury(II) and silver(I) have thus proportional complex formation abilities toward phosphines. The mercury(II) complexes are more stable mainly due to a larger electrostatic contribution to the metal–ligand bond.

The second mercury(II) tricyclohexylphosphine complex, as well as the corresponding silver(I) complex, is slightly weaker than expected. The bulky cyclohexyl groups from different ligand molecules in the second complexes may come in contact with each other, in spite of linear coordination [14]. This destabilizes the second complex thermodynamically and the M–P bonds become weaker.

## Acknowledgement

The support from the Swedish Natural Science Research Council is gratefully acknowledged.

## References

- 1 M. Meier, *Diss. no. 3988*, Eidgenössische Technische Hochschule, Zurich, 1967.
- 2 R. D. Hancock and F. Marciano, *J. Chem. Soc., Dalton Trans.*, 1832 (1976).
- 3 S. Ahrland, T. Berg and P. Bläuenstein, *Acta Chem. Scand., Ser. A*, 32, 933 (1978) and refs. therein.
- 4 S. Ahrland, T. Berg and P. Trinderup, *Acta Chem. Scand., Ser. A*, 31, 775 (1977).
- 5 S. Ahrland, E. Avsar and T. Berg, *J. Organomet. Chem.*, 181, 17 (1979).
- 6 S. Ahrland, F. Hultén and I. Persson, *Acta Chem. Scand., Ser. A*, 40, 595 (1986).
- 7 F. Hultén and I. Persson, *Inorg. Chim. Acta*, 128, 43 (1987) and refs. therein.
- 8 W. Strohmeier and F. J. Müller, *Chem. Ber.*, 100, 2812 (1967).
- 9 C. A. Tolman, *Chem. Rev.*, 77, 313 (1977).
- 10 F. Hultén, *Thesis*, Chalmers University of Technology and University of Göteborg, Göteborg, 1986.
- 11 L. I. Chudinova, *Zh. Prikl. Khim.*, 42, 189 (1969).
- 12 S. Ahrland, I. Persson and R. Portonova, *Acta Chem. Scand., Ser. A*, 35, 49 (1981).
- 13 M. Johnsson and I. Persson, *Inorg. Chim. Acta*, 127, 25 (1987).
- 14 E. C. Aleya, S. A. Dias, G. Ferguson and M. A. Khan, *J. Chem. Res.*, 360 (1979).