

1019. *Ligands containing Elements of Group V. Part I.*

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The acid dissociation constants of *N*-2-carboxyethyldiphenylamine and of its phosphorus and arsenic analogues $[(C_6H_5)_2X(CH_2CH_2CO_2H)]$; $X = N, P, \text{ or } As$] have been measured in 20% (v/v) aqueous dioxan at 20.0° and at constant ionic strength $\mu = 0.1$ (KNO₃). None of these ligands formed complexes of measurable stability with nickel, copper, zinc, or cadmium: only the ligands containing phosphorus and arsenic gave complexes with Ag⁺, and these showed a strong tendency to protonation.

Proton- and metal-stability constants have been measured in water at 20.0° for *NN*-di(carboxymethyl)aniline and its arsenic analogue $[C_6H_5 \cdot Y(CH_2CO_2H)_2]$; $Y = N \text{ or } As$] and for *AsAs*-di-(2-carboxyethyl)-*p*-chlorophenylarsine. Although the ligand containing nitrogen resembled *NN*-di(carboxymethyl)cyclohexylamine in forming strong chelate complexes with nickel, copper, cadmium, and zinc, and a weak complex with Ag⁺, the ligands containing arsenic formed very weak complexes with the transition metals but strong 1:1 complexes, and protonated 1:1 complexes with Ag⁺. Complex formation with mercury(II) and copper(I) was also studied and the results are discussed in terms of the difference in behaviour of metals of class (a) and class (b) towards N, P, and As as donor atoms.

FOR many years it has been recognised that metals acting as acceptors to ligand atoms could be divided into two types: those forming their most stable complexes with the first atoms of each group of the Periodic Table, *i.e.*, nitrogen, oxygen, and fluorine [class (a) metal ions], and those forming more stable complexes with the second or a subsequent atom of any particular group [class (b)].^{1,2} In this context, every oxidation state must be considered as a different acceptor ion. The majority of metals belong to class (a). Since this class also contains the hydrogen ion, the affinities of ligands for class (a) acceptors tend to run approximately parallel to their basicities: hence the relative stabilities of the complexes formed are what would be expected were the complex formation essentially electrostatic in character. The acceptors from class (b) are few, and all lie in a central position in the Periodic Table. There is, however, no rigid boundary between the elements of these two

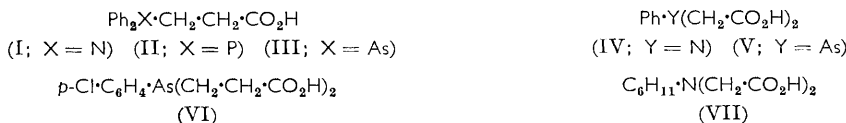
¹ S. Ahrland, J. Chatt, and N. Davies, *Quart. Rev.*, 1958, **12**, 265.

² H. Irving, *Chem. Soc. Special Publ. No. 13*, 1959.

classes,^{1,2} and although much is known about the co-ordinating tendencies of all the ligand atoms of group VII of the Periodic Table,³ quantitative data relating to heavier donor atoms of group V are very sparse.

The first member of group V, nitrogen, is one of the most widely investigated donor atoms, but quantitative measurements of the properties of subsequent members of the group are restricted to only one detailed investigation.⁴ There are two reasons for this: most of the metals of group (b) form inert complexes which, in general, cannot be studied by equilibrium methods; hence only qualitative comparisons of their stabilities can be made. In addition, molecules containing trivalent phosphorus or arsenic as donor atoms tend to be readily oxidised. If this valency state is stabilised by substitution of the donor atoms by suitable aromatic groups, the solubility in water generally becomes impracticably low. Ahrland, Chatt, Davies, and Williams have overcome these difficulties in measurements of the stabilities of complexes of silver with certain unidentate ligands by making these water-soluble by the introduction of one or more sulphonic acid groups into the phenyl groups attached to the donor atoms.⁴ We have now attempted to extend this field of investigation to a wider range of metal ions and to ligands capable of forming chelate rings in which nitrogen has been replaced in turn by phosphorus and arsenic.

For comparison, molecules identical in all but the group V donor atom are required. Such a series was found in *N*-2-carboxyethyldiphenylamine (I) and its phosphorus and arsenic analogues (II and III, respectively). *NN*-Di(carboxymethyl)phenylamine (IV) and its arsenic analogue (V) provided further comparison, but the phosphorus analogue could not be prepared. In addition, complexes of *AsAs*-di-(2-carboxyethyl)-*p*-chlorophenylarsine (VI) and *NN*-di(carboxymethyl)cyclohexylamine (VII) were studied to obtain further information on complexones of the types (IV) and (V). Since it was considered unlikely that six-membered chelate rings would be formed from compounds (I)—(III), they should show the



effects of replacing nitrogen successively by a phosphorus and an arsenic atom. In compounds (IV), (V), and (VII), chelate formation was expected, and comparison of compounds (V) and (VI) would permit some assessment of the effect of an increase in the size of the chelate rings.

The acid dissociation constants of these ligands and the stabilities of their complexes with various metal ions, including Ag^+ , Cu^{2+} , Ni^{2+} , and Zn^{2+} , were calculated from potentiometric titration measurements made at 20.0° in a medium of constant ionic strength (0.1M- KNO_3). In titrations in the presence of Ag^+ ions, a silver/silver iodide electrode was used as well as a glass electrode. All the compounds proved soluble in water to at least 0.002M, with the exception of the diphenyl-substituted derivatives (I)—(III), and all measurements on these three compounds were carried out in 20% v/v aqueous dioxan. The solubility of the arsine derivative (III) in water was found by titration to be $1.16 \times 10^{-4}\text{M}$ at 20.0°.

EXPERIMENTAL

Materials.—*N*-2-Carboxyethyldiphenylamine (I). A method similar to that described by Cookson and Mann was followed.⁵ The nitrile was prepared by heating diphenylamine (40 g.), vinyl cyanide (18 ml.), acetic acid (18 ml.), copper acetate (2 g.), and copper powder (4 g.) to 150° for 8 hr. in a sealed Carius tube. When the reaction mixture had cooled, volatile constituents were removed by distillation under reduced pressure on a water-bath. Free acetic acid was neutralised with anhydrous sodium carbonate and the nitrile, together with unchanged

³ "Inorganic Ligands," *Chem. Soc. Special Publ.* No. 6, Part II, 1958.

⁴ S. Ahrland, J. Chatt, N. Davies, and A. Williams, *J.*, 1958, 264, 276.

⁵ R. Cookson and F. G. Mann, *J.*, 1959, 67.

diphenylamine, extracted with cyclohexane. The cyclohexane was removed by distillation, and the nitrile hydrolysed by heating it under reflux for 4 hr. with potassium hydroxide (40 g.) in water (200 ml.) and ethanol (150 ml.). Ethanol was removed by distillation, the residue cooled, and the unchanged diphenylamine separated and removed. The filtrate was acidified with hydrochloric acid to pH 2.5, the required acid separating as a light brown oil, which slowly

TABLE I.

(a) Titrations in 20% v/v dioxan. Initial volume = 20.0 ml.; alkali = 0.1030N; $\mu = 0.10M$ (KNO_3).

(i) N-(2-Carboxyethyl)diphenylamine (I). $C_L = 0.00100M$.												
Alkali (ml.)	0.00	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22
pH	4.13	4.40	4.59	4.77	4.93	5.09	5.26	5.49	5.74	6.17	8.90	10.00
(ii) P-(2-Carboxyethyl)diphenylphosphine (II). $C_L = 0.00100M$; $C_{Ag} = 0.00100M$.												
Alkali (ml.)	0.00	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22
pH (ligand only)	4.13	4.33	4.52	4.70	4.88	5.05	5.25	5.46	5.65	5.85	6.05	6.25
pH (ligand + Ag)	3.91	4.06	4.20	4.34	4.49	4.65	4.82	5.03	5.20	5.38	5.55	5.72
E_{Ag} (v)	0.3531	0.3522	0.3512	0.3502	0.3493	0.3484	0.3475	0.3466	0.3457	0.3447	0.3437	0.3428
Alkali (ml.)	0.16	0.18	0.20	0.22	0.24	0.26	0.28	0.30	0.32	0.34	0.36	0.38
pH (ligand only)	5.78	6.35	8.60	9.80								
pH (ligand + Ag)	5.31	5.80	8.00									
E_{Ag} (v)	0.3457	0.3447	0.3451	volts								
(iii) As-(2-Carboxyethyl)diphenylarsine (III). $C_L = 0.000875M$; $C_{Ag} = 0.00100M$.												
Alkali (ml.)	0.00	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22
pH (ligand only)	4.22	4.50	4.75	4.96	5.17	5.38	5.63	5.99	7.00			
pH (ligand + Ag ⁺)	3.88	4.03	4.20	4.37	4.55	4.75	5.00	5.36	6.20			
E_{Ag} (v)	0.3390	0.3376	0.3361	0.3348	0.3333	0.3318	0.3298	0.3278	0.3251			

(b) Titrations in water. $\mu = 0.10M$ (KNO_3). Initial volume = 20.0 ml.

(i) AsAs-Di(carboxymethyl)phenylarsine (V). $C_L = 0.00500M$; $C_{Cu} = 0.00250M$; alkali = 0.465N.												
Alkali (ml.)	0.00	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22
pH (ligand alone)	2.97	3.09	3.21	3.34	3.46	3.59	3.71	3.84	3.96	4.10	4.24	4.38
pH (ligand + Cu ²⁺)	2.96	3.07	3.18	3.30	3.42	3.54	3.65	3.78	3.88	4.01	4.13	4.26
Alkali (ml.)	0.24	0.26	0.28	0.30	0.32	0.34	0.36	0.38	0.40	0.42	0.44	0.46
pH (ligand alone)	4.52	4.66	4.79	4.93	5.07	5.22	5.40	5.59	5.87	6.44	9.98	
pH (ligand + Cu ²⁺)	4.38	4.52	4.65	4.77	4.90	5.05	5.20	5.33	5.50	5.70	~6	
$C_L = 0.000966M$; $C_{Ag} = 0.00100M$; alkali = 0.1030N.												
Alkali (ml.)	0.00	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22
pH	3.25	3.29	3.34	3.39	3.45	3.51	3.57	3.64	3.72	3.80		
E_{Ag} (v)	0.3211	0.3203	0.3194	0.3187	0.3173	0.3157	0.3141	0.3121	0.3099	0.3076		
Alkali (ml.)	0.20	0.22	0.24	0.26	0.28	0.30	0.32	0.34	0.36	0.38		
pH	3.89	3.97	4.07	4.19	4.32	4.47	4.67	4.93	5.39	8.75		
E_{Ag} (v)	0.3051	0.3023	0.2991	0.2957	0.2916	0.2870	0.2815	0.2750	0.2674	0.2600		
(ii) AsAs-Di-(2-carboxyethyl)-p-chlorophenylarsine (VI). $C_L = 0.00094M$; $C_{Ag} = 0.00100M$.												
Alkali (ml.)	0.00	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22
pH (ligand only)	3.70	3.80	3.91	4.02	4.13	4.24	4.34	4.44	4.54	4.64		
pH (ligand + Ag)	3.49	3.55	3.62	3.70	3.78	3.86	3.94	4.03	4.11	4.21		
E_{Ag} (v)	0.3220	0.3215	0.3207	0.3198	0.3187	0.3174	0.3161	0.3146	0.3126	0.3103		
Alkali (ml.)	0.20	0.22	0.24	0.26	0.28	0.30	0.32	0.34	0.36	0.38		
pH (ligand only)	4.74	4.84	4.96	5.09	5.23	5.39	5.62	5.94	6.79			
pH (ligand + Ag)	4.31	4.41	4.52	4.65	4.80	4.98	5.24	5.64	6.50			
E_{Ag} (v)	0.3080	0.3056	0.3027	0.2994	0.2959	0.2918	0.2870	0.2818	0.2769			
(iii) NN-Di-(carboxymethyl)cyclohexylamine (VII). $C_L = 0.00100M$; $C_M = 0.00100M$; alkali = 0.1030N.												
Alkali (ml.)	0.00	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22
pH (ligand alone)	3.11	3.16	3.21	3.27	3.34	3.43	3.54	3.68	3.88	4.26		
pH (ligand + Cu ²⁺)	2.88	2.90	2.93	2.95	2.98	3.01	3.05	3.09	3.13	3.18		
Alkali (ml.)	0.20	0.22	0.24	0.26	0.28	0.30	0.32	0.34	0.36	0.38		
pH (ligand alone)	7.31	9.65	9.91	10.13	10.28	10.40	10.50	10.59	10.65	10.70		
pH (ligand + Cu ²⁺)	3.23	3.28	3.35	3.43	3.53	3.65	4.80	4.03	4.44	5.77		
pH (ligand + Zn ²⁺)	4.75	5.21	5.53	5.80	6.05	6.30	6.56	6.87	7.22	7.66 *		
pH (ligand + Ni ²⁺)	4.51	4.86	5.12	5.36	5.57	5.79	6.03	6.26	6.58	6.98		
pH (ligand + Cd ²⁺)	5.09	5.61	5.59	6.21	6.45	6.69	6.94	7.22	7.58	8.00 *		
pH (ligand + Ag ⁺)	6.35	8.00	8.47	8.78 *								

* Precipitation took place.

TABLE I. (Continued.)

(c) Data used in the calculation of the formation constants of the mercury complexes.
 $E^\circ = 0.5965$ v.

(i) Compound (IV).								
$10^4 C_L$ (M)	8.42	8.36	8.34	8.32	8.32			
$10^4 C_{Hg}$ (M)	7.56	7.51	7.48	7.47	7.47			
pH	3.21	4.08	4.51	4.80	5.29			
E_{Hg} (v)	0.3800	0.3371	0.3190	0.3047	0.2760			
(ii) Compound (V).								
$10^4 C_L$ (M)	9.50	9.62	9.48	10.00	9.62	9.93	9.66	9.66
$10^4 C_{Hg}$ (M)	5.95	4.48	2.94	2.98	2.98	2.96	3.00	2.08
pH	1.60	1.83	2.56	2.84	3.14	3.25	3.49	3.69
E_{Hg} (v)	0.3224	0.3078	0.2655	0.2477	0.2274	0.2189	0.2075	0.1887
$10^4 C_L$ (M)	9.88	9.85	0.57	9.83	9.24	9.66	9.82	9.24
$10^4 C_{Hg}$ (M)	2.94	2.93	2.96	2.93	1.46	2.09	2.91	1.46
pH	3.65	4.02	4.12	4.62	4.63	4.77	5.06	5.33
E_{Hg} (v)	0.1930	0.1708	0.1677	0.1424	0.1273	0.1250	0.1297	0.1010
$10^4 C_L$ (M)	9.24	9.61	9.52	9.76	9.24	9.57		
$10^4 C_{Hg}$ (M)	1.46	2.98	2.96	2.90	1.46	2.97		
pH	5.35	5.38	5.45	5.60	6.34	6.90		
E_{Hg} (v)	0.1000	0.1229	0.1222	0.1214	0.0940	0.1151		

crystallised. The acid, when recrystallised three times from aqueous ethanol, and dried at 80° (yield, 15%) had m. p. 210—211° (lit., 211°).

NN-Di(carboxymethyl)aniline (IV).—Redistilled aniline (9.3 g.) was heated at 95° under reflux with sodium chloroacetate prepared from chloroacetic acid (28.2 g.), sodium hydroxide (12 g.), and water (100 ml.). Sodium hydroxide (8.0 g.) in water (10 ml.) was added slowly and at such a rate that the pH was maintained between the change points of phenolphthalein and thymolphthalein. When the resulting solution was cooled and acidified, crystals of the required acid separated. These were filtered off at once and recrystallised from aqueous alcohol (yield 60%; m. p. 154°). The purity was checked by titration with alkali. Acid dissociation constants calculated from the titration curve agreed with those quoted by Schwarzenbach.⁶

P-(2-Carboxyethyl)diphenylphosphine (II), *As*-(2-carboxyethyl)diphenylarsine (III), and *AsAs*-di-(2-carboxyethyl)-*p*-chlorophenylarsine (VI) were gifts from Dr. F. G. Mann of Cambridge University.

AsAs-Di(carboxymethyl)phenylarsine (V) was a gift from Professor W. C. Fernelius, of Pennsylvania State University, U.S.A.

Titration Procedure.—The titration procedure was similar to that described previously.⁷ Both proton- and metal-stability constants were calculated from data obtained by titrating 0.001M solutions (20 ml.) of the appropriate acid with carbonate-free potassium hydroxide in the presence, and in the absence, of metal ions. In all save one case [Table I, titration of (V) with copper] the ionic strengths of solutions were adjusted to 0.10M with potassium nitrate. When titrations were carried out in the presence of silver ions, a salt bridge of 0.1M-potassium nitrate was inserted between the saturated calomel reference electrode and the titration solution. In addition to the pH measurements a silver/silver iodide indicator electrode was used in conjunction with the calomel reference electrode to measure silver ion activities.

Determination of Acid Dissociation Constants.—An attempt was made to determine the dissociation constants of the arsine derivative (V) by using a hydrogen electrode; this proved unsuccessful, since above pH 7 the electrode became poisoned, and it had to be replated before it could be used again. From the results obtained with the glass electrode, acid dissociation constants were calculated by the usual methods,⁸ but a graphical method⁹ had to be employed with compounds (V) and (VI), whose dissociation constants were similar in magnitude so that the buffer regions overlapped considerably. Typical experimental results are recorded in Table I.

Determination of Formation Constants of the Metal Complexes.—Since complexes higher than 1:1 were not encountered with copper(II), nickel, zinc, or cadmium, and since contributions from protonated or hydroxylated species were found to be negligible over the pH range 3—10,

⁶ G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, 1955, **38**, 1147.

⁷ H. Irving and L. Pettit, *J.*, 1963, 1546.

⁸ H. Irving, R. Shelton, and R. Evans, *J.*, 1958, 3540.

⁹ F. J. C. Rossotti and H. Rossotti, "Determination of Stability Constants," McGraw-Hill, New York, 1961, ch. 5.

TABLE 2.
Acid dissociation constants and metal complex formation constants.

Ligand	(I) *	(II) *	(III) *	(IV)	(V)	(VI)	(VII)
p <i>K</i> ₁	5.06	5.03	5.12	2.40 †	3.60	4.17	2.15 ¶
p <i>K</i> ₂				4.96 †	5.03	5.08	10.81 ¶
Copper(II)							
(log <i>K</i> ₁)	n.m.	n.m.	n.m.	6.57 †	2.51	1.5	11.04
Nickel							
(log <i>K</i> ₁)	n.m.	n.m.	n.m.	3.53 †	1.5	n.m.	8.08
Zinc							
(log <i>K</i> ₁)	n.m.	n.m.	n.m.	3.22 †	1.4	n.m.	7.60
Cadmium							
(log <i>K</i> ₁)	n.m.	n.m.	n.m.	2.16 †	1.0	n.m.	6.94
Silver							
(log <i>K</i> ₁)	n.m.	3.80	3.87	1.0	5.37	5.00	4.94 ¶
log <i>K</i> ₂		2.7 (u)					
log <i>K</i> _{MHL} ^M		2.7	2.3		3.73	3.98	
log <i>K</i> _{MHL} ^H		3.9	3.6		3.40	4.06	
Mercury(II)							
log <i>K</i> ₁	u	u	u	(8.3) (u)	14.7 ± 0.1 ‡	u	(13.8) (u)
log <i>K</i> ₂	u	u	u	(3.7) (u)	5.2	u	(9.0) (u)
log β ₂	u	(16.9) (u)	u	12.9	19.92 ± 0.06	u	(22.8) (u)
Copper(I)							
log <i>K</i> ₁					5.6 §		
log <i>K</i> _{MHL}					4.0		

* Measurements in 20% v/v dioxan. † G. Schwarzenbach, R. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, 1955, **38**, 1147. ‡ From a potentiometric determination of mixtures of HgCl₂ and the ligand (V), the values log *K*₁ = 13.4 and log β₂ = 19.2 were obtained. § James and Williams, *J.*, 1961, 2007. ¶ H. Irving and J. J. F. da Silva, *J.*, 1963, 3308. u, Values were unobtainable or are considered unreliable. n.m., Formation constants are too small (log *K* < 1) to be measurable by these methods.

the calculation of formation constants by conventional methods⁸ was straightforward. Typical experimental results are shown in Table 1, and the calculated formation constants in Table 2. The 1 : 1 complex of the substituted arsine (V) formed a bright green precipitate at pH 4.6. Its composition was confirmed by analysis, and by the method of continuous variations by measurements of absorbance at 322 and 350 mμ. No evidence was obtained for complex formation between the arsenic-containing ligands (V) and (VI) and the alkaline-earth metals.

Determination of stability constants for the complexes of the arsines and phosphine with silver ions proved more difficult. Potentiometric titrations of mixtures of the arsine (V) with silver ions were difficult to interpret, since comparisons of figures obtained from different ratios of [total silver] : [total ligand] indicated appreciable concentrations of the protonated species of the simple 1 : 1 complex AgL⁻. These were investigated by titrations with a large excess of silver ions, and also with a constant concentration of silver ions provided by a saturated solution of silver bromate.¹⁰ Solutions of compound (V) in acetate buffers of pH 4.48 and 5.92 were also titrated severally with three different concentrations of silver ions and [Ag⁺] was measured with a silver/silver iodide electrode. Stability constants were then calculated by Leden's method as modified by Fronaeus, graphical integration being employed to obtain the free ligand concentration. Values of \bar{n} tended to rise just above unity at high ligand concentrations, but the predominant complexes were clearly AgL⁻ and AgHL, with no evidence for the participation of bimetallic species.

The method finally used was to titrate a mixture of the ligand and silver ions with alkali, recording simultaneously the pH and pAg of the solution by using glass and silver/silver iodide electrodes, respectively. If *C*_L and *C*_M are the total concentrations of ligand and metal, respectively, and [H] and [M] the hydrogen and metal-ion concentrations when the degree of neutralisation is *a*, it can be shown that:

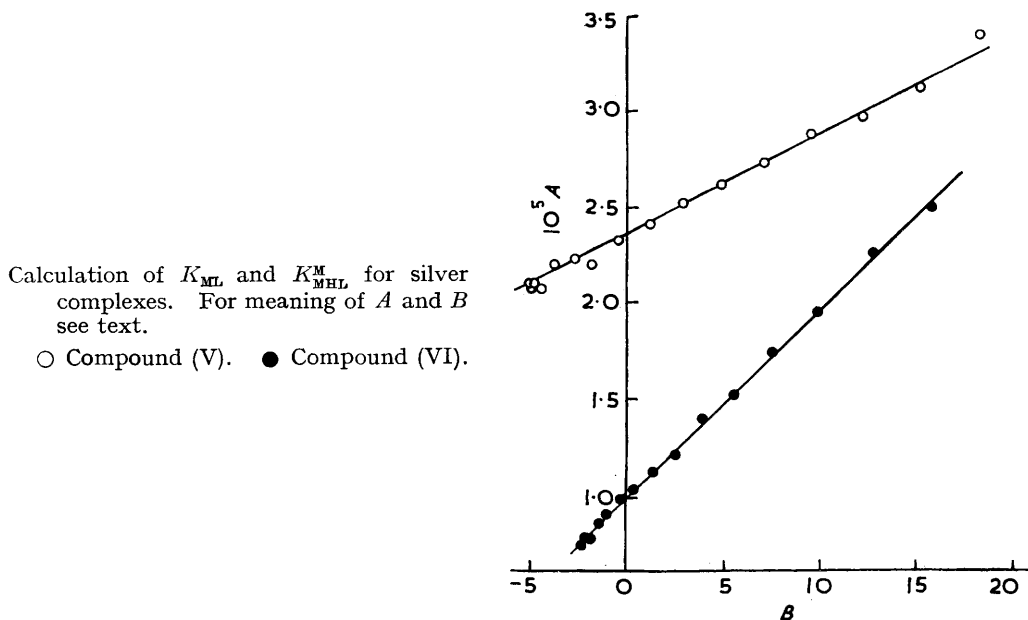
$$\frac{(2 - R) + (1 - R)[H]/K_2 - [H]^2R/K_1K_2}{[M](R - 2)} = \frac{[H](R - 1)K_{MHL}^M}{(R - 2)K_2} + K_{ML}$$

where *R* = (*aC*_L + [H] - [OH])/C_L, *K*_{ML} = [ML]/[M][L], *K*_{MHL}^M = [MHL]/[M][HL], *K*₁ = [H][HL]/[H₂L], and *K*₂ = [H][L]/[HL] (charges have been omitted for simplicity). A plot of

¹⁰ J. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 963.

the left-hand term, (A), against the expression $B = [H](R - 1)/(R - 2)K_2$, gave excellent straight lines in all cases (see Figure), from which K_{ML} could be calculated as the intercept and K_{MHL}^M as the slope. Stability constants calculated by this method were found to be independent of the ratio of total ligand to total silver-ion concentrations.

Measurements of the mercury(II) complexes shown in Table 2 were made entirely by Schwarzenbach's "p[Hg]" method.¹¹ Where results are reported as "unreliable," precipitation



had taken place, casting about on the measurements. However, with compound (V), reproducible results were obtained and these were in good agreement with values calculated from potentiometric titration curves for mixtures of the ligand and mercuric chloride (see Table 2).

RESULTS AND DISCUSSION

The calculated acid dissociation constants and metal complex formation constants are shown in Table 2. Since all measurements of the compounds (I)—(III) were carried out in 20% aqueous dioxan, the results are not directly comparable with others calculated for aqueous solutions. However, it has been shown¹² that the dissociation constants of carboxylic hydrogen atoms are about 0.3 log unit lower in 20% dioxan than in water, *i.e.*, the pK value increases by ~ 0.3 unit. Since the dissociations actually measured must correspond in each case to the removal of the carboxylic-hydrogen atom rather than a quaternary hydrogen atom (this is demonstrated by the high acidity of the species Ph_2NH_2^+ for which $pK = 0.87$), the dissociation constants in water would approximate to that of propionic acid itself ($pK = 4.71$).

In view of the poor donor character of ligands of the type Ph_2XR (where $X = \text{N}, \text{P},$ or As) towards class (*a*) metals, and the further weakening consequent upon replacing R by $\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2^-$, the failure to detect complex formation between class (*a*) metals and the ligands (I)—(III) is not unexpected, in spite of the possibility of the formation of a six-membered chelate ring. However, with silver which is a class (*b*) metal the effect of $d\pi$ bonding is striking. The arsine (III) is reluctant to form more than a 1 : 1 complex; but there was definite evidence that two molecules of the phosphine are co-ordinated with

¹¹ G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, 1957, **40**, 1773.

¹² H. Harned and B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd edn., Reinhold, New York, 1958, p. 662.

approximately equal ease so that there is no marked "step" at $\bar{n} = 1.0$. One striking result is that the measured stabilities are so much lower than those reported for the silver complexes of the ligands studied by Arhland, Chatt, Davies, and Williams.⁴

It is probable that both the acid dissociation constants of the two arsenic derivatives (V) and (VI) correspond to the ionisation of carboxylic-hydrogen atoms; hence the results are not directly comparable with those for the nitrogen analogue (IV), where pK_2 probably refers to the dissociation of the 'onium-hydrogen atom from the zwitterion $\text{Ph}\cdot\text{NH}^+(\text{CH}_2\cdot\text{CO}_2^-)_2$. The calculated values of pK_2 for both compounds (V) and (VI) are almost exactly the same as the values of pK_2 for the carbon analogues in which a methylene group replaces the $\text{PhAs}\langle$ grouping (cf. glutaric acid $\text{HO}_2\cdot\text{C}\cdot\text{CH}_2\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $pK_2 = 5.06$), showing that the arsenic atoms exert little influence on these second dissociations. The first dissociation constants, however, do reflect the electron-attracting nature of the $\text{PhAs}\langle$ grouping [compare $pK_1 = 3.60$ for (V) with $pK_1 = 4.21$ for glutaric acid].

The effect of replacing nitrogen by arsenic is demonstrated very clearly by comparing the formation constants of complexes formed by the ligands (IV) and (V). Since the values of pK_2 for both ligands do not differ much from that of glutaric acid (pK_2 5.08), where the methylene group replacing the nitrogen or arsenic is non-co-ordinating, any increase above the values $K_{\text{CuL}} = 2.40$ or $K_{\text{ZnL}} = 1.60$ reported for glutaric acid¹³ would indicate that bonding through nitrogen or arsenic had occurred. It is clear from Table 2 that bonding through the nitrogen does occur in compound (IV), but that bonding through arsenic in (V) is negligible with class (a) metal ions. This is in accordance with expectations if only σ -bonds are involved. Since comparable data for the nitrogen analogue of (VI) are not available, a similar discussion cannot be applied to this ligand, but comparison of results for (V) demonstrate the effect of increasing the ring size in lowering stability.

The stability order $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^+$, which holds for most nitrogen donors, is illustrated by the new results for *NN*-di(carboxymethyl)cyclohexylamine (VII). Comparison with data for the phenyl analogue (IV) demonstrates the effect of the aromatic ring when attached to nitrogen, for by participating in its delocalised π -bonding system its lone-pair electrons are less available for donor bond formation. Still greater weakness would be predicted for the complexes of an arsenic-containing analogue with class (a) metals.

With silver, however, which is a typical class (b) ion, the situation is clearly reversed for now the Ag-As bond is strengthened by $d\pi$ -bonding involving electrons from the filled $4d$ shell of the silver ion and the unoccupied d orbitals of the arsenic. This effect cannot, of course, occur with nitrogen. Experiment shows that compounds (V) and (VI) form stronger bonds with Ag^+ than even the aliphatic amine (VII). The very small difference in the stabilities of the silver complexes of (V) and (VI) suggests that bonding through the carboxylic-oxygen atoms is negligible in both cases, so that increase in the size of the chelate rings from 5- to 6-membered has become of secondary importance. The *p*-chlorine atom in the arsine (VI) would be expected to have a two-fold effect on the Ag-As bond; the inductive effect could weaken the σ -bond, and the mesomeric effect could reduce any π -bonding, since Chatt and Williams have shown unambiguously that mixing between the d orbitals of large atoms bonded to a benzene ring does take place.¹⁴ The result of both these effects would be a decrease in the formation constant of the complex of the *p*-chloro-derivative. However, at the pH of the measurements, the carboxyl groups in both the arsines (V) and (VI) are almost completely ionised and, if they are not chelated, their inductive effect on the arsenic atoms would cause a lowering of stability, which would be greater in (V) than in (VI) owing to the interposition of the additional methylene groups. The similarity in the magnitudes of the formation constants of the silver complexes of both the ligands, therefore indicates that there is little complex formation through the carboxyl groups, and that the larger inductive effects of the carboxyl groups in (V) are approximately

¹³ R. Cannan and A. Kilbrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314; R. Gregor, L. Luttinger, and E. Loebel, *J. Phys. Chem.*, 1955, **59**, 34.

¹⁴ J. Chatt and A. Williams, *J.*, 1954, 4403.

compensated by the combined inductive and mesomeric effects of the *p*-chlorine atom in (VI). These results are in keeping with the well-known reluctance of silver to form small chelate rings. It is noteworthy that with both ligands there is a marked tendency for the 1 : 1 complex to take up a proton ($\log K_{\text{AgHL}}^{\text{H}} = 3.40$ and 4.06 , respectively), that of the longer chain ligand being the greater. Hence, it appears that, while class (a) cations tend to form bonds almost entirely through the carboxyl groups of these ligands, a typical class (b) cation does so almost entirely through the arsenic atom.

This difference is further supported by investigations on the complexes of the arsine (V) with copper(I) and mercury(II), both of which are class (b) metal ions.¹ From measurements of redox potential, James and Williams showed that noticeable complex formation takes place between the arsine (V) and copper(I) at a pH well below that at which the carboxyl groups are ionised.¹⁵ The complex formed was found to have a high stability ($\log K_1 5.7$) and to be a dibasic acid with dissociation constants $\text{p}K_1 2.70$ and $\text{p}K_2 3.96$.

Stabilities of complexes of mercury(II) with ligands containing arsenic as donor atom have not previously been reported but, in consequence of its pronounced class (b) character, very stable complexes would be expected. This is borne out by the present results (Table 2). The formation constant of the arsine (V) was the only one that could be measured with certainty and confirmed by an alternative method. The complex is certainly far more stable than that of the nitrogen analogue (IV). The greater reluctance to form a di-complex with the arsine acid ($K_1/K_2 = 10^{9.5}$) as compared with the nitrogen analogue ($K_1/K_2 = 10^{4.6}$) is particularly interesting. Neither copper(II) nor cadmium showed any apparent class (b) character in any of the complexes studied.

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¹⁵ B. James and R. Williams, *J.*, 1961, 2007.
