

Studies on Metal Ion Co-ordination in Solution

II. The Complex Formation of Diphenylphosphinobenzene-*m*-sulphonate with Bismuth

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Diphenylphosphinobenzene-*m*-sulphonate, which was used by Ahrland *et al.*^{1,2}, and Salvesen and Bjerrum³ as a phosphorus donor ligand for Ag⁺, Cd²⁺ and Hg²⁺, has been found to be appreciably basic with

$$pK_{LH^+} = 0.13 + 0.50 C_{HClO_4}$$

There is evidence that the ligand undergoes self-association when $[L] + [LH^+] > ca. 0.01 M$, thus limiting the range of concentration useful for determining stability constants. The complex formation between Bi³⁺ and the ligand has been measured using a bismuth amalgam electrode; difficulties with the electrode resulted in low accuracy. A steep formation curve was derived in agreement with the preliminary measurements of Salvesen⁴. The data show that the maximum coordination number is six and only the first and the sixth complex are formed in significant concentration. Stability constants, in 1 M HNO₃ at 25°, are $K_1 = 10^{3.71} \cdot \text{mole}^{-1}$, $\beta_6 = 10^{21.816} \cdot \text{mole}^{-6}$. These findings are consistent with the stability trend observed by Ahrland and Grenthe⁵ for the bismuth halide complexes: Cl⁻ < Br⁻ < I⁻ < P. The ranges of existence of intermediary complexes decreases along this series.

It has been shown by Ahrland and Grenthe⁵ that bismuth(III) is a class (b) metal ion^{6,7}, the stability of its halide complexes increasing in the order Cl⁻ < Br⁻ < I⁻. This paper reports further exploration of the class (b) character of bismuth(III) using the water soluble ligand diphenylphosphinobenzene-*m*-sulphonate. The ligand has a phosphorus donor atom; it forms strong silver(I)¹ and mercury(II)³ complexes and weaker complexes with cadmium(II)². In order to eliminate hydrolysis of the bismuth ion⁸ and to maintain a constant salt concentration, 1 M nitric acid has been used as the medium. Salts of the ligand $m\text{-(C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{SO}_3^-$ show higher solubility as the acid concentration is increased, hence the ligand is appreciably basic. A

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UV spectrophotometric method has been used to determine pK_{LH}^+ in perchloric acid solutions. Complex stability constants can then be calculated with respect to the unprotonated ligand. A preliminary report of this work has been published with Salvesen as co-author⁴.

EXPERIMENTAL

Materials and analysis. $m\text{-(C}_6\text{H}_5\text{)}_2\text{PC}_6\text{H}_4\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$ has been described previously^{1,3}. The ligand decomposes slowly in water and therefore fresh solutions were prepared by weight for each E.M.F. measurement. The spectrophotometric measurements were made using the same stock solution of ligand (0.000616 M); a small correction ($\sim 3\%$ in 2 h) was made for decomposition.

Bismuth solutions were prepared by dissolving pure Merck bismuth nitrate crystals in 1 M HNO_3 and analysing the bismuth gravimetrically as $\text{BiOI}^3,5$.

Pure concentrated nitric acid was diluted to 5 M, boiled to remove nitrous acid, then diluted by trial to 1 M and determined by titration with standard sodium hydroxide. Perchloric acid solutions were prepared by dilution and standardisation of Merck p.a. 70% HClO_4 .

Bismuth amalgam (2%) was prepared by electrolysis of a solution of $\text{Bi(NO}_3\text{)}_3$ in nitric acid, using a mercury pool as cathode and it was stored in a separatory funnel under distilled water and nitrogen.

Spectrophotometric measurements were made with a Cary 11MS-50 instrument at $25 \pm 2^\circ$, using 1 cm silica cells. The reference cell contained the same concentration of perchloric acid as the sample cell, in order to correct for the small background absorption of HClO_4 .

Potentiometric measurements. The cell was



A stream of purified nitrogen¹⁰ was passed through the test solution (25 ml) in the electrode vessel. The amalgam was contained in a J-tube of 2 mm bore with a 10 mm cup opening on the short arm immersed in the solution. The longer arm of the J-tube contained a platinum wire which made contact with the amalgam. This design avoided interference caused by a film of solution between the platinum and amalgam: similar precautions have been taken by Holloway and Reilley¹¹. Solutions for measurement were transferred to the electrode vessel in the thermostat and nitrogen passed for 20 min. The J-tube electrode was then filled with amalgam and placed in the solution quickly to avoid atmospheric oxidation of the bismuth. The reference electrode, which was a bright platinum foil in 1 M HNO_3 saturated with quinhydrone, was connected by a syphon bridge to the main electrode vessel. Tests of several such reference electrodes against each other showed that their potentials were reproducible and stable for 2–3 h within ± 0.1 mV. Other details have been described in Part I³.

Table 1 shows measurements on solutions containing no ligand to test the Nernst law according to the formula valid at 25°C :

$$E = E^\circ + 0.0197 \log [\text{Bi}^{3+}] \quad (2)$$

E° is seen to be a constant for bismuth concentrations between 20.1 mM and 2.01 mM, but below this concentration the potentials are too positive by 1–2 mV. This may be caused by dissolution of small amounts of bismuth from the amalgam during brief exposure to the air. The mean E° of the four highest bismuth concentrations (-423.7 mV) has been used to calculate E at the bismuth concentrations used in all subsequent experiments.

In the presence of the ligand it took about 40 min. to reach the equilibrium potential and the reproducibility was poor, as shown in Fig. 3, where C_{L} is plotted against E_{M} . E_{M} is defined as the potential of the half-cell: $\text{Hg, Bi} | C_{\text{Bi}}, C_{\text{L}} |$ relative to a ligand-free half-cell with the same C_{Bi} , and the directly measured potentials on cell (1) were converted to E_{M} by means of the above given mean value for E° (-423.7 mV).

Table 1. Nernst law test for the bismuth amalgam electrode in 1 M HNO₃ at 25°. Measurements of the cell:

(-) Hg,Bi	1 M HNO ₃ C _{Bi}	1 M HNO ₃	1 M HNO ₃ quinhydr. sat.	Pt (+)
	C _{Bi} mM	-E mV	-E° mV	
	20.1	457.0	423.5	
	10.05	463.2	423.8	
	4.02	470.9	423.6	
	2.01	476.9	423.7	
	1.21	480.4	422.9	
	0.804	482.2	421.1	
	0.402	488.6	421.6	
	0.402	488.2	421.2	

A titration procedure was not used; each solution was prepared and measured individually to reduce errors due to ligand decomposition and slow electrode reactions. Preliminary measurements were made using 1 M HClO₄ medium; but 1 M HNO₃ was used in the present work because it was hoped that the electrode reaction might be faster in the presence of nitrate¹².

BASICITY OF DIPHENYLPHOSPHINOBENZENE-*m*-SULPHONATE

Fig. 1 shows the UV spectra of the ligand in water, dilute sodium hydroxide and a series of perchloric acid concentrations. The spectra can be simply interpreted as an acid-base equilibrium between two absorbing species, giving an isobiestic point at 241 mμ.

$$\text{LH}^+ = \text{L} + \text{H}^+$$

$$\text{p}K_{\text{LH}^+} = -\log \frac{(\epsilon - \epsilon_{\text{LH}^+})C_{\text{HClO}_4}}{(\epsilon_{\text{L}} - \epsilon)} \quad (3)$$

ϵ_{L} is the molar extinction coefficient for the ligand anion determined in water and dilute sodium hydroxide. ϵ_{LH^+} is the extinction coefficient of the protonated

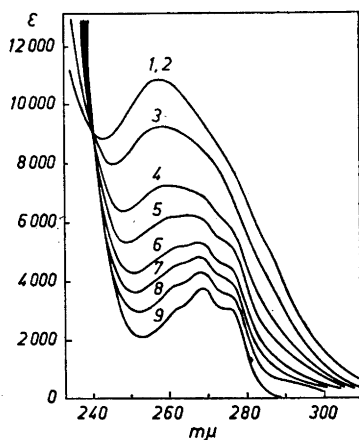


Fig. 1. UV spectra of diphenylphosphinobenzene-*m*-sulphonate in dilute NaOH (1), water (2) and a series of perchloric acid concentrations: 0.184 M (3), 0.415 M (4), 0.599 M (5) 0.829 M (6), 1.00 M (7), 1.38 M (8) and 9.22 M HClO₄ (9). The concentration of phosphine ligand was 0.123 mM in all solutions.

Table 2. Spectrophotometric determination of the acid dissociation constant of m - $(C_6H_5)_2PH^+(C_6H_4SO_3^-)$ in perchloric acid at 25°C.

Solution Curve in Fig. 1	C_{HClO_4} M	$(\epsilon - \epsilon_{LH^+})/(\epsilon_L - \epsilon)$ at:				pK_{LH^+}	
		252	257	269	276 $m\mu$	exptl.	calc.
3	0.184	3.22	3.33	3.03	3.03	0.24	0.22
4	0.415	1.10	1.19	1.09	1.18	0.33	0.34
5	0.599	0.63	0.67	0.65	0.69	0.40	0.43
6	0.829	0.33	0.34	0.31	0.36	0.56	0.54
7	1.00	0.22	0.25	0.22	0.24	0.63	0.63
8	1.38	0.098	0.118	0.076	0.109	0.86	0.82

ligand, which is assumed to be completely formed in 9.22 M $HClO_4$. ϵ is the observed extinction coefficient at intermediate acid concentrations. Table 2 gives the ratio $(\epsilon - \epsilon_{LH^+})/(\epsilon_L - \epsilon)$ measured at four wavelengths. These agree satisfactorily and the mean is used to obtain pK_{LH^+} .

It is known that the pK values of many weak bases in strong acid media are linearly dependent on the concentration of acid¹³.

In the present case it is found that

$$pK_{LH^+} = 0.13 + 0.50 C_{HClO_4} \quad (4)$$

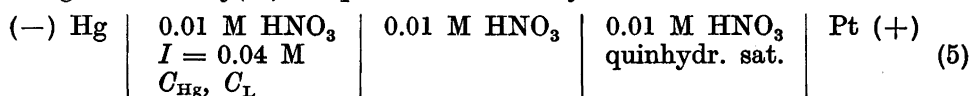
pK_{LH^+} calculated from this expression is given in Table 2 for comparison. Nitric acid is not a suitable medium for UV spectral measurements therefore it is assumed that the degree of protonation of the ligand in 1 M HNO_3 is 0.8; *i.e.* the same as in 1 M $HClO_4$.

The sulphonate group is known to be a very weak base¹⁴ and hence it is certain that m - $(C_6H_5)_2PC_6H_4SO_3^-$ protonates on the phosphorus atom. Henderson and Streuli¹⁶ estimate the pK_{LH^+} of $(C_6H_5)_3P$ in water as 2.73, which is consistent with the present work since a *meta* sulphonate group is known to have an acid strengthening effect¹⁵.

SELF-ASSOCIATION OF DIPHENYLPHOSPHINOBENZENE-*m*-SULPHONATE

The structure of the ion m - $(C_6H_5)_2PC_6H_4SO_3^-$ suggests that it is likely to show self-association of the micelle type at higher concentrations, which would interfere with equilibrium studies. The accurate equilibrium measurements of Ahrland *et al.*¹ with the silver ion show that there is no self-association in a neutral medium of ionic strength $I = 0.1$ M, when $C_L < 0.01$ M.

In the present investigation, self-association of the ligand was studied by using the mercury(II) complex and a mercury electrode in the cell:



The results of Part I³ show that when $[L] > 0.002$ M, the mercury is present almost entirely as the *tetra* complex and in this case:

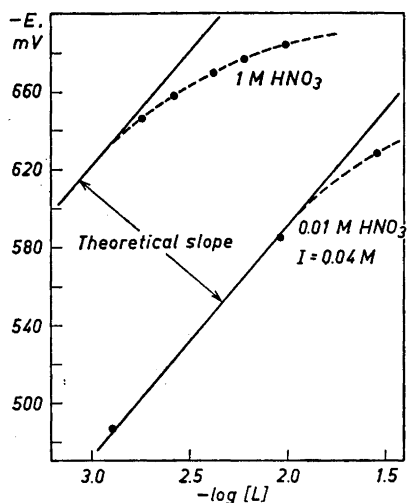


Fig. 2. The potential of cell (5) as a function of $\log [L]$ at 25°C. The straight lines have the theoretical slope expected for the tetra complex of Hg^{2+} with $m\text{-(C}_6\text{H}_5)_2\text{-PC}_6\text{H}_4\text{SO}_3^-$. The mercury concentration was fixed at $C_{\text{Hg}} = 0.191 \text{ mM}$.

$$E = \text{const.} - \frac{RT}{2F} \ln [L]^4 \quad (6)$$

if C_{Hg} is fixed, and $[L] = C_L - 4 C_{\text{Hg}}$. A graph of E against $\log [L]$ should be a straight line with a slope of $4 \times 0.0296 = 0.1184 \text{ V}$. A decreasing slope as $\log [L]$ increases will indicate ligand self-association. Fig. 2 shows that for the conditions of cell (5) self-association occurs above $[L] = 0.01 \text{ M}$. Cell (5) has also been used with 1 M HNO_3 as medium and the results are shown in Fig. 2. In this case $[L] = 0.2 (C_L - 4C_{\text{Hg}})$; the factor 0.2 correcting for the protonation of the ligand. In 1 M HNO_3 there is a larger divergence from the theoretical slope; this corresponds to greater self-association and may be caused by self-association of the protonated species or a salt effect on the self-association process. From these preliminary experiments one learns that in 1 M HNO_3 it is not possible to use solutions with $[L] > 0.001 \text{ M}$ for equilibrium measurements.

COMPLEXING OF DIPHENYLPHOSPHINOBENZENE-*m*-SULPHONATE WITH BISMUTH IONS

The general method and notation has been described in Part I³. In 1 M HNO_3 there is partial protonation of the non-complexed ligand:

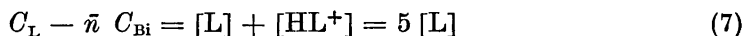


Table 3 gives the results of measurements on cell (1), and they are shown graphically in Fig. 3. From the graphs of C_L versus E_M for each bismuth concentration C_{Bi} , it was possible to interpolate at selected E_M values to obtain corresponding values of C_L and C_{Bi} . A graph of C_L versus C_{Bi} at constant E_M is a straight line with slope $= \bar{n}$ and intercept $= 5 [L]$, as shown by eqn. (7). Table 4 gives corresponding values of \bar{n} and $[L]$ determined in

Table 3. Measurements of E_M (the potential relative to a ligand-free reference cell with same bismuth concentration) for increasing values of C_L at four different bismuth concentrations. Concentrations are in mM and potentials in mV.

$C_{Bi} = 0.402$		$C_{Bi} = 0.804$		$C_{Bi} = 1.61$	
C_L	E_M	C_L	E_M	C_L	E_M
0.79	4	1.16	3	1.02	0.7
1.14	5	2.19	7	1.68	2.0
2.03	11	2.91	10	2.10	2.9
2.51	19	3.65	17	2.65	4.1
2.60	33	3.87	30	3.31	6.6
2.67	31	4.20	42		
2.86	35	4.31	47	$C_{Bi} = 2.41$	
2.90	44	4.74	48	C_L	E_M
3.04	52	5.52	60	1.89	1.0
3.51	61	6.62	68	2.40	2.1
3.52	58	8.12	85	3.07	3.3
4.73	75			3.48	5.2
4.92	74				
5.63	86				
6.13	88				
7.18	99				

this way; the formation function is plotted in Fig. 4. The smallest values of \bar{n} estimated in this manner are less reliable than the remainder, because they are derived from small, uncertain values of E_M . They are ignored when calculating the constants.

The step formation curve shows that the maximum co-ordination number is six, and that the concentrations of complexes intermediate between *mono*

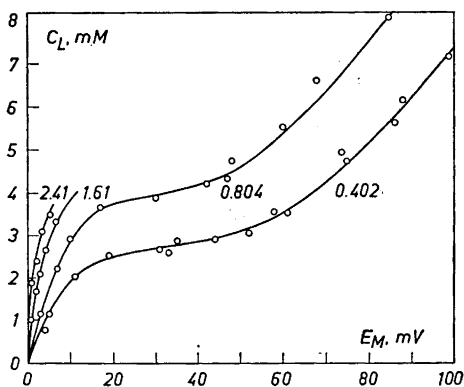


Fig. 3. Graphs of C_L against E_M for the experimental data in Table 3. The bismuth ion concentrations are given in mM for each curve.

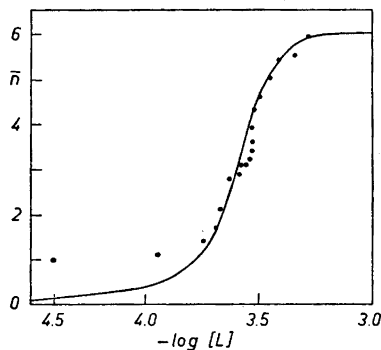


Fig. 4. The complex formation curve of bismuth ions and diphenylphosphinebenzene-*m*-sulphonate. ● Experimental points. The full curve is calculated from the constants $K_1 = 5 \times 10^3 \text{ l}\cdot\text{mole}^{-1}$, $\beta_6 = 6 \times 10^{21} \text{ l}^6\cdot\text{mole}^{-6}$.

Table 4. Corresponding values of [L] and \bar{n} determined graphically from the data of Table 3. Concentrations in mM and potentials in mV.

E_M	[L]	\bar{n}	E_M	[L]	n
2	0.032	1.0	40	0.300	3.4
4	0.116	1.1	45	0.300	3.6
6	0.184	1.4	50	0.304	3.9
8	0.208	1.7	55	0.31	4.3
10	0.220	2.1	60	0.33	4.6
15	0.240	2.8	65	0.36	5.0
20	0.264	2.9	70	0.40	5.4
25	0.272	3.1	75	0.47	5.5
30	0.280	3.1	80	0.54	5.9
35	0.296	3.2			

and *hexa* are small. The experimental formation curve can be best fitted by the constants:

$$K_1 = 5 \times 10^3 \text{ l} \cdot \text{mole}^{-1}, \quad \beta_6 = 6 \times 10^{21} \text{ l}^6 \cdot \text{mole}^{-6}.$$

The formation function can be calculated with these constants:

$$\bar{n} = \frac{K_1[L] + 6\beta_6[L]^6}{1 + K_1[L] + \beta_6[L]^6}$$

It is compared with the experimental points in Fig. 4.

The sluggish electrode reaction and the ligand self-association, already mentioned, limit the accuracy of the results. There is also the possibility that mercury may reduce Bi^{3+} in the presence of the ligand, as discussed by Ahrlund and Grenthe⁵. But this reaction is likely to be slow and unimportant in the time taken for each measurement. Treatment of the data by the X_1 functions of Fronæus or the Bodländer equation as discussed in Part I³ is unprofitable because of the low precision; but such treatments are consistent with the above constants.

DISCUSSION

Since co-ordination by the sulphonate group¹ or the benzene nucleus¹⁷ is generally very weak, there is undoubtedly co-ordination by a phosphorus donor atom in the present case. The co-ordination number of six found here for the phosphine ligand agrees with that determined by other workers for the halide⁵ and thiocyanate ions¹⁸. It is remarkable that there seems to be no steric hindrance of the formation of the *hexa* complex of $m\text{-(C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{SO}_3^-$. It is reasonable to assume that this is connected with the relatively small C—P—C angle in tertiary aryl phosphines¹⁹ and the relatively large size of the phosphorus atom.

Fig. 5 shows the distribution of bismuth between the various complexes for those systems for which data are available. From this it can be clearly seen that the bismuth ion has a greater affinity for phosphorus than for the halides, confirming the class (b) character of bismuth(III). The ranges of existence of the intermediary complexes decrease from chloride to iodide; and for the phosphine the ranges of existence have decreased so much that

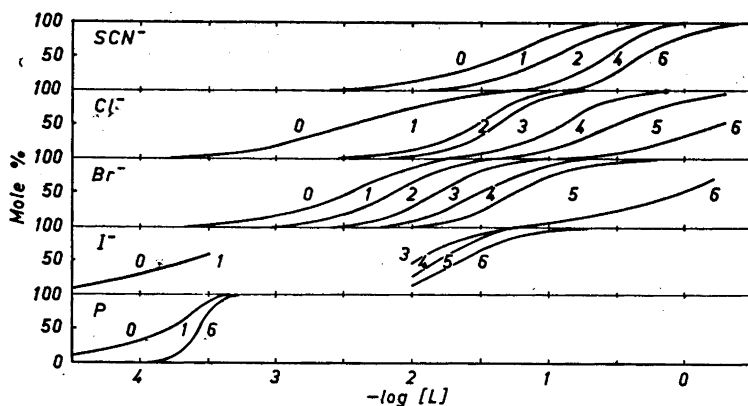


Fig. 5. The distribution of bismuth between the various complexes as a function of $\log [L]$. Conditions: thiocyanate complexes¹⁸ in 0.4 M HClO_4 at 20–25°; chloride bromide and higher iodide complexes⁵ in 1 M HClO_4 , 1 M NaClO_4 at 25°; *mono*-iodide complex²¹ in 1 M HClO_4 at 25°. The $m\text{-(C}_6\text{H}_5)_3\text{PC}_6\text{H}_4\text{SO}_3^-$ complexes in 1 M HNO_3 at 25°. Note: Ahrlund and Grenthe⁵ have incorrectly calculated β_5 and β_6 for the bismuth chloride complexes. In this diagram we have used the corrected constants²²: $\log \beta_5 = 6.72$ and $\log \beta_6 = 6.56$.

we are able to describe the system completely neglecting the complexes intermediary between *mono* and *hexa*. Thus the behaviour of the phosphine as a ligand for bismuth ions can be regarded as an extrapolation of the halide series Cl^- , Br^- , I^- . Similarly previous workers^{1,3,4} have shown that for the class (b) metal ions Ag^+ and Hg^{2+} , the phosphine behaves as a halide with properties beyond that of iodide. The thiocyanate ion¹⁸ does not fit into the halide-phosphine series and this may be accounted for by the resonance of the ion SCN^- .

The stability constant data for the halide and phosphine complexes of Ag^+ and Hg^{2+} show an enhanced stability of the *mono* complexes with the heavier donor atoms. Such large and systematic deviations from the statistical ratios of consecutive stability constants indicate that there are important orbital changes accompanying complex formation. Ahrlund, Chatt *et al.*¹ have discussed the case of the silver ion in terms of the d_{π} acceptor properties of the ligand and the hybridisation of the silver ion. Similar considerations apply to the mercuric ion^{3,4}. The bismuth ion stability constants deviate from the statistical ratios in the opposite sense to that of Ag^+ and Hg^{2+} . The orbital requirements for π -dative bonding in a *hexa* complex thus appear to be quite different from that in ions of lower co-ordination number.

Williams²⁰ has suggested that the high polarising power of class (b) metal ions, relative to their size and charge, explains the stability order of complexes of these cations. He has proposed an empirical function of the metal ionisation potential which correlates the data for the phosphine ligand with Ag^+ , Cd^{2+} , Hg^{2+} and Bi^{3+} within $\pm 2 \log K_1$ units. However, this correlation applies only to the stability of the *mono* complexes and ignores the relationships

between successive constants. It seems that the symmetry of the orbitals and the overall electronegativity are both important in the stability of class (b) metal complexes.

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