

Studies on Metal Ion Co-ordination in Solution

III. The Complex Formation of Triphenylarsine with Silver(I) and with Mercury(II) Chloride in Mixed Water-Methanol Solvents

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The complexing properties of triphenylarsine ($\phi_3\text{As}$) with silver (I) ion and with mercury(II) chloride in mixed water-methanol solvents were studied using spectrophotometric methods. It was found that silver (I) forms a 1:1 complex over a large range of ligand to metal-ion ratios. The stability constant of this complex was determined to be $10^{5.70}$ in 75.4 wt %, and to be $10^{5.81}$ in 55.6 wt % methanol at 25°C. The mercury (II) chloride, on the other hand, takes up more than one arsine ligand. The complete formation curve could not be determined due to the insolubility of the complexes formed. Job plots indicate that in the absence of added chloride, a 3:1 complex is formed, while in 0.050 M chloride, a 2:1 complex is formed. Stability constants for some of the complexes identified were determined.

Adducts of mercury(II) halides and arsines have been known for many years,^{1,2} but no studies of the complex formation between a mercury(II) salt and an arsine have been performed in solution. The complex formation between tri-(*m*-sulphophenyl)arsine and silver nitrate in aqueous solution has recently been studied by Ahrlund, Chatt *et al.*³ with silver-silverhalide electrodes. In order to further examine the formation of silver and mercuric arsine compounds, spectrophotometric studies have been made of the complex formation of these metals with unsubstituted triphenylarsine in aqueous methanol solutions.

EXPERIMENTAL

Materials. Merck anhydrous methanol *p.a.* was used. The mercuric chloride was recrystallized Riedel-de Haën. Silver nitrate and other chemicals were all of analytical grade.

Silver trifluoroacetate was prepared from silver oxide and trifluoroacetic acid. The purity of the salt was confirmed by C and Ag analysis. (Found: C 10.86; Ag 48.4. Calc. for $\text{AgO}_2\text{C}_2\text{F}_3$: C 10.88; Ag 48.4).

Triphenylarsine. A commercial product was recrystallized several times from 95 % ethanol. Analysis of the ligand confirmed its purity. (Found: C 70.6; H 4.93. Calc. for $(C_6H_5)_3As$: C 70.6; H 4.94).

Solutions. Triphenylarsine is insoluble in water, but sufficiently soluble in aqueous methanol. The spectrum in methanol solutions up to 1 M in trifluoroacetic acid is unchanged, indicating that protonation of the ligand in this acid range can be neglected.

Methanol solutions of triphenylarsine are stable towards air oxidation, but it was found that oxygen absorbed in the methanol solutions created a strong band in the ultraviolet beginning at about 280 $m\mu$ and with its peak below 200 $m\mu$. Passage of a stream of air through the solvent increased the absorbance due to this band, while passing nitrogen through the solution decreased it. In the preliminary experiments this effect was partly eliminated by using the same solvent in the reference cells as in the solutions to be measured. But in all later experiments possible errors due to this extra absorbance were completely eliminated by preparing all solutions in a dry box with a circulating nitrogen atmosphere using solvents through which a stream of nitrogen had been passed.

The mixed solvents were prepared by weight, and concentrations of dissolved substances are given in moles per liter.

Spectra. The preliminary spectra were taken with a Cary 14 recording spectrophotometer, and the absorbance measurements at selected wavelengths with a Beckman DU spectrophotometer. All work was done at 25°C.

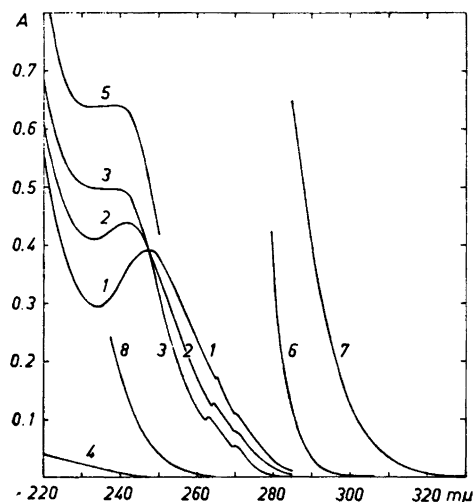


Fig. 1. Spectra of the following solutions in 1 cm cells. Reference cell with the same methanol solvent. L = triphenylarsine, T = trifluoroacetate.

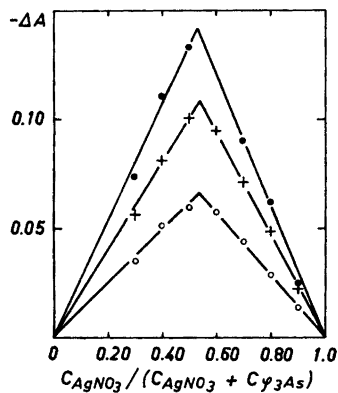
| curve | $C_L \times 10^4$ | $C_{AgT} \times 10^4$ | $C_{HgCl_2} \times 10^4$ | wt % CH_3OH |
|-------|-------------------|-----------------------|--------------------------|---------------|
| 1 | 0.294 | 0 | | 93.8 |
| 2 | 0.294 | 0.218 | | 93.8 |
| 3 | 0.294 | 0.654 | | 93.8 |
| 4 | 0 | 0.436 | | 93.8 |
| 6 | 4.17 | | 0 | 74.2 |
| 7 | 4.17 | | 7.75 | 74.2 |
| 8 | 0 | | 4.65 | 74.2 |

Curve 5 gives the absorbance of the silver-arsine complex in 75.4 % CH_3OH for a chosen concentration, $[AgL] = 0.4 \times 10^{-4}$ M. The spectrum was obtained from solutions with a great excess of silver trifluoroacetate, the absorbance of which was corrected for using the same silver concentration in the reference solutions.

THE SILVER (I)-TRIPHENYLARSINE SYSTEM

When silver trifluoroacetate is added to a methanol-water solution of triphenylarsine its ultraviolet spectrum shifts due to complexation (see Fig. 1). In this figure the curves 1–3 with the same ligand concentration and varying concentration of silver trifluoroacetate has an isosbestic point, and curve 4 shows that the absorption of silver trifluoroacetate itself is very small in the range examined. From this it can be concluded that only one silver complex is formed. A Job continuous variations study⁴ was made at three wavelengths, 255, 264, and 271 $m\mu$ where in all cases a decrease in the absorbance due to

Fig. 2. Job plot for the system silver nitrate-triphenylarsine in 93.8 wt % methanol. The excess absorbance ΔA (per cm cell length) is plotted versus the mole fraction of the components for the wavelengths 255 $m\mu$ ●, 264 $m\mu$ +, 271 $m\mu$ ○. ΔA is defined as the difference between the absorbance of the mixed solution and the absorbance that the solution would have had if there had been no reaction on mixing the components. The total concentration of silver nitrate and triphenylarsine in the solutions was 10^{-4} M.



complexation occurs. The plot is given in Fig. 2, and shows, in agreement with the findings of Ahrlund, Chatt *et al.*³ for the sulphonated ligand, that a 1:1 complex is formed. The maxima are not situated exactly at the "mole fraction" 0.5, but the deviations which would correspond to the existence of complexes with less than one arsine molecule per silver ion are probably within the uncertainty of the method.

The stability of the silver-arsine complex in two different solvents, 75.4 wt % CH_3OH and 55.6 wt % CH_3OH , were determined from absorbance readings at 233 and 238 $m\mu$. Silver trifluoroacetate was assumed to be completely dissociated, and concentrations were used for the species in question. The results are given in Table 1. The extinction coefficients of triphenylarsine ϵ_L were obtained from absorbance readings in the two solvents, and the extinction coefficients of the silver-arsine complex ϵ_1 from absorbance readings of solutions containing a large enough excess of silver ions to bind all of the ligand present (*cf.* curve 5 in Fig. 1). An expression for the stability constant K_1 was derived as follows. Denoting the absorbance per cm cell length by A , the following set of equations is available for the estimation of K_1 :

$$\begin{aligned} A &= \epsilon_L[\text{L}] + \epsilon_1[\text{AgL}^+] \\ C_L &= [\text{L}] + [\text{AgL}^+] \\ C_{\text{Ag}} &= [\text{Ag}^+] + [\text{AgL}^+] \\ [\text{AgL}^+] &= K_1[\text{Ag}^+][\text{L}] \end{aligned}$$

Table 1. Spectrophotometric estimation of the stability constant for the complex formation between silver trifluoroacetate and triphenylarsine in mixed water-methanol solvents at 25°C. Absorbance readings were taken in 5 cm quartz cells with a Beckman DU at 233 and 238 m μ . Reference cell contained silver salt in the same concentration as the complex solution. A = absorbance per cm cell length.

| 75.4 wt % CH ₃ OH | | $\left\{ \begin{array}{l} 233 \text{ m}\mu : \epsilon_L = 1.01 \times 10^4, \\ 238 \text{ m}\mu : \epsilon_L = 1.09 \times 10^4, \end{array} \right.$ | | $\left. \begin{array}{l} \epsilon_{AgL} = 1.60 \times 10^4 \\ \epsilon_{AgL} = 1.61 \times 10^4 \end{array} \right\}$ | | |
|------------------------------|----------------------|---|-----------|---|--------------------|--------------------|
| No. | $C_{Ag} \times 10^6$ | $C_L \times 10^6$ | A_{233} | A_{238} | log K_1 (233) | log K_1 (238) |
| 1 | 9.16 | 5.47 | 0.0786 | 0.0806 | 5.70 | 5.74 |
| 2 | 8.68 | 4.10 | 0.0594 | 0.0606 | 5.71 | 5.72 |
| 3 | 8.68 | 5.47 | 0.0760 | 0.0780 | 5.54 | 5.55 |
| 4 | 8.68 | 7.75 | 0.1088 | 0.1108 | 5.76 | 5.72 |
| 5 | 8.68 | 10.0 | 0.1358 | 0.1402 | 5.71 | 5.75 |
| 6 | 8.68 | 11.4 | 0.1526 | 0.1568 | 5.73 | 5.71 |
| Av. | | | | | 5.69 | 5.70 |
| 55.6 wt % CH ₃ OH | | $\left\{ \begin{array}{l} 233 \text{ m}\mu : \epsilon_L = 1.01 \times 10^4, \\ 238 \text{ m}\mu : \epsilon_L = 1.08 \times 10^4, \end{array} \right.$ | | $\left. \begin{array}{l} \epsilon_{AgL} = 1.65 \times 10^4 \\ \epsilon_{AgL} = 1.65 \times 10^4 \end{array} \right\}$ | | |
| No. | $C_{Ag} \times 10^6$ | $C_L \times 10^6$ | A_{233} | A_{238} | log K_1 (233) | log K_1 (238) |
| 7 | 8.40 | 5.92 | 0.0892 | 0.0892 | 5.96 | 5.88 |
| 8 | 6.00 | 4.14 | 0.0562 | 0.0570 | 5.50 | 5.45 |
| 9 | 6.00 | 5.33 | 0.0740 | 0.0758 | 5.71 | 5.72 |
| 10 | 6.00 | 5.92 | 0.0830 | 0.0850 | 5.83 | 5.80 |
| 11 | 6.00 | 8.88 | 0.1192 | 0.1222 | 5.90 | 5.89 |
| 12 | 6.00 | 11.8 | 0.1534 | 0.1570 | 6.11 | 5.99 |
| Av. | | | | | 5.83 | 5.79 |

When the concentrations of ligand [L], silver complex [AgL⁺], and silver ion [Ag⁺] are eliminated from these equations one gets the following expression:

$$\frac{1}{K_1} = \left(\frac{C_{Ag}}{A - \epsilon_L C_L} - \frac{1}{\epsilon_1 - \epsilon_L} \right) (\epsilon_1 C_L - A)$$

in which the reciprocal stability constant is expressed by the measurable optical quantities A , ϵ_L , ϵ_1 , and the total concentrations of ligand (C_L), and silver ion (C_{Ag}).

Table 1 shows that the values of K_1 determined at the two wavelengths agree well with each other for the same solution, but that the determinations show considerable variations from solution to solution. However, better agreement can hardly be expected. The average values for K_1 are found to be $10^{5.70}$ in 75.4 % and $10^{5.81}$ in 55.6 % CH₃OH. Extrapolation from these data would suggest the value of about 10^6 l-mole⁻¹ for K_1 in aqueous solution. As the ligand is uncharged, then in dilute solution this value can be assumed to be nearly independent of the ionic strength.

Ahrland, Chatt *et al.*³ determined K_1 for the tri-(*m*-sulphophenyl)arsine-silver complex in aqueous solution at the ionic strength 0.2 to be $10^{5.36}$ at 25°C. Considering that substitution of sulphonic groups weakens the coordinating affinity,³ this result is consistent with our values for the complexing tendency of the unsubstituted ligand.

THE MERCURY (II) CHLORIDE-TRIPHENYLARSINE SYSTEM

When mercuric chloride is added to a methanol solution of triphenylarsine only a small change of the ligand absorption occurs, in effect, a broadening of the band with no change in its maximum, or peak intensity. However, at the foot of the band for wavelengths higher than 300 $m\mu$ a large increase in absorbance occurs. As shown in Fig. 1 in this wavelength range not only the absorbance of mercuric chloride (curve 8), but also that of triphenylarsine (curve 6) is negligible compared with that of the complexes formed (curve 7). For this reason solutions with different concentrations of mercuric chloride and arsine, having the same mean extinction coefficient $\epsilon = A/C_{\text{HgCl}_2}$, fulfil the necessary conditions for what one of the authors⁵ has called "corresponding solutions". This principle has been used to determine the first part of the formation curve for the take up of the arsine molecules by mercuric chloride. The wavelength chosen was 307 $m\mu$.

When the arsine ligand is taken up, chloride ions are displaced from the complex, but we have no quantitative knowledge to what extent this happens. It was therefore decided to determine the formation curve for the mercuric chloride-triphenylarsine system at well-defined concentrations of chloride ions. Experiments were made both in 0.01 M and 0.05 M NaCl solutions; in both cases the ionic strength was adjusted to 0.10 M with NaClO_4 . The experiments in 0.01 M chloride solutions were made in a solvent with 74.5 wt % CH_3OH . The data are given in Table 2. For the solutions Nos. 1–8, $\bar{\epsilon}_{307}$ was measured and matched with identical values on an adjustment curve where $\bar{\epsilon}_{307}$ was plotted *versus* C_L using solutions with $C_{\text{HgCl}_2} = 2.53 \times 10^{-4}$ M. The ligand number \bar{n} and the concentration of the free ligand $[L]$ were obtained from the expressions⁵

Table 2. Data used to estimate the formation curve of the mercury(II) chloride-triphenylarsine system in 74.5 wt % methanol at 25°C. Corresponding solutions were obtained by means of an adjustment curve $\bar{\epsilon}_{307}$ vs C_L with $C_{\text{HgCl}_2} = 2.53 \times 10^{-4}$ M.

| $C_{\text{NaCl}} = 0.0101$ M, $C_{\text{NaClO}_4} = 0.09$ M | | | | | | |
|---|---------------------------------|-------------------|--|-------------------------|-----------|-------------|
| No. | $C_{\text{HgCl}_2} \times 10^4$ | $C_L \times 10^4$ | $\bar{\epsilon}_{307}(\text{corr.})^*$ | $C_L^\circ \times 10^4$ | \bar{n} | $-\log [L]$ |
| 1 | 8.26 | 3.68 | 29.0 | 2.35 | 0.232 | 3.754 |
| 2 | 8.26 | 5.89 | 58.0 | 3.87 | 0.352 | 3.528 |
| 3 | 8.26 | 7.38 | 80.2 | 4.85 | 0.441 | 3.439 |
| 4 | 5.36 | 4.82 | 56.2 | 3.81 | 0.357 | 3.538 |
| 5 | 5.36 | 6.02 | 80.4 | 4.85 | 0.413 | 3.420 |
| 6 | 5.36 | 7.22 | 103 | 5.80 | 0.502 | 3.343 |
| 7 | 5.36 | 9.64 | 151 | 7.73 | 0.675 | 3.221 |
| 8 | 5.36 | 12.0 | 204 | 9.75 | 0.796 | 3.119 |

* $\bar{\epsilon}_{307}$ is corrected for the very small absorption of the ligand not bound to mercuric chloride. This was easily done after a preliminary calculation of the formation curve has been carried through.

$$\bar{n} = \frac{C_L^\circ - C_L}{C_{\text{HgCl}_2}^\circ - C_{\text{HgCl}_2}}$$

$$[L] = \frac{C_{\text{HgCl}_2}^\circ C_L - C_{\text{HgCl}_2} C_L^\circ}{C_{\text{HgCl}_2}^\circ - C_{\text{HgCl}_2}}$$

where C° corresponds to concentrations from the adjustment curve. The formation curve obtained from these calculations is shown in Fig. 3 (curve A) together with the result of similar experiments in 0.05 M chloride solutions (curve B) in a 88.0 wt % methanol solvent.

Addition of chloride should exert a diminishing influence on the tendency to take up arsine molecules, and it is satisfying to see that the shift of the formation curve with the chloride concentration is about what would be expected if the uptake of an arsine molecule is followed by the displacement of one chloride ion. The shift is on average 0.6 log [L]-units, and theoretically should

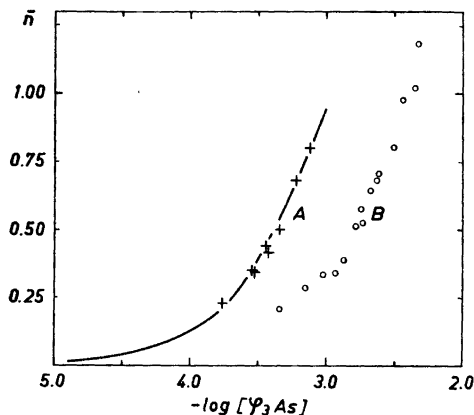


Fig. 3. Formation curves in the system mercury(II) chloride-triphenylarsine in methanol-water mixtures.

Curve A: 74.5 wt % CH_3OH , $[\text{Cl}^-] = 0.01 \text{ M}$, $\mu = 0.1$ ($\text{NaClO}_4 + \text{NaCl}$), 25°C . Experimental points +. The full-drawn curve is calculated with:

$$K_1 = \frac{[\text{HgCl}_{n-1}(\varphi_3\text{As})][\text{Cl}^-]}{[\text{HgCl}_n] \times [\varphi_3\text{As}]} = 13 \text{ l-mole}^{-1}$$

$$K_2 = \frac{[\text{HgCl}_{n-2}(\varphi_3\text{As})_2][\text{Cl}^-]}{[\text{HgCl}_{n-1}(\varphi_3\text{As})][\varphi_3\text{As}]} = 6.8 \text{ l-mole}^{-1}$$

Curve B: 88.0 wt % CH_3OH , $[\text{Cl}^-] = 0.05 \text{ M}$, $\mu = 0.1$ ($\text{NaClO}_4 + \text{NaCl}$), 25°C . Experimental points O.

be expected to be 0.7 log [L]-units in case the solvent media had the same composition. Curve B shows some irregularities in the lower part of the curve, and we have used curve A to estimate the order of magnitude of the formation constants for the equilibria:

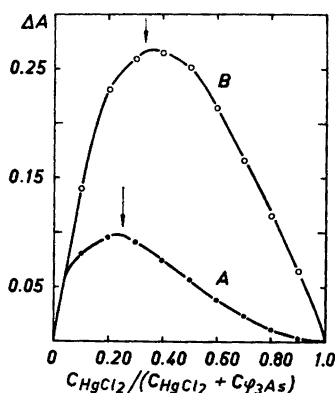
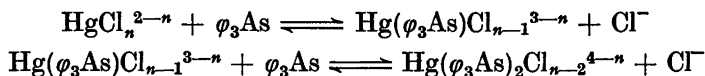


Fig. 4. Job plots for the system mercury(II) chloride-triphenylarsine in methanol-water mixtures at 25°C . The excess absorbance ΔA is plotted versus the mole fraction of the components for the wavelength $307 \text{ m}\mu$.

Curve A: 75.7 wt % CH_3OH , $C_{\text{HgCl}_2} + C_{\varphi_3\text{As}} = 10^{-3} \text{ M}$.

Curve B: 88.0 wt % CH_3OH , $C_{\text{HgCl}_2} + C_{\varphi_3\text{As}} = 2 \times 10^{-3} \text{ M}$, $C_{\text{NaCl}} = 0.05 \text{ M}$, $C_{\text{NaClO}_4} = 0.05 \text{ M}$.



This has been done graphically by plotting the equation:

$$\frac{\bar{n}}{(1-\bar{n})[\varphi_3\text{As}]} = \frac{K_1}{[\text{Cl}^-]} + \frac{K_1K_2(2-\bar{n})[\varphi_3\text{As}]}{[\text{Cl}^-]^2(1-\bar{n})}$$

and inserting 0.01 for the chloride ion concentration. From a good straight line plot K_1 was found to be 13, and K_2 to be 6.8. The full-drawn curve in Fig. 3 is calculated from these values, while the points are the experimental values. The agreement is seen to be good.

Only the first part of the formation curve until $\bar{n} \sim 1$ could be determined because complex compounds began to precipitate at higher ligand concentrations. In the hope of getting some information about the existence of higher complexes, continuous variations studies were made with and without added chloride (NaCl). The plots are shown in Fig. 4, and that for 75.7 wt % methanol without added chloride (curve A) is seen to have a flat maximum approximately at a value of 0.25 for the "mole fraction of mercuric chloride", indicating the addition of 3 triphenylarsine molecules to the mercury central ion. In the plot for 88.0 wt % methanol, 0.05 M in chloride (curve B), the maximum is situated at 0.34 indicating the addition of two arsine molecules per mercury atom. These results predict some range of existence for the complexes in question, but no quantitative conclusions can be drawn.⁶ On the other hand, it has been shown quantitatively that the monoarsine-chloro-mercury(II) complex has a very small range of existence. This result was quite unexpected,⁷ considering that the aquomercury(II)-phosphine system⁸ has a pronounced stop for $\bar{n} = 1$, and is worthy of further study.

Two experiments were carried out in order to determine the composition of the solids which separated from the solutions at high enough concentrations of the components. In the first, equal volumes of 4×10^{-3} M HgCl_2 and 4×10^{-3} M $\varphi_3\text{As}$ in 74 wt % methanol, were mixed. A white precipitate formed, which was filtered, washed with the solvent, and dried. Analysis indicated that it was $\text{Hg}(\varphi_3\text{As})\text{Cl}_2$. (Found: C 37.0; H 2.79; Cl 12.0. Calc.: C 37.4; H 2.62; Cl 12.3).

In the second experiment, solid mercuric chloride was mixed with a 4×10^{-3} M $\varphi_3\text{As}$ solution so that a 3-fold excess of ligand over HgCl_2 was present. Analysis of the precipitate formed corresponded to the formula: $\text{Hg}(\varphi_3\text{As})_{1.5}\text{Cl}_2$. (Found: C 43.4; H 3.10; Cl 9.68. Calc.: C 44.5; H 3.10; Cl 9.72).

The compound $\text{Hg}(\varphi_3\text{As})\text{Cl}_2$ has been prepared before by Mann and coworkers.¹ $\text{Hg}(\varphi_3\text{As})_{1.5}\text{Cl}_2$ seems not to have been prepared before, but other mercury(II) arsine compounds of this type are known.¹ Mann and coworkers¹ have prepared the compounds $\text{Hg}(\varphi_3\text{As})_2\text{X}_2$ with X = Br and I, but have tried in vain to prepare this type of compound with X = Cl.

The compounds formulated with 1 and 1.5 arsine molecule per Hg-atom are generally assumed^{1,2} to be bridged dimers in the crystal lattice, but one cannot draw conclusions from the structure of the isolated solids about the kind of species which exist in the very dilute solutions considered in this paper.

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