# THE SYNTHESIS OF SOME NEW LIGANDS CONTAINING SULPHUR AND ARSENIC AS DONOR ATOMS AND A STUDY OF THEIR COMPLEXES WITH THE PROTON, SILVER AND SOME DIVALENT METAL IONS

## G. J. FORD, L. D. PETTIT and C. SHERRINGTON

Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT, England

## (Received 17 March 1971)

Abstract – A number of new chelating ligands containing sulphur(11) or arsenic(111) as donor atoms has been synthesised and their proton, silver, copper(11), nickel, zinc and cadmium complex formation constants measured at 25°C. For metal ions the stability order was found to be Ag > Cu > Ni > Cd > Zn for all the ligands studied. Equilibria in the presence of silver ions were particularly complicated with the formation of both protonated and unprotonated species AgL,  $Ag_2L$  and  $AgL_2$ . A computer based computational method for treating the data is described.

## INTRODUCTION

As DONOR atoms sulphur(II) and arsenic(III) are markedly "soft" in character. Organic sulphides and arsenides therefore tend to form more stable complexes with metal ions such as  $Ag^+$  and  $Hg^{2+}$  than with divalent metal ions from the first transition series. The nature of the bonding between the silver ion and sulphur [1-3] and arsenic[4] has been investigated by studying trends in the thermodynamic properties of the complexes as substituents on the ligands were varied. The trends found could be explained in terms of inductive  $\sigma$ -bonding effects only and produced no real evidence for the presence of extensive back co-ordination from the metal ion to the ligand. Complexes formed between a number of organic sulphides and "hard" divalent metal ions have been studied by Suzuki *et al.* [5, 6] and Schunzel *et al.*[7]. In general they found the complexes to be weak and often ill-defined.

We wish to report the synthesis of a number of new chelating ligands containing arsenic or sulphur as donor atoms and a direct comparison of their complexes with the proton, silver and a range of divalent metal ions. Silver complexes, in particular were found to be numerous so that refined itterative procedures had to be used to fit the experimental data satisfactorily. In all the following ligands were prepared and, where possible, their complexes studied.

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## **EXPERIMENTAL**

*Materials*. The ligands were prepared by modifications of existing synthetic routes which are summarised below. Melting points and analyses are listed in Table 1.

Dithiocatehol was prepared from 2-aminobenzenesulphonic acid by the following route, described by Guha and Chaklader[8],

$$o-SO_{3}H \cdot C_{6}H_{4} \cdot NH_{2} \xrightarrow{(i) KNO_{2}/H_{2}SO_{4}} o-SO_{3}H \cdot C_{6}H_{4} \cdot S \xrightarrow{S} OEt \xrightarrow{(i) KOH/alc} o-SO_{3}H \cdot C_{6}H_{4} \cdot S \xrightarrow{S} OEt \xrightarrow{(i) KOH/alc} o-SO_{3}H \cdot C_{6}H_{4} \cdot SH \xrightarrow{(i) O_{2}} (o-SO_{2}Cl \cdot C_{6}H_{4} \cdot S-)_{2} \xrightarrow{Sn/HCl} o-C_{6}H_{4}(SH)_{2}$$

Dithiocatechol was steam-distilled from the reaction mixture. (If steam-distillation was continued for longer than 30 min, the thiol decomposed to give a red solid). Overall yield 8 per cent.

o-Phenylenebis(thioacetic acid)(1). Dithiocatechol (3g), chloroacetic acid (4g) and potassium hydroxide (2g) in water (20 ml) were refluxed for 2 hr the solution was cooled in ice, and acidified to Congo red with conc. hydrochloric acid which precipitated the required acid. It was recrystallised from water. Yield 62 per cent.

4-Methyl-o-phenylenebis(thioacetic acid)(11) was prepared, similarly from its corresponding dithiol.

*p-Phenylenebis(thioacetic acid)(III)* was prepared by the method of Behagel[9], and purified by recrystallisation from water. Yield 19 per cent.

Ethanebis(thioacetic acid)(IV) and thiobis(ethanethioacetic acid)(V) were prepared by re-

8. P. C. Guha and M. N. Chaklader, J. Indian chem. Soc. 2, 324 (1925).

9. O. Behagel, J. prakt. Chem. 114, 288 (1926).

fluxing the parent thiol with chloroacetic acid and potassium hydroxide in 25% aqueous alcohol. The product, obtained by distilling off the alcohol, diluting the solution with ice, and acidifying with conc. hydrochloric acid to Congo red, was recrystallised from water.

Bis(carboxymethyl)-(methylthiophenyl) arsines(VI-VIII) were prepared by the methods of Mann and Braunholtz[10]. The o- and p-ligands were obtained from the corresponding thioanisoles via the arsonic acids. Both arsonic acids are soluble in dilute hydrochloric acid and their precipitation from the reaction mixture was facilitated by saturation with solid sodium chloride. (*m*-Methylthio)phenylarsonic acid was prepared by nitrating phenylarsonic acid and reducing the nitrocompound with iron filings in sodium chloride solution[11] to give *m*-aminophenylarsonic acid. This acid was diazotised, converted to the o-dithiocarbonate ester with potassium o-dithiocarbonate, and this ester hydrolysed in ethanol with potassium hydroxide to give the thiol, which was refluxed for 3 hr with an excess of dimethylsulphate. Addition of sodium hydroxide hydrolysed the methyl ester of the arsonic acid which was precipitated by acidification with conc. hydrochloric acid and saturation of the reaction mixtures with solid sodium chloride. All the ligands were recrystallised from water.

*o-Phenylenebis(di-2-carboxyethyl)arsine(IX). o-Phenylenebis(arsonic acid)* was prepared from *o*-nitroaniline via the Bart reaction reducing *o*-nitrophenylarsonic acid with iron filings and then treating the amino derivative as described by Kalb[12].

$$o - \operatorname{NO}_2 \cdot \operatorname{C}_6 \operatorname{H}_4 \cdot \operatorname{N}_2 \operatorname{H}_2 \frac{(i) \operatorname{NaNO}_2/\operatorname{HCl}}{(ii) \operatorname{As}_2\operatorname{O}_3/\operatorname{Na}_2\operatorname{CO}_3} o - \operatorname{NO}_2 \cdot \operatorname{C}_6 \operatorname{H}_4 \cdot \operatorname{AsO}_3 \operatorname{H}_2 \frac{(i) \operatorname{Fe}/\operatorname{NaCl}}{(ii) \operatorname{As}_2\operatorname{O}_3/\operatorname{KOH}} on \operatorname{diazo-salt} o - \operatorname{C}_6 \operatorname{H}_4(\operatorname{AsO}_3 \operatorname{H}_2)_2 \frac{\operatorname{Zn}/\operatorname{HCl}}{\operatorname{Hg}} o - \operatorname{C}_6 \operatorname{H}_4(\operatorname{AsH}_2)_2 \frac{\operatorname{C}_2\operatorname{H}_2 - \operatorname{C}_2\operatorname{H}_2\operatorname{C}_2\operatorname{C}_2}{\operatorname{H}_2 - \operatorname{C}_2\operatorname{H}_2\operatorname{C}_2\operatorname{C}_2} o - \operatorname{C}_6 \operatorname{H}_4(\operatorname{AsCH}_2\operatorname{CH}_2\operatorname{C}_2\operatorname{C}_2\operatorname{H}_2)_2 \frac{(i) \operatorname{KOH}/\operatorname{water}}{(ii) \operatorname{HCl}/5^\circ} o - \operatorname{C}_6\operatorname{H}_4(\operatorname{AsCH}_2\operatorname{C}_2\operatorname{CO}_2\operatorname{H}_2)_2$$

o-Phenylenediarsine was prepared by the reduction of the diarsonic acid with amalgamated zinc and hydrochloric acid in 95 per cent aqueous ethanol. Isolation of the pure arsine was not attempted, but exposure to air of 1 drop of an ether solution of the arsine turned yellow. o-Phenylenebis(di-2cyanoethyl)arsine was prepared by refluxing the diethyl ether solution of the arsine with a large excess of vinyl cyanide. Distillation of the ether, and the vinyl cyanide, under reduced pressure, yielded a yellow-brown syrup which defied all attempts at recrystallisation. It was characterised as the palladium complex which was recrystallised from absolute alcohol, and analysed for 1 molecule of the solvent; Found C, 36·1; H, 3·6; Pd, 16·0. C<sub>20</sub>H<sub>25</sub>N<sub>4</sub>As<sub>2</sub>O·PdCl<sub>2</sub> requires: C, 36·2; H, 3·9; Pd, 16·0%.

o-Phenylenebis(di-2-carboxyethyl)arsine was prepared by refluxing the cyanoarsine with a large excess of sodium hydroxide in 50 per cent ethanol. On completion of the reaction (ammonia evolution ceased), the solution was filtered and the ethanol distilled off. Ice was added and the solution acidified to pH 6 with conc. hydrochloric acid at 0° (carbon dioxide is evolved at 20°). The filtrate was further acidified to pH 2 and the solid precipitate recrystallised from a large volume of warm (50°) water decarboxylation of the acid occurred at higher temperatures).

1,2-Di(Phenyl-2-carboxyethylarsino)ethane(X) was prepared as for IX from ethane-1,2-bisphenylarsinic acid, which was obtained by the method of Chatt and Mann[13]. It was recrystallised from ethanol



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11. F. G. Mann and A. J. Wilkinson, J. chem. Soc., 3336 (1957).

- 12. L. Kalb, Annalen 423, 74 (1921).
- 13. J. Chatt and F. G. Mann, J. chem. Soc. 610 (1939).

	M.P.(°C)	C(%)		H(%)		S(%)	
Compound	Found	Found	Req.	Found	Req.	Found	Req.
I	209d	46.3	46.5	3.9	3.9	25.0	24.8
II	170d	48.5	48.5	4.4	4.4	23.4	23.5
III	215	46.5	46.5	4.1	3.9	24.9	24.8
IV	109	34.2	34.3	4.9	<b>4</b> ·8	30.3	30.5
V	114	35.8	35.6	5.2	5.2	35.9	35.6
VI	157	<b>41</b> ·7	41.7	4.1	4.1	10-2	10.1
VII	109	41.5	41.7	3.9	4.1	10.0	10.1
VIII	148	42.0	41.7	4.4	<b>4</b> ·1	9.9	10.1
IX	157	41.9	41.7	4.8	4.7		
Х	> 250	50.0	50.2	4.8	5.0		
Arsonic acids							
o-SCH <sub>3</sub>	157	33.9	33.9	3.6	3.6	12.9	12.9
m-SCH <sub>3</sub>	101	33.9	33.9	3.6	3.6	12.7	12.9
p-SCH <sub>3</sub>	> 250	34.2	33.9	3.9	3.6	12.6	12.9
Dichloroarsines							
o-SCH <sub>3</sub>	52	31-3	31.2	2.6	2.6	11.7	11.9
p-SCH <sub>3</sub>	68	31.0	31.2	2.7	2.6	11.9	11.9
Carboxymethyl- chloroarsines							
o-SCH <sub>3</sub>	99	36.6	36.9	3.4	3.6	11.3	10.9
p-SCH₃	112	36.5	36.9	3.6	3.6	10.8	10.9

Table 1.

## Methods of measurement and calculation

Acid dissociation constants (expressed as proton complex formation constants) were calculated from titrations of solution of the acids (approximately  $10^{-3}$  M with the ionic strength adjusted to 0.1 M) with alkali in the apparatus described previously[4]. Formation curves (corresponding values of  $\bar{n}$ , the degree of formation of the protonated complexes, and pH) were calculated from the relationship:

$$\bar{n} = (N-a) - \{[H] - [OH]\}/C_L$$
(1)

where N is the basicity of the acid, of total concentration  $C_L$  and a the degree of neutralization. Proton complex formation constants,  $\beta_n$  where  $\beta_n = [H_n L]/[H]^n[L]$ , were then calculated from the relationship:

$$\bar{n} = \sum_{1}^{N} n[\mathbf{H}]^{n} \beta_{n} / \sum_{0}^{N} [\mathbf{H}]^{n} \beta_{n}.$$
<sup>(2)</sup>

Constants for dibasic acids were calculated by the method described previously[4]. The tetrabasic acid (1X) was only very sparingly soluble in water  $(2 \times 10^{-4} \text{ M})$  but reproducible titration curves were obtained and the four complex formation constants were calculated from Equation (2) by assuming that to a first approximation over selected parts of the formation curve, two complex species may be ignored. Equation (2) can then be solved for two constants only. The regions selected were (i)  $\bar{n} > 2.6$  ( $\beta_3$  and  $\beta_4$  only) (ii)  $\bar{n} < 1.8$  ( $\beta_1$  and  $\beta_2$  only) and (iii)  $1.8 < \bar{n} < 2.5$  ( $\beta_2$  and  $\beta_3$  only). Having calculated temporary values for the four constants there were refined in pairs, using the latest values for the remaining two constants, until self-consistent results were obtained. The values were later checked by using a computer-based itterative least-squares minimisation procedure which calculated a theoretical formation curve from the refined constants (Procedure Hyperplane). The constants agreed excellently with those calculated by the above method (better than  $\pm 0.02$  log units) and the theoretical

рН	<i>n</i> (meas.)	pН	$\bar{n}$ (calc.)
3.995	3.391	4.00	3.355
4.221	3.073	4.20	3.112
4.346	2.881	4.40	2.827
4.578	2.543	4.60	2.517
4.789	2.209	4.80	2.199
4.963	1.960	5.00	1.895
5.263	1.541	5.20	1.617
5.478	1.272	5.40	1.373
5.580	1.163	5.60	1.158
5.863	0.889	5.80	0.967
6.081	0.723	6.00	0.791
6.222	0.612	6.20	0.627
6.412	0.454	6.40	0.478
6.610	0.332	6.60	0.349
6.731	0.276	6.80	0.246
6.930	0.220	7.00	0.167
7.160	0.164	7.20	0.111

Table 2. The formation curve for proton complexes of ligand IX

The	calculated	ñ	values	assume	the	formation
constant	ts given in T	`ab	le 4.			

curve fitted the experimental curve throughout its entire length [14]. The experimental formation curve is given in Table 2. The dibasic acid (X) was too insoluble in water to permit titration and, in alkali, appeared to decarboxylate slowly making back titration impractical. It was therefore impossible to get reliable constants.

Stability constants of metals other than silver. The procedure used was essentially that described for the acid dissociation constants since the initial co-ordination step was expected to be largely through the carboxyl groups. The ligand was titrated with alkali in the presence of the metal ion (approximate ratio 1:1) under study. The solutions of the metal ions were standardised with EDTA. Ligands studied by this technique were the chelating ligands II, IV, V, and VI. The chelating arsenic ligand, IX, was insufficiently soluble to give meaningful results.

It was found that the data for the ligands II, IV and V could be treated adequately on the assumption that the only complex species present was the mono-complex, *ML*. Complex formation constants  $(\beta_{ML})$  were calculated by the normal method[15] and were found to be sensibly constant throughout the titration with no discernable drifting in value. With the ligand VI (bis(carboxymethyl)-o-(methyl-thio)phenylarsine), however, there was a marked drift in apparent  $\beta_{ML}$  values as the pH increased, suggesting the presence of a protonated complex *MHL*. Values for  $\beta_{ML}$  and  $\beta_{MRL}$  were therefore calculated simultaneously by computer using the Powell 64 procedure[16]. For each experimental point (a total of *N*) a function is selected which can be calculated from measured quantities ( $f_{meas}$ ). A value for the same function is then calculated using the estimated values for the formation constants ( $f_{calc}$ ) and the difference sum.

$$\sum_{1}^{N} \{(f_{\text{meas}} - f_{\text{calc}})\omega(n)\}^2,$$

where  $\omega(n)$  is the empirical weighting factor  $f_{\text{meas}}(N)/f_{\text{meas}}(n)$ , minimised by the Powell procedure. For a dibasic ligand, H<sub>2</sub>L, and assuming the complex species *ML* and *MHL* only the relationship

$$(2-a)C_L + [OH] - [H] = [L] \{ [H]\beta_{HL} + 2[H]^2\beta_{H_2L} + [M][H]\beta_{MHL} \}$$
(3)

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- 15. H. Irving, R. Shelton and R. L. Evans, J. chem. Soc. 3540 (1958).
- 16. M. J. Powell, Computer J. 7, 155 (1964).

may be derived, where [M] and [L] can be expressed in terms of  $\beta_{ML}$  and  $\beta_{MRL}$  and measured quantities. The left hand side of Equation (3) was therefore selected as  $f_{meas}$  and the right hand side as  $f_{calc}$ . This procedure gave good and consistent values for both  $\beta_{ML}$  and  $\beta_{MRL}$  with values for  $(f_{calc}-f_{meas})$  being smaller than 1 per cent of  $f_{calc}$  for all data points.

Silver complexes of the ligands. A different procedure had to be adopted for the silver complexes since co-ordination would be predominantly through the sulphur or arsenic atoms. Solutions of the ligand were added, by titration, to a solution of silver nitrate and changes in silver ion activity were followed with a silver/silver chloride reference electrode. All titrations were carried out in acetate buffer solutions of ionic strength 0.20 M and pH 1.5 and 5.95 so that the formation of fully protonated and fully ionized complex species could be followed. Full experimental details have been given previously[1]. It was found that ligands I, II and III discoloured rapidly in acid solution making titration impossible and ligands IX and X were too insoluble to study. In "neutral" solution (pH 5.95) ligands III, VII and VIII formed an immediate precipitate with silver ions, probably as a result of polymer formation. Ligands I and II formed simple monomeric complexes, AgL, only since the experimental data could be fitted by the introduction of an AgL complex alone. Other ligands formed a greater variety of complex species and formation constants were evaluated using the "Powell 64" minimisation procedure [16] with

 $f_{\text{meas}} = (C_{\text{Ag}} - [\text{Ag}])/[\text{Ag}]$  and  $f_{\text{calc}} = [L]\beta_{\text{AgL}} + 2[\text{Ag}][L]\beta_{\text{AgL}} + [L]^2\beta_{\text{AgL}}$ 

where [L] may be obtained as the positive root to the equation:

$$C_L = [L](1 + [\mathrm{Ag}]\beta_{\mathrm{AgL}} + [\mathrm{Ag}]^2\beta_{\mathrm{AgaL}}) + 2[L]^2[\mathrm{Ag}]\beta_{\mathrm{AgL}}.$$

The most satisfactory constants were taken to be the minimum number which satisfied the condition  $(f_{calc} - f_{meas})/f_{calc} < 0.01$  (i.e. < 1 per cent) for all points. The complex species AgL, Ag<sub>2</sub>L and AgL<sub>2</sub> (or their fully protonated equivalents) were found to satisfy the experimental data for all ligands except V and IX. In ligand V there appeared to be a small contribution from the species Ag<sub>3</sub>L (i.e. a silver ion co-ordinated to each sulphur atom). Ligand IX was far from its fully ionized form at pH 5.95 and, while reproducible titration data were obtainable indicating very stable complexes, the multiplicity of possible and partly protonated complex species made reliable computation of formation constants impractical. For ligands in which  $\beta_{HL}$  was greater than 4.00 (i.e. in which there would be > 1 per cent HL species at pH 6.00) a correction was included to allow for an HL present on the assumption that its complexing ability would be negligible at such low concentrations. A sample set of data (the silver complexes of ligand VI at pH 1.5) is shown in Table 3.

#### **RESULTS AND DISCUSSION**

Measured proton complex formation constants are given in Table 4, together with those quoted by Suzuki and Yamasaki for the ligand IV[5]. The aryldi (thioacetic) acids I–III have very similar acidities indicating that the positions of substituents in the aromatic ring are of surprisingly little importance. The difference between the stepwise constants (0.70 log units) is very close to the expected statistical factor of 0.60. The aliphatic ligands IV and V also show the same difference with log  $\beta_{H_{2L}}$  for IV being somewhat larger than that previously reported. On statistical grounds the result we report is more satisfactory. The acidities of the *o*, *m* and *p* series of ligands (VI–VIII) are in agreement with the trend expected from the Hammett functions for the SMe group. The constants for the ligand IX all overlap considerably although log  $\beta_{HL}$  – log  $\beta_{H_{2L}}$  (1.19) is considerably greater than any of the other differences. This may be the result of the accumulation of negative charges as protons are ionized.

Silver complex formation constants which could be determined with reasonable precision are shown in Table 5. Complex formation will be predominantly

Vol.	-E	$f_{\rm meas}$	$f_{calc}$	$(f_{\rm calc} - f_{\rm meas})/f_{\rm calc}$
(ml)	(mV)	(× 10¹)	(× 10 <sup>1</sup> )	(%)
1.00	61.44	0.5445	0.5422	-0.43
2.00	63.04	1.115	1.122	0.55
3.00	64.70	1.746	1.744	-0.11
4.00	66.36	2.413	2.410	-0.11
5.00	68·03	3.124	3.124	0.01
6.00	69.73	3.894	3.893	-0.03
7.00	71.45	4.721	4.719	-0.04
8.00	73.17	5·599	5.605	0.12
9.00	74.93	6.556	6.564	0.12
10.00	76.72	7.594	7.600	0.08
11.00	78.53	8.713	8.720	0.08
12.00	80.37	9.928	9.933	0.05
14.00	<b>84</b> ·16	12.702	12.689	-0.10
16.00	<b>88</b> ·04	15.960	15.938	-0.14
18.00	92.02	19.810	19.787	-0.12
20.00	96.12	24.401	24.375	-0.11
22.00	100.30	29.833	29.825	-0.03
25.00	106.70	39.908	39.980	0.18

Table 3. Experimental data for the addition of VI ( $1.622 \times 10^{-3}$  M solution, pH 1.5) to 103 ml AgNO<sub>3</sub> ( $2.911 \times 10^{-4}$  M, pH 1.5) at 25°C and I 0.20 M (HNO<sub>3</sub> + CH<sub>3</sub>CO<sub>2</sub>H buffer).  $E_o = 0.14928$  V.

where log  $\beta_{AgHL} = \log [AgHL]/[Ag][HL] = 4.635 \pm 0.007$ ; log  $\beta_{AggHL} = \log [Ag_{2}HL]/[Ag]^{2}[HL] = 6.82 \pm 0.04$ ; log  $\beta_{Ag}(HL)_{2} = \log [Ag(HL)_{2}]/[Ag][HL]^{2} = 8.73 \pm 0.03$ .

Table 4. Proton complex formation constants at 25°C and I = 0.10 M (estimated standard deviations (o values) 0.01 unless stated)

Ligand	$\log \beta_{\mathrm HL}$	$\log \beta_{\text{H}_{2}l.}$	р <i>К<sub>Н2</sub>L</i>
I	3.90	7.11	3.21
П	3.89	7.08	3.19
Ш	3.89	7.06	3.17
IV	4.06*	7.40*	3.34
V	4.03	7.34	3.31
VI	5.35	9.24	3.89
VII	5.13	8.95	3.82
VIII	5.06	8.73	3.67
IX†	6.29(2)	11.47(2)	5.18

\*Values quoted in ref. 5 are log  $\beta_{HL} = 4.10$ , log  $\beta_{HaL} = 7.26$ .

 $^{\dagger}\text{Log }\beta_{\text{H}_{3L}} = 16.08(3), \text{ log }\beta_{\text{H}_{4L}} = 20.13(4).$ 

due to silver-sulphur or silver-arsenic bonding with bonding through the carboxyl groups being almost negligible—hence the high stabilities of protonated complexes. The silver complex of II would be expected to be more stable than that of I as a result of the inductive effect of the methyl group. The difference ( $\Delta$  log

Ligand	$\log \beta_{AgL}$	$\log \beta_{AE_2L}$	$\log \beta_{AB3L}$	$\log \beta_{\text{AgH}_{2L}}^{\text{H}_{2L}}$	$\log \beta^{\mathrm{H}_{2L}}_{\mathrm{Ag_{2H_{2}L}}}$	$\log \beta_{Ag(H_2L)_2}^{H_2L}$
I	3·97(2)	nm		d		
III	4·1/(2) ppt	nm		a ppt		
IV	4·95(1)	7.01(3)		4.45(1)	6·16(4)	8.24(5)
V	8.52(1)	10·99(3)	12.2(3)	5.47(1)	7.48(1)	nm
VI	5-14(3)	<b>7·88</b> (5)		4·64(1)	6.82(4)	8.73(3)
VII	ppt					
VIII	ppt					

Table 5. Silver complex formation constants at 25°C and 1 = 0.20 M (estimated deviations( $\sigma$ -values) in brackets)

ppt-precipitation; nm-not measurable; d-decomposes.

 $\beta_{AgL} = 0.20$ ) is close to that expected for the combined effect of a *meta* and *para* methyl substituent[17]. The reaction of silver ions with ligand IV, which is comparable with diaminoethane, is far more complicated than anticipated by Larsson who gave the value log  $\beta_{AgL} = 6.9[18]$ . The species  $Ag_2L$  presumably has the structure:



analogous to the silver complex of diaminoethane detected by Schwarzenbach [19]. Ligand V, which contains three sulphur atoms, appears to even form an  $Ag_3L$  species. The complex  $AgL_2$  was not detected in neutral solution since precipitation occurred before the ligand concentration was sufficiently high. A comparison of log  $\beta_{AgL}$  for ligands I and IV shows that the phenyl group decreases the stability by a factor of 10, very close to that found in earlier studies[2]. The unprotonated complexes of V are considerably more stable than those of IV. This may be a result of chelation through all three sulphur atoms or more likely, due to linear S-Ag-S coordination in the complex of V while it is sterically impossible in IV.

With "harder" transition metal ions the ligands II, IV and V only formed the mono-complex ML in detectable concentration since single formation constants explained the experimental data adequately. Protonated complexes, MHL, were clearly present with ligand VI. Calculated formation constants for all the ligand-metal combinations are shown in Table 6. As with the silver complexes, the presence of a phenyl ring reduced the stability by up to an order of magnitude. The values found for ligand IV are close to those reported by Suzuki and Yamasaki[5] showing the same order of stability, i.e.

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- 18. E. Larsson, The Svedberg, Uppsala, p. 311 (1944).

<sup>19.</sup> G. Schwarzenbach, H. Ackermann, B. Maissen and G. Anderegg, *Helv. Chim. Acta* 35, 2337 (1952).

Ligand	log K <sub>CuL</sub>	$\log K_{\text{Ni}L}$	$\log K_{CdL}$	$\log K_{\text{Zn}L}$	
11	3.90	2.97	2.40	2.20	· · ·
IV	5.33	4.31	2.65	2.55	
V	5.68	4-42	2.55	2.25	
VI $(\log K_{ML})^*$	3.68	3.27	3.22	3.20	
VI $(\log K_{MHL}^{HL})^*$	2.19	2.64	2.51	2.52	
VIII	2.83	2.92	1.5		
*Additional re	sults for ligand	IVI were:			
log K <sub>CoL</sub>	$\log K_{COHL}$	log K <sub>FeL</sub>	log K <sub>FeHL</sub>	log K <sub>MnL</sub>	log K <sub>MnH</sub>
2.93	2.37	3.80	2.32	2.86	2.35

Table 6. Metal complex formation constants<sup>†</sup> at 25° and I = 0.10 M

 $\pm$ Estimated standard deviations are 0.02 for Cu, 0.03 for Ni, 0.09 for Cd and 0.10 for Zn complexes.

A similar order is found for ligand V which forms a rather more stable complex with Cu(II) and weaker complex with Zn(II).

The ligand ethanediylidinetetra(thio)acetic acid,  $(HO_2C\cdot CH_2S)_2CH\cdot CH (SCH_2\cdot CO_2H)_2$  (ETTA) is comparable to ligands IV and V and data for the copper and nickel complexes have been published recently[20]. The values quoted were log  $\beta_{CuL} = 5.72$  and log  $\beta_{NiL} = 4.17$  with, in addition, significant contributions from the CuHL and NiHL species. These values are very close to the values we have found for ligands IV and V, suggesting that the bonding is essentially similar in all complexes.

Chelation through at least one sulphur atom contributes noticeably to the stabilities found. Evidence for this is provided by the weaker complexes formed by the *para*-ligand, VIII, compared to the *ortho*-ligand, VI, and by a comparison of stabilities with ligand IV and V with comparable values for glutaric acid in which no sulphur donors are present (log  $\beta_{CuL} = 2.4$ , log  $\beta_{NIL} = 1.6$ ). As a result of the electron donating properties of the CH<sub>2</sub>CO<sub>2</sub><sup>-</sup> group, sulphur atoms bonded to these groups will be more able donors than the central sulphur atom in ligand V. If it is assumed that the initial bonding is through the carboxyl groups followed by sulphur atoms bonded to these groups then similar stabilities are to be expected since steric effects alone would tend to limit the coordination number with such polydentate ligands. The results for ETTA demonstrate this clearly.

A greater range of complexes of the arsenic-sulphur ligand VI was studied. The stability order is essentially that found for the other ligands with Fe(II) giving an exceptionally high value. Oxidation to Fe(III) must be suspected although it is difficult to understand why this should take place in the presence of a reducing ligand. The high formation constant found, however, was reproducible over several days and remarkably consistent throughout the entire titration range used. The protonated copper complex (Log  $K_{AgHL}^{HL} = 2.19$ ) appears to be abnormally weak.

20. W. J. Geary and D. E. Malcolm, J. chem. Soc. A, 797 (1970).