

55. *The Relative Affinities of Co-ordinating Atoms for Silver Ion. Part II.*<sup>1</sup> *Nitrogen, Phosphorus, and Arsenic.*<sup>2</sup>

By STEN AHRLAND, J. CHATT, N. R. DAVIES, and A. A. WILLIAMS.

The stability constants of some sulphonated anilines, a sulphonated triphenylphosphine and a sulphonated triphenylarsine with silver(I) ion have been determined in aqueous solution. The affinity of silver ion (as  $\Delta G^\circ$ ) for the phosphine is some 10 kcal. mole<sup>-1</sup>, and for the arsine 6 kcal. mole<sup>-1</sup>, greater than for the anilines. The shapes of the complex-formation curves of a wide variety of ligands with silver ion are remarkable for their variety, and because few of them have the "stop" or inflection, hitherto considered characteristic of silver ion, at  $\bar{n} = 2$ . The shapes are interpreted in terms of  $d_\pi$ -bonding by the co-ordinating atoms. They indicate that the  $d_\pi$ -bonds formed by the phosphine, arsine, and iodide ion are strong compared with those formed by sulphides and selenides, and by chloride ion and bromide ion.

STABILITY constants of a sulphonated aromatic ether, three sulphonated aromatic sulphides, and a selenide with silver ion are known.<sup>1</sup> We now describe corresponding measurements for the sulphonated amines, phosphine, and arsine listed in Table I together with their stability constants. The experimental method and notation are those of Part I except that the highly complex-forming phosphine and arsine necessitated Ag-AgI electrodes for measuring the concentration of silver ion at high ligand concentrations, and indeed even

<sup>1</sup> Part I, preceding paper.

<sup>2</sup> This work was briefly reported at the 10th Solvay Conference (1956), and in *Nature*, 1957, **179**, 1187.

these electrodes were stripped of their silver iodide at the highest concentration of phosphine tried. The constants for the amines were calculated by Leden's method as developed by Fronaeus;<sup>3</sup> as this could not be used for the phosphine and arsine Fronaeus's alternative method (Appendix) was used.

The sulphonated ligands used are not exactly analogous but the differences between their constants are so great that there can be no doubt about the relative affinities of similar amines, phosphines, and arsines for silver ion.

TABLE I. Concentration stability constants,  $K$  (l. mole<sup>-1</sup>) of the ligands, L, with silver ion at an ionic strength  $I$  (M) and 25°.

L	$I$	$K_1$	$K_2$	$K_3$	$K_4$	$\log K_1$
$p\text{-H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	0.1	13.7	9	—	—	1.14
	1	10.7	4.4	2.5	0.8	1.03
$p\text{-Me}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	0.1	5.7	4	—	—	0.76
$m\text{-H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	1	17	8	1.5	1.3	1.23
$m\text{-Ph}_2\text{P}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	0.1	$1.4 \times 10^8$	$0.9 \times 10^6$	$2.5 \times 10^6$	—	8.15
$\text{As}(\text{C}_6\text{H}_4\cdot\text{SO}_3^-m)_3$ .....	0.2	$2.3 \times 10^6$	—	—	—	5.36

The tendency of silver ion to form its strongest complexes with the second or a subsequent, rather than with the first, co-ordinating atom in each Group is evidently very marked in Group V.

The highest constants  $K_1$  for unidentate amines (*e.g.*, ethylamine) are  $< 2.5 \times 10^3$ , whereas the phosphine has the exceptionally high constant of  $1.4 \times 10^8$  l. mole<sup>-1</sup> and the arsine of  $2.3 \times 10^5$  l. mole<sup>-1</sup>. These high constants are remarkable when we consider that they refer to a completely aromatic phosphine and similar arsine, which are known qualitatively to have much weaker affinities than aliphatic derivatives for most acceptor atoms. In Part I we observed that the replacement of the phenyl by an ethyl group in *p*-phenylthiobenzenesulphonate increases the stability constant  $K_1$  with silver ion by a factor of 9, so it seems probable that the aliphatic phosphines might have first stability constants a few orders greater than  $10^8$ . Sulphonation weakens the co-ordinating affinity of *p*-phenylthiobenzenesulphonate<sup>1</sup> ion and of aniline (see below) by a factor of about 2 in the stability constant, so it seems likely that an arsine strictly comparable with the diphenylphosphinobenzenesulphonate ion would have a constant  $K_1$  of about  $10^6$  l. mole<sup>-1</sup>.

The complex between silver ion and the monosulphonated triphenylarsine would thus be weaker than its phosphorus analogue by a factor of about 100 in  $K_1$ . This contrasts with the situation when the co-ordinating atoms belong to Groups VI and VII; the selenide and bromo-complexes of silver(I) are stronger than their sulphide and chloro-analogues respectively (Fig. 2). Nevertheless, it is in keeping with all qualitative evidence regarding the relative stabilities of tertiary arsine and phosphine complexes. There appears to be no example of a complex compound which, with arsenic as its co-ordinating atom, is more stable than its phosphorus analogue.

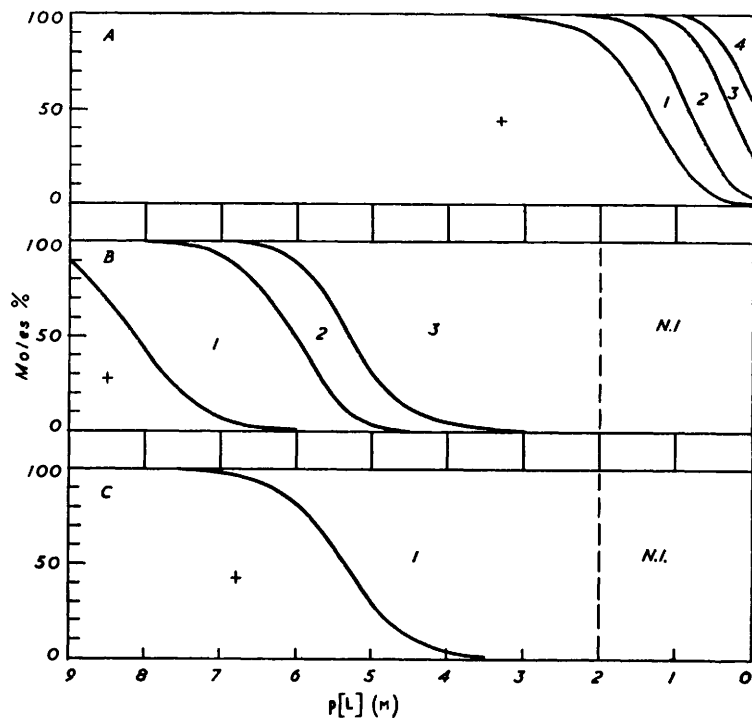
The sulphonated amines are exceptionally weak, as amines, in their co-ordinating affinities for silver ion, largely because the lone pair of electrons on the nitrogen atom is strongly conjugated with the aromatic system. This may be seen on comparing ethylamine<sup>4</sup> ( $K_1 = 2340$  l. mole<sup>-1</sup> in 0.5M-KNO<sub>3</sub> at 25°) with aniline<sup>5</sup> ( $K_1 = 27.5$  in 0.5M-KNO<sub>3</sub> at 25°). The sulphonate ion group must account for the further slight weakening compared with aniline. The values of the stability constants ( $K_1$ , Table I) of the sulphanilate and metanilate are in the sequence expected from their affinities for hydrogen ion (reciprocal of their acid dissociation constants) but the constant  $K_1$  of the *N,N*-dimethylsulphanilate is relatively much smaller ( $1/K_a$  at  $I = 0$  and 25°; sulphanilic acid<sup>6</sup>  $1.6 \times 10^3$ , dimethylsulphanilic acid  $4.0 \times 10^3$ ; metanilic acid<sup>6</sup>  $5.0 \times 10^3$ ). Such weakening of an amine

<sup>3</sup> Fronaeus, "Komplexsystem hos Koppar," Gleerupska Univ.-Bokhandeln, Lund, 1948. See Appendix to Part I.

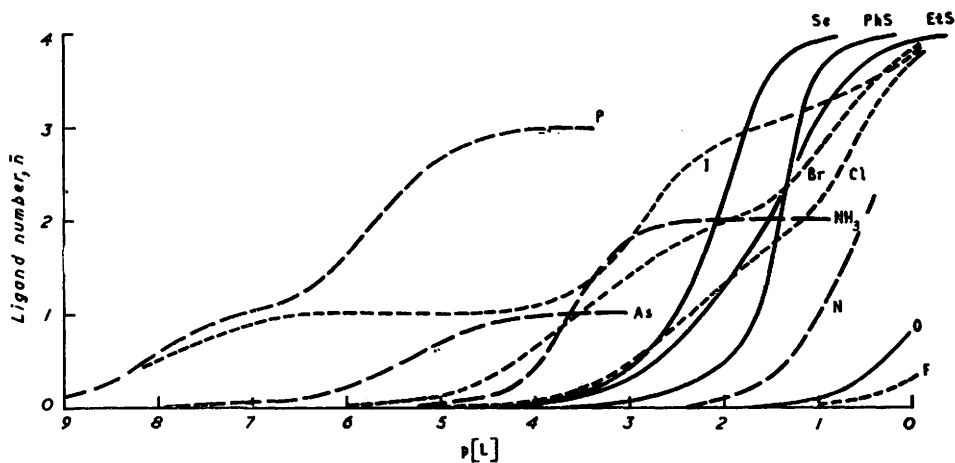
<sup>4</sup> Bruhlman and Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401.

<sup>5</sup> Golombic, *ibid.*, 1952, **74**, 5777.

<sup>6</sup> Beilstein's Handbuch, H 689, 696; E I 718, 720.

FIG. 1. *Regions of stability of the complex ions  $\text{AgL}_n$ , showing the percentages of the total silver content in the form of the various complexes and their variation with  $[\text{L}]$  at 25°.*


A.  $\text{L} = m\text{-H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ ;  $I = 1\text{M}$ .  
 B.  $\text{L} = m\text{-Ph}_2\text{P}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ ;  $I = 0.1\text{M}$ .  
 C.  $\text{L} = \text{As}(\text{C}_6\text{H}_4\cdot\text{SO}_3^- - m)_3$ ;  $I = 0.2\text{M}$ .  
 N.I., not investigated.

 FIG. 2. *Complex-formation curves of silver ion with various unidentate ligands.*


- - - - - Group V co-ordinating atoms (N, P, As).  
 ———— Group VI co-ordinating atoms and groups (O, SEt, SPh, Se).  
 - - - - - Group VII co-ordinating ions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ).

towards complex formation with a metal, compared with hydrogen ion, is usually observed on its complete alkylation.<sup>7</sup>

The sulphanilate and metanilate ion systems are remarkable in that there is no sign of a stop in complex formation at  $\bar{n}$  (ligand number) = 2; previous workers have never reported any evidence that aqueous systems of a monoamine and silver ion contain any other than the species  $\text{AgL}$  and  $\text{AgL}_2$ ; this is the first record of the types  $\text{AgL}_3$  and  $\text{AgL}_4$ .

None of the systems which we have investigated shows any stop in the formation of silver complexes at  $\bar{n} = 2$ . This is emphasised in the diagrams (Fig. 1) which show the regions of stability of the various complexes. They indicate that the  $\text{AgL}_2$  type of complex has no more than an average region of stability and in the case of the phosphine it has by far the smallest region of stability. In the case of the arsine complex the region of the second complex, if it exists, was not reached.

Our measurements, together with Leden's,<sup>8</sup> supply quantitative data concerning the formation of silver ion complexes with a greater variety of co-ordinating atoms than are available for any other metal ion or acceptor molecule. In Fig. 2 the formation curves are shown together with Bjerrum's<sup>9</sup> curve for ammonia. The variety of shapes of formation curves could hardly be greater. They are of three main types: (1) those ( $\text{NH}_3$ , Cl, Br) which have a stop or inflection at  $\bar{n} = 2$ ; (2) an intermediate type (S, Se) where the formation of complexes proceeds uniformly to  $\bar{n} = 4$ ; and (3) those (P, As, I) with a stop or inflection at  $\bar{n} = 1$  and  $\bar{n} = 3$ . Cyanide,<sup>10</sup> azide,<sup>11</sup> and thiocyanate<sup>12</sup> ions also give curves of type (1).

Until now type (1) has been considered characteristic of silver ion, and generally amines appear to have formation curves of this type.<sup>4</sup> Nevertheless, the sulphonated anilines have curves of type (2), and further investigation may show this to be true of other amines, particularly aromatic amines. Evidently the linear  $\text{AgL}_2$  type of complex whose special stability would cause an inflection at  $\bar{n} = 2$  is not favoured by phosphorus, sulphur, selenium, or iodide ion as co-ordinating atoms, or even by nitrogen in the sulphonated amines. Probably arsenic, antimony, and tellurium will behave similarly to phosphorus, sulphur, and selenium. Evidently silver(I) can no longer be regarded as having a characteristic co-ordination number of 2, which is sometimes supplemented by further addition of one or two weakly held ligands. In fact, silver(I) changes its co-ordination number according to the nature of the co-ordinating atoms: 4 is found for more types of co-ordinating atoms than either 2 or 3, so if any is to be considered as characteristic of silver it must be 4. Perhaps it is better to recognise that silver has no characteristic co-ordination number but that the number of unidentate ligand molecules which can be accommodated by silver ion is very sensitive to the nature of the co-ordinating atoms.

The shapes of the formation curves appear to be connected with the  $d_\pi$ -bonding characteristics of the co-ordinating atoms.

The accumulation of qualitative evidence now suggests that with transition-metal ions such as platinum(II) and silver(I), the tendencies of the co-ordinating atoms in their alkyls to form  $d_\pi$ -bonds increase in the order amines < selenides ~ sulphides < arsines < phosphines<sup>13,14</sup> and of the halide ions in the order Cl < Br < I.<sup>15,16</sup>

The chloride and bromide ions probably fit into the first series near the selenides, or in

<sup>7</sup> Chatt and Gamlen, *J.*, 1956, 2371.

<sup>8</sup> Leden, *Svensk kem. Tidsskr.*, 1953, **65**, 88; *Z. Naturforsch.*, 1953, **8a**, 719; *Acta Chem. Scand.*, 1956, **10**, 812.

<sup>9</sup> Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 131.

<sup>10</sup> Jones and Penneman, *J. Chem. Phys.*, 1954, **22**, 965.

<sup>11</sup> Leden and Schön, *Trans. Chalmers Univ. Technology*, Nr. 144, 1954.

<sup>12</sup> Leden and Nilsson, *Z. Naturforsch.*, 1955, **10a**, 67.

<sup>13</sup> Ahrlund and Chatt, *J.*, 1957, 1379 and references quoted therein.

<sup>14</sup> Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

<sup>15</sup> Chatt, Duncanson, and Venanzi, *J.*, 1956, 2712 and references quoted therein.

<sup>16</sup> Chatt and Wilkins, *J.*, 1956, 525.

the case of chloride between the amines and selenides. The iodide ion probably fits between the arsines and phosphines.

The selenides and sulphides and the chloride ion appear to have only a slight tendency to form  $d_{\pi}$ -bonds, and the arsines a definitely lower tendency than the phosphines. The  $d_{\pi}$ -bonding tendencies of sulphides are thus lower than was originally supposed.<sup>17</sup> Our evidence for the above order is mainly from equilibria and infrared spectroscopy. The low position of the sulphide is in agreement with Backhouse, Foss, and Nyholm's observation that dialkyl and alkyl aryl sulphides do not cause electron pairing in nickel(II),<sup>18</sup> and of the arsines relative to the phosphines by our recent observation that the acetylene  $C_2(p-C_6H_4NO_2)_2$  (ac) will displace the chelate  $o-C_6H_4(AsMe_2)_2$  from  $[o-C_6H_4(AsMe_2)_2PtPPh_3]^0$  in preference to the unidentate  $PPh_3$  to give  $[(Ph_3P)_2Pt ac]$  as a product. In a low valency state such as Pt(0)  $d_{\pi}$ -bonding doubtless contributes substantially to stabilise the Pt-P bond.<sup>19</sup>

Against this background it can be seen that the ligands with little or no  $d_{\pi}$ -bonding capacity have formation curves of type 1 tending to type 2; those of rather more  $d_{\pi}$ -bonding capacity have type 2 and those of still greater  $d_{\pi}$ -bonding capacity have type 3.  $p_{\pi}$ -Bonding capacity on the part of the co-ordinating atom does not alter the shape of the formation curve in the same manner; thus CN forms stable  $[Ag(CN)_2]^-$  ions as well as higher species. The fact that the thiocyanate ion has a curve of type 1 suggests that the  $[Ag(SCN)_2]^-$  species in solution is an equilibrium mixture having Ag-N as well as Ag-S bonds.<sup>20</sup>

The way in which  $d_{\pi}$ -bonding on the part of co-ordinating atoms can affect the shape of the formation curve can be explained if we suppose that in the absence of  $d_{\pi}$ -bonding the linear  $AgL_2$  ion such as occurs in solid salts of  $[Ag(NH_3)_2]^+$  and  $[Ag(CN)_2]^-$  is particularly stable. The first ligand molecule to be attached to the aquated silver ion to give the aquated complex,  $AgL$ , will have its attachment strengthened by any dative  $\pi$ -bonding from metal to ligand which might occur.  $d_{\pi}$ -Bonding by the ligand atom on the  $x$  co-ordinate would involve the  $d_{xy}$ - and  $d_{xx}$ -orbitals of the metal probably hybridised with the  $p_y$ - and  $p_x$ -orbitals respectively. These orbitals and electrons in them would also have to be used for  $d_{\pi}$ -bonding to a second ligand molecule if it were attached in the diametrically opposite position to the first. However, since they are already used in bonding to the first they are not so readily available for the second and so its attachment will be delayed. Indeed, if  $d_{\pi}$ -bonding by the ligand atom contributes significantly to bond strength, the second ligand molecule may not attach itself at all in the diametrically opposed position, but rather in a trigonal or tetrahedral position. It can be seen that strong  $d_{\pi}$ -bonding on the part of the co-ordinating atom will lower the stability of the linear complex,  $AgL_2$ , and increase that of the first complex,  $AgL$ ; hence the inflection at  $n = 1$ , when strong  $d_{\pi}$ -bonding occurs to the ligand atom.

The reason for the inflection at  $\bar{n} = 3$  in the case of the stronger  $d_{\pi}$ -bonding ligands is not so clear. It may be connected with the combination of the  $p_x$ - with the  $d_{xx}$ - and  $d_{yz}$ -orbitals of the silver ion to give three trigonally directed  $\pi$ -type orbitals, but electrons are available from the  $d_{xx}$ - and  $d_{yz}$ -orbitals to form only two strong  $\pi$ -type bonds with the ligands.<sup>21</sup> It seems unlikely that this would lead to a very stable trigonal complex, although it may be stabilised relative to the linear complex. In the case of the phosphine complex steric effects are probably largely responsible for the stop in complex formation at  $\bar{n} = 3$ .

Strong  $p_{\pi}$ -bonding by the co-ordinating atoms should not lead to curves of type 3. In such a case the attachment of the first ligand molecule will involve only the electrons from one  $d$ -orbital on the silver ion, say the  $d_{xy}$ , and so those from the  $d_{xx}$ -orbital will

<sup>17</sup> Cf. Chatt and Williams, *J.*, 1951, 3061.

<sup>18</sup> Backhouse, Foss, and Nyholm, *J.*, 1957, 1714.

<sup>19</sup> Chatt, Rowe, and Williams, *Proc. Chem. Soc.*, 1957, 208.

<sup>20</sup> Cf. Lindqvist and Strandberg, *Acta Cryst.*, 1957, 10, 173.

<sup>21</sup> Chatt and Ahrland, *Chem. and Ind.*, 1955, 96.

remain available to attach the second ligand molecule in the diametrically opposed position. Thus the special stability of the linear  $\text{AgL}_2$  type of complexes is not destroyed by  $p_\pi$ -bonding on the part of the ligand atom as the existence of the stable  $[\text{Ag}(\text{CN})_2]^-$  ion shows.

The great variety of formation curves formed by the various ligand molecules with silver ion is as much a property of the silver ion as of the ligand atoms. They arise because silver ion can form stable complexes of linear  $sp$ , trigonal  $sp^2$ , and tetrahedral  $sp^3$  hybridisations, and the solution could contain an equilibrium mixture of hydrated ions of these types. The relative stabilities of these will be altered markedly by the electronegativities, and  $d_\pi$ -type bonding characteristics of the co-ordinating atoms, especially the stability of the  $\text{AgL}_2$ , will be decreased, and those of all forms of  $\text{AgL}$  increased, by  $d_\pi$ -bonding. Our experiments indicate also that the stability of  $\text{AgL}_3$  is increased relative to  $\text{AgL}_2$  by  $d_\pi$ -bonding.

This work was started with the object of determining the relative  $d_\pi$ -bonding capacities of the various donor atoms of Groups V and VI by observing the stabilisation of the  $\text{AgL}$  type of complex relative to the  $\text{AgL}_2$ , but then we did not expect to find evidence of species other than  $\text{Ag}(\text{H}_2\text{O})_2$ ,  $\text{AgL}\cdot\text{H}_2\text{O}$ , and  $\text{AgL}_2$ . The existence of further complexes complicates the situation, but the ratio  $K_1/K_2$  may nevertheless supply some rough measure of the relative  $d_\pi$ -bonding capacities of analogous ligands of the same charge. When ligands carry a higher charge, such as  $\text{S}(\text{C}_6\text{H}_4\cdot\text{SO}_3^-)_2$  or more especially  $\text{As}(\text{C}_6\text{H}_4\cdot\text{SO}_3^-)_3$ , the electrostatic repulsion of the ligands may have a great additional influence on the value of  $K_1/K_2$ . Indeed, for the arsine we have no evidence that more than one ligand was ever taken up over the range of concentrations studied. The ratios  $K_1/K_2$  are given in Table 2.

TABLE 2. The ratio  $K_1/K_2$  for silver ion with a number of ligands containing co-ordinating atoms from Groups V, VI, and VII at  $25^\circ$  ( $\text{NH}_3$ ,  $22^\circ$ ).

L	I	$K_1/K_2$	L	I	$K_1/K_2$
Group V			Group VII		
$\text{NH}_3$ .....	2.0	0.3			
$p\text{-H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	0.1	1.5	$\text{Cl}^-$ .....	0.2	9
	1	2.4		5	6
$p\text{-Me}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	0.1	1.4	$\text{Br}^-$ .....	0.1	15
$m\text{-H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	1	2.1		5	$\approx 20$
$m\text{-Ph}_2\text{P}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	0.1	160	$\text{I}^-$ .....	4	$\approx 10^5$
Group VI			Polysulphonates		
$p\text{-MeO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	1	1	$\text{As}(\text{C}_6\text{H}_4\cdot\text{SO}_3^-m)_3$ .....	0.2	$> 10^4$
$p\text{-EtS}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	0.1	9	$\text{S}(\text{C}_6\text{H}_4\cdot\text{SO}_3^-p)_2$ .....	0.2	3
	0.2	8			
$p\text{-PhS}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	0.1	2.1			
	0.2	3.9			
$p\text{-PhSe}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ .....	0.1	2.4			

The ratios ( $K_1/K_2$ ) of the phosphine<sup>1</sup> and iodide ion are by far the highest amongst ligands of their respective types. This agrees with all our previous experience of the complex chemistry of platinum(II) and palladium(II) with phosphines and iodide ion as ligands, *viz.*, that the  $d_\pi$ -bonding capacity of a phosphine appears to be greater than that of all other ligand atoms in similar circumstances of combination ( $\text{AsR}_3$ ,  $\text{SR}_2$ , etc.) and that of iodide ion is much greater than that of the other halide ions.

#### EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney, of these laboratories.

*Preparation of Ligands.*—The three sulphonates derived from aniline were commercial products recrystallised from water until analyses (C and H) and equivalent weights were correct.

*Sodium diphenylphosphinobenzene-m-sulphonate.* Triphenylphosphine (10 g.) was added slowly with cooling to a mixture of 20%  $\text{SO}_3\text{-H}_2\text{SO}_4$  (19 c.c.) and 65%  $\text{SO}_3\text{-H}_2\text{SO}_4$  (1 c.c.).

The phosphine dissolved and the solution was heated on a water-bath. The solution was tested at intervals by adding one drop to water (2–3 c.c.) until a test drop gave a clear or only slightly cloudy aqueous solution ( $\frac{1}{2}$ –2 hr. depending on the acid strength). The acid solution was cooled, poured cautiously into water (200 c.c.) and neutralised with saturated sodium hydroxide solution. The product separated as fine, white, shining leaves. This may be contaminated by large crystals of sodium sulphate if the solution is allowed to stand too long or is chilled in ice. It was centrifuged off and the soluble part extracted with water. The aqueous extract was evaporated at 100° to crystallisation and cooled; the crystalline product which separated was recrystallised from a small amount of ethyl alcohol (yield 5 g.). Recrystallised from water and dried (50% sulphuric acid), it gave the *dihydrate* (Found: equiv. by ion exchange, 401, 404.  $C_{18}H_{14}O_3SPNa, 2H_2O$  requires equiv., 400). It was characterised as its *benzylisothiuronium salt*, m. p. 146–148° (Found: C, 61.15; H, 5.0; N, 5.5.  $C_{26}H_{25}O_3N_2SP$  requires C, 61.4; H, 4.95; N, 5.5%).

*Trisodium salt of tri-(m-sulphophenyl)arsine (trisodium triphenylarsine-mm'm'-trisulphonate).* Triphenylarsine (20 g.) in 65%  $SO_3-H_2SO_4$  (30 c.c.) was heated on a water-bath for 1½ hr., then poured into water (250 c.c.), and the slight insoluble precipitate which formed was filtered off. The filtrate contains  $Na_3[AsO(C_6H_4SO_3)_3]$ .<sup>22</sup> This arsine oxide was reduced by addition of concentrated hydrobromic acid (150 c.c.) and a few crystals of potassium iodide followed by passage of sulphur dioxide for 19 hr. The dissolved sulphur dioxide was then removed by blowing nitrogen through the solution for 5½ hr. The solution was neutralised with barium hydroxide and finally barium carbonate, the precipitated sulphate was removed from the hot solution and the filtrate taken to dryness.

The white residue was extracted with methanol in a Soxhlet apparatus for 6 hr. to remove barium bromide, ground, and then extracted further with methanol (100 c.c.). To remove the last traces of bromide, the solid was dissolved in the minimum amount of hot water and reprecipitated with a large excess of methanol. The filtered precipitate was then dissolved in hot water (150 c.c.) and caused to crystallise by the addition of methanol (100 c.c.) and cooled. The pure hygroscopic barium salt (8.7 g.) separated, and was converted into the *sodium salt* as previously described, then dried at 130°<sup>23</sup> (Found: C, 34.1; H, 2.3%; equiv., 203.  $C_{18}H_{12}O_9S_3AsNa_3$  requires C, 33.7; H, 2.0%; equiv., 204).

*Orientation of the sulphonated triphenylphosphine and arsine.* The very high heat of solution of triphenylphosphine in sulphuric acid and its resistance to sulphonation leave no doubt that it was sulphonated in the form of the triphenylphosphonium ion. A *meta*-orientation is thus highly probable.

Attempts to obtain the monosulphonated triphenylarsine by using concentrated sulphuric acid in place of  $SO_3-H_2SO_4$  gave triphenylarsine oxide. Evidently the arsine is not sufficiently basic to be protected against oxidation by forming the arsonium salt but is first oxidised and then sulphonated (cf. ref. 22). The AsO group is *meta*-directing and so a *meta*-orientation of the trisulphonate is also highly probable.

We are indebted to Dr. L. A. Duncanson for an infrared investigation of the two sulphonic acids. The absorption bands in the appropriate region of the spectrum are listed in Table 3. Neither substance has bands in the 820  $cm^{-1}$  region where *para*-substituted benzenes have strong bands, but both spectra are consistent with either *meta*- or *ortho*-orientations. To check that *para*-substituted arsines do have strong bands in the 820  $cm^{-1}$  region a number were examined, as follows: (*p*- $Ph_2As \cdot C_6H_4 \cdot SO_3$ )<sub>2</sub>Ca, 823  $cm^{-1}$ , *p*- $Ph_2As \cdot C_6H_4 \cdot NH_2 \cdot HCl$ , 819  $cm^{-1}$ , and *p*- $Ph_2As \cdot C_6H_4 \cdot Br$ , 814  $cm^{-1}$ . The sulphonated phosphine and trisulphonated arsine are certainly not *para*-derivatives, and all available evidence is strongly in favour of a *meta*-orientation for both acids.

TABLE 3. *Infrared spectra of sodium diphenylphosphinobenzene-m-sulphonate and the trisodium salt of tri-(m-sulphophenyl)arsine.*

$Ph_2P \cdot C_6H_4 \cdot SO_3Na, 2H_2O$ ...	794w	784 *	785m	772s	763s	752s	738s	723s	~690m
$As(m-C_6H_4 \cdot SO_3Na)_3$ .....	799s	788s	753m	746s	738s	700 *	691s	673m	

\* Shoulders.

*Determination of Stability Constants.*—These were determined by the titration method described in Part I. The method of calculating stability constants described there was also

<sup>22</sup> Michaelis, *Annalen*, 1902, **321**, 186.

<sup>23</sup> Chatt and Williams, *J.*, 1956, 3246.

used for the present amine systems. It could not be used for the phosphine and arsine because their affinities for silver ion are too high. In these circumstances  $[L]$  in all solutions, except where complex formation is almost complete, is so small compared with  $C_L$ , that all the  $C_L$ - $C_M$  lines pass through the origin within experimental error (see Part I, Fig. 4). Then the intercepts which are necessary for determining the constants cannot be obtained. The method described in Part I can be used for the determination of all the constants  $\beta_1$ ,  $\beta_2$ , etc., only when  $\beta_1 < 1500$  l. mole<sup>-1</sup>. When  $\beta_1$  is higher, an alternative method must be used,<sup>24</sup> and since this has appeared only in Swedish we give the essentials of the method in an Appendix.

*Experimental Technique.*— $[Ag^+]$  was measured by means of silver-silver halide electrodes as described in Part I. Chloride and bromide electrodes were used for the amine complexes and in the initial stages of a titration of silver solutions with the phosphine. Iodide electrodes were essential in the later stages of the phosphine measurements and were used throughout the arsine experiments. In the case of the phosphine even the iodide electrode was used to its limit, and an attempt to extend the range of measurements by using a pure silver electrode failed. The iodide electrodes were prepared analogously to Brown's chloride electrodes,<sup>25</sup> and were brownish-yellow. They were as good as the chloride and bromide electrodes when they were properly prepared but had a shorter life and tended to become erratic more easily. In the amine systems, and in the phosphine and arsine systems at lower ligand concentrations, the reproducibility of the e.m.f. was from 0.1 to 0.4 mv, but often in the latter systems  $E_M$  at high values of  $C_L$  could not be determined with better accuracy than  $\pm 2$  mv. Evidently the rate of the electrode reaction is slowed down very much when  $Ag^+$  is strongly co-ordinated by the phosphine and arsine.

*Systems Investigated.*—Sodium sulphanilate was investigated at  $I = 0.1M$ , to get constants under conditions directly comparable with those of the phosphine. The complexes were so weak, however, that a higher ionic strength  $I = 1M$  had to be used to cover a sufficient range of  $[L]$  to prove the existence of the third and fourth complexes,  $AgL_3$  and  $AgL_4$ . This difference in ionic strength altered the constants very little (Tables 4 and 5). Titrations were also performed with buffer solutions, which besides sulphanilate of the concentration  $C_L'$  also contained sulphanilic acid of a concentration =  $1/5 C_L'$ . These buffer solutions gave the same results as the pure sulphanilate indicating that the silver salt had not been hydrolysed by the more basic sulphanilate solutions.

Sodium dimethylsulphanilate was investigated at  $I = 0.1M$ . It forms weak complexes and only two were formed in appreciable amounts within the range of  $[L]$  used (Table 6). There was no sign of a stop at  $\bar{n} = 2$  and our results do not preclude the existence of higher complexes in solutions of greater  $[L]$ .

The acid dissociation constant was determined for comparison with those of sulphanilic and metanilic acids. Using the quinhydrone electrode at  $I = 0.1M$  and  $25^\circ$  we obtained the value of  $K_a = 4.25 \times 10^{-4}$ . This was corrected to  $K_a = 2.5 \times 10^{-4}$  at  $I = 0$  and  $25^\circ$  by using the Debye-Hückel law.

Sodium metanilate was investigated only at  $I = 1M$  (Table 6) since the influence of ionic strength on the constants could be reasonably estimated from the sulphanilate measurement.

Sodium diphenylphosphinobenzene-*p*-sulphonate was investigated at  $I = 0.1M$  because it is so sparingly soluble that the sodium-ion concentration had to be kept low. Nevertheless, since it forms strong complexes the whole range of complex formation could be followed up to a constant value of  $\bar{n} = 3 = N$ . The upper limit of  $[L]$  was not set by the low ionic strength but by the failure of the  $Ag$ - $AgI$  electrodes. The sodium salt of the third complex  $Na_2[Ag(Ph_2P \cdot C_6H_4 \cdot SO_3)_3]$  was sparingly soluble and so complete titrations could be performed only when  $C_M' \leq 5$  mM. When  $C_L' = 10$  mM, this salt was precipitated as soon as  $C_L$  exceeded ca. 3 mM (Found:  $Ag$ , 8.7%  $C_{12}H_{10}O_9S_3P_3AgNa_2$  requires  $Ag$ , 9.21%). The titrations also had to be abandoned before the formation of complexes was complete when  $C_M' = 1$  mM because the reproducibility of  $E_M$  was too poor at the higher values of  $C_L$  for such a low value of  $C_M'$ .

In spite of these limitations the silver complexes of the phosphine are so strong that the curves of  $C_A$  against  $E_M$  show a pronounced inflection when  $C_L/C_M \approx 3$ , indicating that complex formation is complete. Since  $[L]$  is significant compared with  $[ML_3]$  at this point, about 2% excess of the ligand over the three equivalents is necessary to reach the inflection point.

In Table 8,  $C$  the last two values of  $\beta_3$  should be discarded as the  $Ag$ - $AgI$  electrodes are

<sup>24</sup> Ref. 3, p. 21.

<sup>25</sup> Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 646.



TABLE 4. *The system silver ion-sulphanilate ion ( $C_L' = 0.1M$ ;  $I = 0.1M$ ).*

A. $E_M$ as a function of $C_L$ .						B. Calculation of [L] and derived stability constants.						
$C_M' \rightarrow 10$			$C_M' \rightarrow 10$			$C_M' \rightarrow 10$			0			
$C_L$	$E_M$	$E_M$	$C_L$	$E_M$	$E_M$	$E_M$	$C_L$	$C_L$	$C_L = [L]$	$X$	$X_1$	$X_2$
1.32	0.5	0.5	16.7	5.9	6.1	2	5.8	5.5	5.5	1.081	14.7	
2.60	1.0	1.0	21.1	7.2	7.6	4	12.0	11.1	10.9	1.169	15.5	
3.85	1.4	1.5	25.0	8.6	9.2	6	17.9	16.7	16.4	1.263	16.0	
5.07	1.8	1.9	28.6	9.9	10.5	8	23.5	22.2	21.9	1.366	16.7	137
6.26	2.0	2.1	34.8	11.9	12.5	10	29.1	27.7	27.4	1.476	17.3	131
9.09	3.3	3.5	40.0	13.8	14.5	12	35.0	33.2	32.8	1.595	18.1	134
11.8	4.0	4.3	50.0	18.8	19.8	15	43.6	41.3	40.7	1.793	19.5	143
14.3	4.9	5.2	62.5	21.4	23.0	20	58.0	55.0	54.2	2.178	21.7	148

$\beta_1 = 13.7 \pm 0.8 \text{ l. mole}^{-1}$ ,  $K_1 = \beta_1$ ,  
 $\beta_2 = 120 \pm 20 \text{ l.}^2 \text{ mole}^{-2}$ ,  $K_2 = 9 \text{ l. mole}^{-1}$ ,  
 $\beta_3 \approx 500 \text{ l.}^3 \text{ mole}^{-3}$ .

TABLE 5. *The system silver ion-sulphanilate ion ( $C_L' = 1M$ ;  $I = 1M$ ).*

A. $E_M$ as a function of $C_L$ .						B. Calculation of [L] and derivation of the stability constants.								
$C_M' \rightarrow 17.5$			10			5			$C_M' \rightarrow 10$			5		
$C_L$	$E_M$	$E_M$	$C_L$	$E_M$	$E_M$	$C_L$	$E_M$	$E_M$	$C_L$	$E_M$	$E_M$	$C_L$	$E_M$	$E_M$
6.62		1.5		1.6		1.7		166.7		37.9		38.9		38.9
13.17		3.1		3.2		3.4		189.3		42.3		43.4		43.4
19.62		4.5		4.7		5.0		210.5		46.4		47.5		47.5
26.0		6.1		6.4		6.7		250		53.6		54.8		54.8
38.5		8.9		9.3		9.7		286		59.8		61.1		61.1
50.7		11.7		12.3		12.8		348		69.8		71.0		71.0
62.6		14.3		15.0		15.6		400		77.7		78.9		78.9
90.9		20.8		21.7		22.5		444		83.9		85.1		85.1
117.8				27.7		28.6		500		91.3		92.7		92.7
142.9				33.0		34.0								

$\beta_1 = 10.7 \pm 0.8 \text{ l. mole}^{-1}$ ,  $K_1 = \beta_1$ ,  
 $\beta_2 = 47 \pm 5 \text{ l.}^2 \text{ mole}^{-2}$ ,  $K_2 = 4.4 \text{ l. mole}^{-1}$ ,  
 $\beta_3 = 120 \pm 20 \text{ l.}^3 \text{ mole}^{-3}$ ,  $K_3 = 2.5 \text{ l. mole}^{-1}$ ,  
 $\beta_4 = 100 \pm 30 \text{ l.}^4 \text{ mole}^{-4}$ ,  $K_4 = 0.8 \text{ l. mole}^{-1}$ .

TABLE 6. *The system silver ion-NN-dimethylsulphanilate ion ( $C_L' = 0.1M$ ;  $I = 0.1M$ ).*

A. $E_M$ as a function of $C_L$ .						B. Calculation of [L] and derivation of the stability constants.						
$C_M' \rightarrow 10$			$C_M' \rightarrow 10$			$C_M' \rightarrow 10$			0			
$C_L$	$E_M$	$E_M$	$C_L$	$E_M$	$E_M$	$E_M$	$C_L$	$C_L$	$C_L = [L]$	$X$	$X_1$	$X_2$
1.32	0.2	0.3	28.6	4.2	4.3	1	7.4	6.8	6.7	1.040	6.0	
3.85	0.5	0.6	40.0	5.9	6.0	2	14.4	13.7	13.5	1.081	6.0	
6.26	0.8	0.9	50.0	7.4	7.5	3	21.2	20.4	20.2	1.124	6.1	20
11.8	1.6	1.8	62.5	9.4	9.6	4	27.7	26.9	26.7	1.169	6.3	22
16.7	2.3	2.4	70.0	10.5	10.7	6	40.8	40.0	39.8	1.263	6.6	23
21.1	3.0	3.1				8	53.8	53.1	52.9	1.366	6.7	23
						10	66.4	65.8	65.6	1.476	7.25	24

$\beta_1 = 5.7 \pm 0.3 \text{ l. mole}^{-1}$ ,  $K_1 = \beta_1$ ,  
 $\beta_2 = 23 \pm 5 \text{ l.}^2 \text{ mole}^{-2}$ ,  $K_2 = 4 \text{ l. mole}^{-1}$ .

beginning to fail. The mean of the remaining values is  $\beta_3 = 3 \times 10^{-10} \text{ l.}^3 \text{ mole}^{-3}$ . In this range of  $[L]$ , where complex formation is complete, a value of  $E_M = 600 \text{ mv}$  was chosen, corresponding to  $X([L]_a) = 1.39 \times 10^{10}$  and  $[L]_a = 0.77 \text{ mM}$  [(eqn. (1))]. These values were then used for the calculation of the constants  $\beta_1$  and  $\beta_2$  (Table 8, D). It is to be noted that the value of  $\beta_3$  (Table 8, C) agrees well with that from the  $X$  functions at lower  $[L]$  (Table 8, D).

The trisodium salt of tri-(*m*-sulphophenyl)arsine was investigated at  $I = 0.2M$ . In this case no precipitate was formed even when  $C_M' = 15 \text{ mM}$  up to a ligand concentration of  $C_L \approx 17 \text{ mM}$ . Higher values of  $C_L$  could not be used because the Ag-AgI electrodes failed, although no dissolution of halide took place (cf. p. 277). Thus when  $C_L$  was plotted against  $C_M'$ , good straight lines were not obtained at the highest values of  $E_M$ ; moreover the slopes of the lines, so

TABLE 7. The system silver ion-metanilate ion ( $C_L' = 1M$ ;  $I = 1M$ ).

A.  $E_M$  as a function of  $C_L$ .

$C_M' \rightarrow$	20	10	5	$C_M' \rightarrow$	20	10	5
$C_L$	$E_M$	$E_M$	$E_M$	$C_L$	$E_M$	$E_M$	$E_M$
13.16	4.3	5.0	5.3	285.7	75.1	78.1	79.2
38.47	12.5	14.1	15.0	318.2	81.2	84.0	85.0
62.5	19.9	22.3	23.5	347.9	86.3	88.9	90.0
117.6	36.3	39.7	40.7	400.0	94.8	97.1	98.3
166.6	49.1	52.5	53.7	444.4	101.2	103.6	104.8
210.5	59.5	62.7	63.9	500	109.4	111.2	112.4
250.0	68.0	71.0	72.2				

B. Calculation of  $[L]$  and derivation of the stability constants.

$C_M' \rightarrow$	20	10	5	0					
$E_M$	$C_L$	$C_L$	$C_L$	$C_L = [L]$	$X$	$X_1$	$X_2$	$X_3$	$X_4$
3	9.2	8.0	7.2	6.6	1.124	18.8			
5	15.2	13.2	12.4	11.6	1.215	18.5	129		
7	21.3	18.8	17.6	16.4	1.314	19.1	128		
10	30.6	27.0	25.3	23.6	1.476	20.2	136		
15	46.4	41.0	38.5	35.9	1.793	22.1	142		
20	62.6	55.6	52.4	49.0	2.178	24.0	143		
30	96.0	86.4	82.8	79.0	3.214	28.0	139		
40	132	119	115	110	4.745	34.0	155	227	245
50	170	157	152	146	7.002	41.1	165	240	274
60	212	199	193	187	10.33	49.9	176	246	245
70	260	245	239	232	15.28	61.6	192	267	289
80	311	296	290	283	22.51	76.0	208	276	269
90	370	355	348	340	33.24	94.8	229	291	268
100	435	420	411	403	49.20	119.6	255	310	273
110	505	490	482	474	72.45	150.7	282	321	255

$$\beta_1 = 17 \pm 2 \text{ l. mole}^{-1}.$$

$$\beta_2 = 130 \pm 20 \text{ l.}^2 \text{ mole}^{-2}.$$

$$\beta_3 = 200 \pm 30 \text{ l.}^3 \text{ mole}^{-3}.$$

$$\beta_4 = 250 \pm 50 \text{ l.}^4 \text{ mole}^{-4}.$$

$$K_1 = \beta_1.$$

$$K_2 = 8 \text{ l. mole}^{-1}.$$

$$K_3 = 1.5 \text{ l. mole}^{-1}.$$

$$K_4 = 1.3 \text{ l. mole}^{-1}.$$

far as they could be determined, tended to decrease with increasing  $E_M$ . However, a constant value of  $\bar{n} = 1$  had been reached at lower values of  $E_M$ . This indicates almost complete formation of the first complex and values of  $X_1 = \beta_1$  calculated from  $[L]$ , found as intercepts, are fairly constant (Table 9, B). As the upper values of  $\beta_1$  were suspect the mean was not taken in this case, but a value of  $X([L]_a) = 507.0$ , corresponding to  $E_M = 160 \text{ mv}$  was chosen as the upper limit of integration of eqn. (3). This value was chosen because the corresponding value of  $[L]_a$  was obtained as the intercept of a good straight  $C_L$ - $C_M$  line; also the intercept was sufficiently large to be determined fairly accurately. The values of  $X_1$  resulting from the integration are in the last column of Table 9, B. The constancy is good and also the agreement with the values found from the intercepts. The mean value of  $X_1$  may therefore be taken as an accurate value of  $\beta_1$ .

#### APPENDIX

*Fronaenus's Method for the Determination of Stability Constants when  $\beta_1$  is Greater than or Equal to 1500 l. mole<sup>-1</sup>.*—The notation is defined in the Appendix to Part I (preceding paper). This method by which  $\beta_1$ ,  $\beta_2$  etc. are determined (p. 274) uses the fact that the

TABLE 8. *The system silver ion-diphenylphosphinobenzene-p-sulphonate ion* ( $C_L' = 0.03M$ ;  $I = 0.1M$ ).A.  $E_M$  as a function of  $C_L$ .

$C_M' \rightarrow$	10	5	2	1	$C_M'$	5	2
$C_L$	$E_M$	$E_M$	$E_M$	$E_M$	$C_L$	$E_M$	$E_M$
0.199	—	1.0	2.7	6.0	5.27	—	512
0.395	1.2	2.2	5.7	13.4	5.41	—	551
0.588	—	—	9.1	23.5	5.67	117.6	585
0.779	2.4	4.6	13.1	40.4	6.32	136.4	623
0.968	—	—	17.6	71.7	6.68	—	633
1.154	3.5	7.2	23.2	108.0	7.50	172.5	644
1.338	—	—	—	129.3	8.57	216.5	—
1.52	4.8	10.0	38.7	145.7	9.08	248	—
1.875	6.1	13.1	69.8	173.8	9.55	294	—
2.22	—	16.8	105.8	210.5	9.83	338	—
2.39	—	—	—	235.9	10.00	382	—
2.725	—	23.4	132.3	—	10.18	450	—
3.22	—	—	154.6	—	10.26	482	—
3.53	—	39.3	170.8	—	10.35	510	—
3.99	—	—	199.3	—	10.43	534	—
4.28	—	69.0	224.5	—	10.61	566	—
4.72	—	—	282.6	—	10.86	592	—
5.00	—	97.8	366	—	11.25	616	—
5.13	—	—	445	—	12.00	638	—

B. Determination of  $\bar{n}$  over the whole range of complex formation.

$C_M' \rightarrow$	10	5	2	1	$C_M'$	5	2
$E_M$	$C_L$	$C_L$	$C_L$	$C_L$	$E_M$	$C_L$	$E_M$
2	0.67	0.36	0.16	—	2	0.67	0.36
5	1.58	0.83	0.35	0.17	5	1.58	0.83
10	2.86	1.52	0.63	0.31	10	2.86	1.52
15	3.86	2.05	0.87	0.43	15	3.86	2.05
20	4.67	2.48	1.04	0.53	20	4.67	2.48
30	—	3.12	1.34	0.68	30	—	3.12
40	—	3.55	1.53	0.78	40	—	3.55
70	—	4.31	1.88	0.97	70	—	4.31
100	—	5.05	2.15	1.09	100	—	5.05
125	—	5.92	2.58	1.31	125	—	5.92
150	—	6.77	3.12	1.60	150	—	6.77
175	—	7.56	3.61	1.89	175	—	7.56
200	—	8.23	4.00	2.14	200	—	8.23
230	—	8.82	4.36	2.35	230	—	8.82
280	—	9.44	4.71	2.68	280	—	9.44
350	—	9.87	4.93	2.89	350	—	9.87
450	—	10.18	5.14	3.00	450	—	10.18

C. Determination of  $\beta_3$  from solutions of high  $C_L$  where complex formation is complete.

$C_M' \rightarrow$	5	2					
$E_M$	$C_L$	$C_L$	$C_L = [L]$	$\bar{n}$	$X$	$10^{-19}\beta_3$	
500	10.31	5.25	0.24	3.03	$2.85 \times 10^8$	2.1	
550	10.50	5.42	0.39	3.1	$2.0 \times 10^9$	3.3	
580	10.72	5.62	0.56	3.2	$6.5 \times 10^9$	3.7	
600	10.96	5.86	0.80	3.2	$1.4 \times 10^{10}$	3.2	
620	11.33	6.27	1.25	3.1	$3.1 \times 10^{10}$	(1.6)	
640	12.10	7.20	2.35	3.1	$6.8 \times 10^{10}$	(0.52)	

D. Calculation of  $[L]$  and derivation of  $\beta_1$  and  $\beta_2$ .

$E_M$	$\bar{n}$	$\log [L]_a/[L]$	$[L]$	$X$	$10^{-8}X_1$	$10^{-14}X_2$	$10^{-19}X_3$
2	0.068	6.154	$0.54 \times 10^{-6}$	1.081	1.5	—	—
5	0.168	5.704	$1.52 \times 10^{-6}$	1.215	1.43	—	—
10	0.318	5.344	$3.48 \times 10^{-6}$	1.476	1.37	—	—
15	0.443	5.120	$5.83 \times 10^{-6}$	1.793	1.36	—	—
20	0.550	4.950	$8.63 \times 10^{-6}$	2.178	1.37	—	—
30	0.695	4.678	$1.61 \times 10^{-5}$	3.214	1.37	—	—
40	0.805	4.460	$2.67 \times 10^{-5}$	4.745	1.40	—	—
70	1.00	3.904	$9.6 \times 10^{-5}$	15.28	1.49	1.25	—
100	1.15	3.428	$2.87 \times 10^{-4}$	49.04	1.68	1.08	—
125	1.45	3.096	$6.17 \times 10^{-4}$	129.7	2.08	1.15	—
150	1.74	2.832	$1.13 \times 10^{-3}$	343.5	3.03	1.47	2.4
175	1.98	2.604	$1.91 \times 10^{-3}$	908	4.75	1.77	3.0
200	2.22	2.404	$3.04 \times 10^{-3}$	2405	7.92	2.16	3.2
230	2.42	2.186	$5.01 \times 10^{-3}$	7730	15.4	2.80	3.2
280	2.68	1.852	0.0108	54,100	50.2	4.52	3.1
350	2.89	1.432	0.0285	$8.26 \times 10^5$	290	10.15	3.1
450	3.00	0.846	0.1096	$4.04 \times 10^7$	3690	33.7	3.0
500	3.0	0.564	0.210	$2.83 \times 10^8$	13,500	64.3	3.0
600	3	0	$[L]_a = 0.77$	$X([L]_a) = 1.39 \times 10^{10}$	—	—	—

$$\beta_1 = 1.4 \pm 0.2 \times 10^8 \text{ l. mole}^{-1}.$$

$$\beta_2 = 1.2 \pm 0.2 \times 10^{14} \text{ l.}^2 \text{ mole}^{-2}.$$

$$\beta_3 = 3 \pm 0.5 \times 10^{19} \text{ l.}^3 \text{ mole}^{-3}.$$

$$K_1 = \beta_1.$$

$$K_2 = 0.9 \times 10^6 \text{ l. mole}^{-1}.$$

$$K_3 = 2.5 \times 10^5 \text{ l. mole}^{-1}.$$

slopes of the  $C_L$ - $C_M$  lines, which are equal to the ligand number  $\bar{n}$ , can be determined more accurately when the complexes formed are strong than when they are weak. This arises because the family of curves of  $C_L$  against  $E_M$  at constant  $C_M$  (see Part I, Fig. 3) is better spaced. Also, when strong complexes are formed,  $\bar{n}$  will usually reach its maximum value  $N$  within the range of  $[L]$  available. Hence at a sufficiently high  $[L]$  the  $C_L$ - $C_M$

TABLE 9. The system silver ion-trianion of tri-(m-sulphophenyl)arsine ( $C_L' = 0.0333M$ ;  $I = 0.2M$ ).A.  $E_M$  as a function of  $C_L$ .

$C_M' \rightarrow 15$					$C_M' \rightarrow 10$				
$C_L$	$E_M$	$E_M$	$E_M$	$E_M$	$C_L$	$E_M$	$E_M$	$E_M$	$E_M$
0.44	0.9	1.3	2.7	6.8	7.55	—	88.5	—	—
0.87	1.8	2.8	5.7	15.4	7.82	—	109.1	—	—
1.28	2.6	4.1	8.8	28.8	8.07	—	124.4	—	—
1.69	—	5.6	12.6	55.7	8.33	37.3	135.0	179.0	191.3
2.08	4.5	7.0	16.8	101.3	8.93	46.5	151.4	—	—
2.47	—	8.6	21.8	125.0	9.51	59.9	161.4	186.4	197.0
2.84	—	10.4	28.0	137.7	10.07	85.1	—	—	—
3.03	7.1	—	31.9	142.2	10.60	122.5	174.1	192.0	201.3
3.21	—	12.2	36.2	145.9	11.10	143.6	—	—	—
3.57	—	14.1	48.1	152.3	11.58	155.4	182.4	196.5	205.1
3.74	—	—	57.3	—	12.49	169.7	188.5	200.1	—
3.92	9.9	16.3	65.9	157.5	13.32	178.8	193.3	203.4	211.4
4.26	—	—	96.5	—	14.09	185.4	—	206.1	—
4.76	12.9	22.3	127	166.8	14.80	190.4	200.6	208.6	216.2
5.55	16.4	29.7	148.8	174.2	15.46	194.6	—	210.8	—
6.30	20.3	40.7	—	—	16.08	198.0	—	212.8	—
7.01	25.0	58.8	168.0	184.1	16.65	200.9	208.1	214.5	222.1
7.28	—	70.9	—	—	—	—	—	—	—

B. Calculation of  $[L]$  and derivation of  $\beta_1$ .

$C_M' \rightarrow$	15	10	5	2	0							
$E_M$	$C_L$	$C_L$	$C_L$	$C_L$	$C_L = [L]$	$X$	$10^{-5}X_1^*$	$\bar{n}$	$\log \frac{[L]_a}{[L]}$	$[L]$	$10^{-5}X_1^\dagger$	
1	0.50	0.33	0.16	0.08		1.040		0.034	4.3039	$1.20 \cdot 10^{-4}$	(3.3)	
2	1.00	0.65	0.32	0.16		1.081		0.068	3.9519	$2.70 \cdot 10^{-4}$	(3.0)	
3	1.44	0.96	0.48	0.22		1.124		0.100				
4	1.88	1.24	0.62	0.28		1.165		0.131	3.5960	$6.13 \cdot 10^{-4}$	2.7	
6	2.62	1.80	0.91	0.40		1.263		0.190				
8	3.32	2.32	1.18	0.51		1.365		0.249				
10	3.95	2.76	1.41	0.61		1.476		0.299	3.1050	$1.90 \cdot 10^{-3}$	2.51	
15	5.24	3.71	1.92	0.85		1.792		0.416				
20	6.25	4.46	2.34	1.03		2.178		0.514	2.6786	$5.07 \cdot 10^{-3}$	2.32	
30	7.60	5.58	2.94	1.31		3.215		0.665	2.3831	$1.00 \cdot 10^{-2}$	2.22	
40	8.51	6.26	3.34	1.54		4.744		0.768	2.1483	$1.72 \cdot 10^{-2}$	2.18	
50	9.10	6.72	3.61	1.64		7.003		0.838				
60	9.50	7.05	3.80	1.75		10.34		0.888	1.7431	$4.37 \cdot 10^{-2}$	2.14	
80	9.98	7.42	4.08	1.90		22.52		0.934				
100	10.26	7.72	4.30	2.07		49.04		0.959	1.0387	$2.21 \cdot 10^{-1}$	2.17	
120	10.55	7.97	4.59	2.38	0.60	106.8	(1.75)	0.975	0.6899	$4.94 \cdot 10^{-1}$	2.14	
140	11.01	8.49	5.10	2.92	1.15	232.7	2.02	0.981	0.3446	1.094	2.12	
160	11.85	9.40	6.33	4.10	2.41	507.0	2.10	0.980	0	$2.41 = [L]_a$	2.10	
170	12.52	10.22	7.20	5.05	3.40	748.1	2.20	0.983				
180	13.44	11.21	8.48	6.37	4.90	1104	2.25	0.983				
190	14.69	12.72	10.18	8.02	7.05	1630	2.31	—				
200	16.45	14.65	12.41	10.21	9.60	2405	2.50	—				
210	—	17.2	15.21	12.92	12.70	3550	(2.80)	—				

$$\beta_1 = K_1 = 2.3 \pm 0.3 \times 10^6 \text{ l. mole}^{-1}.$$

\* Calculated from values of  $[L]$  found by extrapolation to  $C_M = 0$ .

† Calculated from values of  $[L]$  found from eqn. (3).

lines at constant  $E_M$  (see Part I, Fig. 4) will run parallel, with their slopes equal to  $N$ , which can thus be determined.

As  $C_L$  increases and complex formation approaches completion, *i.e.*,  $\bar{n} \rightarrow N$ ,  $[L]$  will sooner or later become comparable in magnitude to  $C_L$ . It will then be possible again to determine  $[L]$  from the intercept of the  $C_L$ - $C_M$  curves. In the case of extremely strong complexes such as those formed by the phosphine, this happens only when  $C_L > N \times C_M$ . In such solutions the highest complex  $ML_N$  is completely dominating and  $C_M = [ML_N]$ . The function  $X$ , which is directly calculated from  $E_M$  [see Part I, eqns. (1), (2), and (7)], can then be simplified to

$$X = \beta_N [L]^N \quad \dots \quad (1)$$

where corresponding values of  $X$  and  $[L]$  and the constant  $N$  are known, and hence  $\beta_N$ .

In order to find the lower constants  $\beta_1, \beta_2$ , etc., eqn. (10) of Part I is transformed to give eqn. (2):

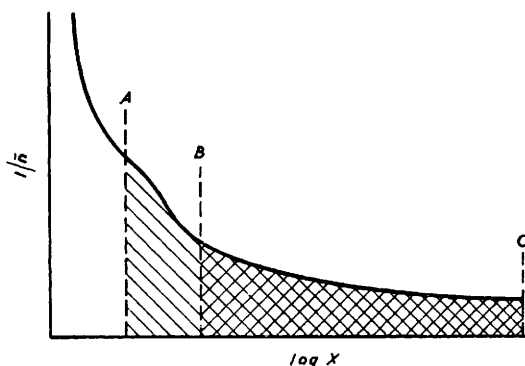
$$\bar{n} = \frac{\sum_{n=1}^N n\beta_n[L]^n}{X} = \frac{[L] \frac{dX}{d[L]}}{X} = \frac{dX}{X} / \frac{d[L]}{[L]} = \frac{d \log X}{d \log [L]} \quad \dots \quad (2)$$

On integration this gives eqn. (3):

$$\log \frac{[L]_a}{[L]_j} = \int_{X([L]_j)}^{X([L]_a)} \frac{1}{\bar{n}} d \log X \quad \dots \quad (3)$$

If the corresponding values  $[L]_a$  and  $X([L]_a)$  are chosen within a range where  $[L]_a$  can be determined as the intercept of a  $C_L$ - $C_M$  line, it is possible to find the value of  $[L]_j$  corresponding to any chosen value  $X([L]_j)$  by evaluating the integral of eqn. (3). This is conveniently done graphically by plotting  $1/\bar{n}$  as a function of  $\log X$  to give a curve as shown in Fig. 3, and measuring the areas under the curve from a fixed limit,  $\log X([L]_a)$  ( $A$  in Fig. 3), to various lower limits,  $\log X([L]_j)$  ( $B, C$  in Fig. 3). Corresponding values of  $X$  and  $[L]_j$  are thus obtained over the whole range of complex formation and the stability constants of the lower complexes are calculated as usual [Part I, eqns. (3) and (4)]. The best values of  $[L]_a$  and  $X([L]_a)$  to serve as the fixed upper limit can be obtained from the value of  $\beta_N$  found above. In the range of  $[L]$  (or  $E_M$ ) where the relation  $X = \beta_N[L]^N$  holds, a value of  $E_M$  is chosen and corresponding values of  $X([L]_a)$  and  $[L]_a$  are calculated.

FIG. 3.



If polynuclear complexes exist the slopes of the  $C_L$ - $C_M$  lines are no longer equal to  $\bar{n}$  but to a quantity less than  $\bar{n}$ . The above method therefore presumes that polynuclear complexes are not formed. This is not easy to prove experimentally, but an indication can be obtained by the method described in Part I over the range where  $[L]$  can be determined by the intercept method. Even if no polynuclear complexes are formed in this range of high  $[L]$  it cannot be assumed that they are not formed at lower values of  $[L]$  and our main arguments for supposing that they are not formed in our phosphine and arsine systems are (i) that there is only one strong donor atom in each ligand molecule and (ii) that the analogous sulphides and selenide were shown experimentally not to give polynuclear complexes although they were in equilibrium with a much higher  $[Ag^+]$  at low  $[L]$  than the phosphine and the arsine.