The Linear Free-energy Relation in the Thermodynamics of Complex Formation. Part 2.‡ Analysis of the Formation Constants of Complexes of the Large Metal Ions Silver(I), Mercury(II), and Cadmium(II) with Ligands Having 'Soft' and Nitrogen-donor Atoms

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A potentiometric and calorimetric study has been made of the complex formation of Ag^I, Hg^{II}, and Cd^{II} with ligands containing 'soft' and N-donor atoms. It has been found that linear enthalpy relations exist, and that they mirror quite closely the division of the free-energy data into separate groups for the 'soft' and N-donor atom ligands, for the pair of metal ions Ag^I–Hg^{II} and for Ag^I–Cd^{II}. It seems that a linear entropy relation also exists, to within experimental error, for the pair Ag^I–Hg^{II} which has a gradient and intercept that can be rationalised in terms of the Powell–Latimer–Cobble semi-empirical theory of ionic entropy. The entropy contributions are small compared with those of the enthalpy in these predominantly enthalpy-stabilised complexes. The significance of the relatively simple behaviour of the free energies compared with their enthalpy and entropy components is discussed.

IT has been shown [1,2] that, for the d^{10} metal ions Cu^I, Ag^I, Au^I, Hg^{II}, and Cd^{II}, fairly simple behaviour is observed when linear free-energy relations (l.f.e.r.s) are plotted involving the standard reduction potential or the associated stability constants of complexes of these metal ions with unidentate ligands. Separate relations are obtained for different classes of ligand donor atom. For example, it has been found that a single l.f.e.r. contains all the 'soft' ligands, *i.e.* ligands containing P, As, S, Se, $[CN]^-$, and I^- as donor groups or atoms, whereas ligands having an N-donor atom belong to a separate relation, as do ligands containing an O-donor atom.[1] One of these l.f.e.r.s, that relating the stability constants of Ag^I and Hg^{II} with 'soft' ligands, has been analysed into its enthalpy and entropy components [3] and it has been shown that underlying the l.f.e.r. was a linear enthalpy relation (l.e.r.) which closely resembled the l.f.e.r. A common feature of l.f.e.r.s is that, unlike l.e.r.s, they often pass through or near to the origin, and this was explained [3] in terms of a cancellation of the enthalpy and entropy effects accompanying desolvation of metal ions on complex formation in aqueous solution.

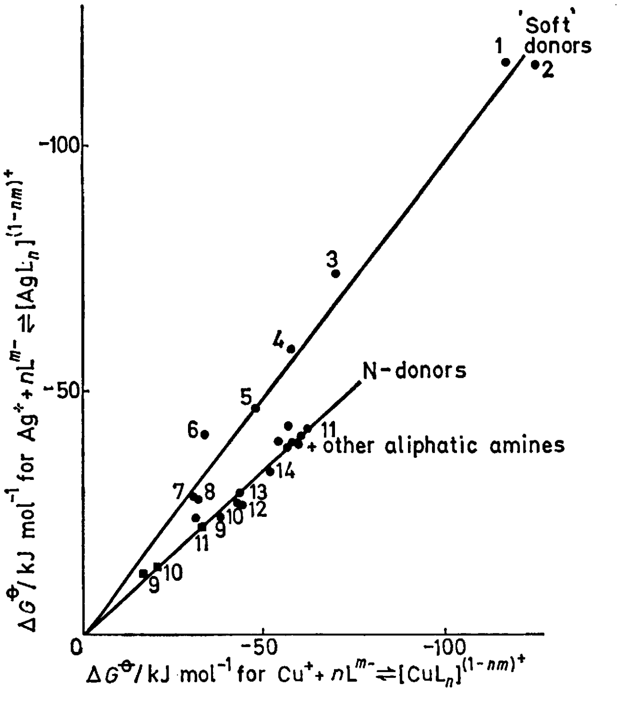

FIGURE 1 Linear free-energy relations for corresponding complex-formation reactions of Ag^I and Cu^I. L = $PEt_2(CH_2CH_2OH)$ (1), $[CN]^-$ (2), $[S_2O_3]^{2-}$ (3), dithioglycol (4), $[SO_3]^{2-}$ (5), Br^- (6), $[AgPh(CH_2CO_2H)_2]$ (7), Cl^- (8), py (9), 2Me-py (10), NH_3 (11), 3Me-py (12), 4Me-py (13), $MeNHCH_2CO_2H$ (14). Circles and squares refer to quantities determined for ML_2 and ML complexes, respectively

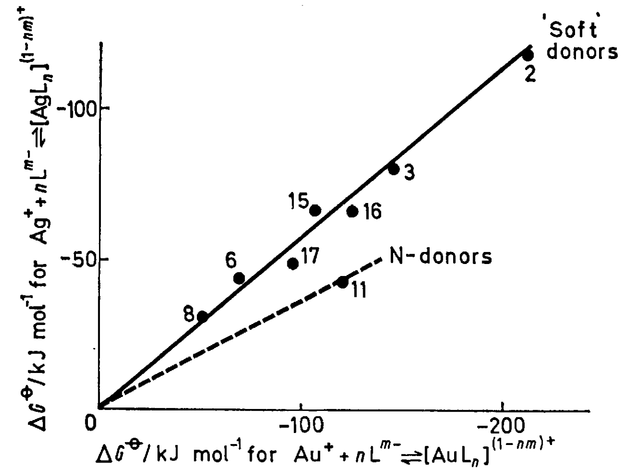

FIGURE 2 Linear free-energy relations for corresponding complex-formation reactions of Ag^I and Au^I. L as in Figure 1 except for I^- (15), thiourea (16), and $[SCN]^-$ (17)

We have noted that l.f.e.r.s of the type described above apply also to non-d^{10} transition-metal ions although, for these metal ions, complexes involving 'soft' ligands are rare. In particular, l.f.e.r.s have recently been shown to apply also to the platinum-group metals Pt^{IV} and Pd^{II}.[4] Some typical l.f.e.r.s involving

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‡ Part 1 is ref. 3.

[1] R. D. Hancock and N. P. Finkelstein, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 477.

[2] R. D. Hancock, N. P. Finkelstein, and A. Evers, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2539.

[3] R. D. Hancock and F. Marsicano, *J.C.S. Dalton*, 1976, 1832.

[4] R. D. Hancock, A. Evers, and N. P. Finkelstein, 'Stability Constants and Linear Free-energy Relations for the Platinum-group Metals,' National Institute for Metallurgy, Johannesburg, Report No. 1822, 1976.

the metal ions Ag^{I}, Cu^{I}, Au^{I}, Cu^{II}, Co^{II}, Hg^{II}, and Bi^{III} are shown in Figures 1—5.

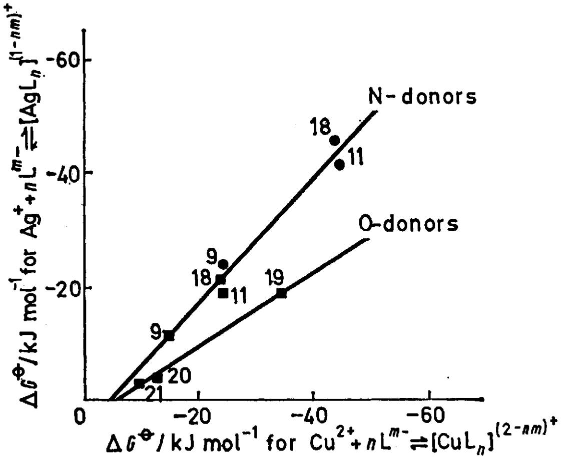

FIGURE 3 Linear free-energy relations for corresponding complex-formation reactions of Ag^{I} and Cu^{II}. L as in Figure 1 except for imH (18), [OH^{-}] (19), [MeCO$_2$]$^{-}$ (20), and [PhCO$_2$]$^{-}$ (21)

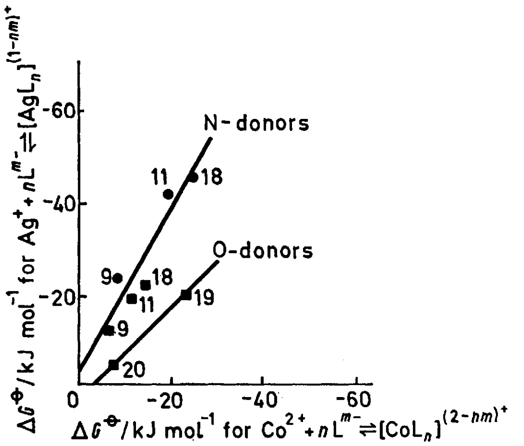

FIGURE 4 Linear free-energy relations for corresponding complex-formation reactions of Ag^{I} and Co^{II}. L as in previous Figures

It is of interest to determine in general whether the division of the free-energy data into separate groups involving ' soft ', N-, and O-donors is a result of simple enthalpy and entropy behaviour, or whether it is the result of complex compensatory effects between enthalpy and entropy. In order to provide a partial answer to this question, and also to check certain predictions made in Part 1 of this series[3] concerning entropy-change relations to be expected when comparison is made between the metal ions Ag^{I} and Hg^{II}, a calorimetric study of the enthalpies of formation of several N-donor complexes of Ag^{I}, Hg^{II}, and Cd^{II} was undertaken. This paper describes the determination of the enthalpies of complex formation of Ag^{I} with 2,2′-iminodiethanol (ide), of Hg^{II} with pyridine (py), imidazole (imH), ide, and piperidine (pip), and of Cd^{II} with ide and imH. Data for the protonation reactions of imH and pip were also determined. These results, together with those previously determined for ' soft '-ligand complexes of Ag^{I}, Hg^{II}, and Cd^{II},[3,5] are used for the analysis of the l.f.e.r.s for these three metal ions in terms of enthalpy and entropy changes on complex formation.

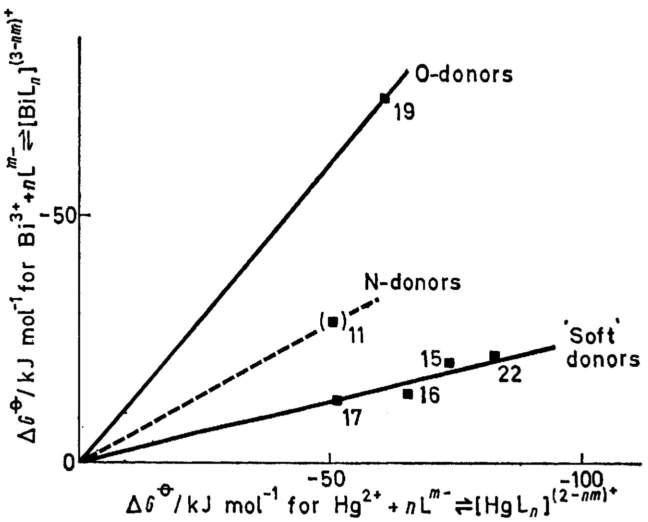

FIGURE 5 Linear free-energy relations for corresponding complex-formation reactions of Bi^{III} and Hg^{II}. L as in previous Figures except for 4-(diphenylphosphino)benzenesulphonate (22)

EXPERIMENTAL

All the measurements were made at 298.15 ± 0.05 K in an aqueous medium of ionic strength $I = 0.5$ mol dm^{-3}. Where necessary, the ionic strength was made up to 0.5 mol dm^{-3} with the use of the perchlorate or nitrate salt of the protonated amine in order to buffer the solutions to a pH value low enough to suppress hydrolysis of the metal ions. In other cases the background electrolyte was Na[ClO$_4$].

Materials.—Stock solutions of the metal ions were prepared as described previously.[5] Pyridine (AnalaR grade) was purchased from B.D.H. and used without further purification. Imidazole (G.R.), 2,2′-iminodiethanol, and piperidine were purchased from E. Merck. Solutions of imH, ide, py, and pip were standardised by potentiometric titration against standard perchloric acid solution.

Potentiometry.—Stability constants were determined by the use of an electrochemical cell having a Radiometer G202B glass electrode, with a low sodium-ion error at high pH. The Ag–AgCl–Cl^{-} reference electrode and salt bridge used have been described previously.[5]

Calorimetry.—The enthalpy changes were determined with the use of a titration calorimeter, which has been described previously,[6] as has the calibration and data reduction.[5,6]

Calculations.—Stability constants were calculated from potentiometric data with the use of the LETAGROP ETITR[7] and the MINIQUAD programs.[8] Enthalpy

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[5] F. Marsicano and R. D. Hancock, *J. Co-ordination Chem.*, 1976, **6**, 21.

[6] K. Lowe, A. W. Forbes, F. Marsicano, and N. P. Finkelstein, ' The Construction and Testing of a Precision Calorimeter,' National Institute for Metallurgy, Johannesburg, Report No. 1582, 1973.

[7] P. Brauner, L. G. Sillén, and R. Whiteker, *Arkiv. Kemi*, 1969, **31**, 365.

[8] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.

changes on complex formation were calculated from the calorimetric data with the use of LETAGROP KALLE.[9] In favourable instances, data obtained from titration calorimetry can be used for the determination of both stability constants and enthalpy changes,[9] but this method was not used generally since it was found that cross-correlation between the stability constants and the enthalpy changes was high particularly for the weaker complexes. In most cases the enthalpy changes were calculated from the calorimetric data and known values of the stability constants.

Corrections were made for any side reactions known to be taking place in the experiment, as described previously.[3] In correcting for metal hydrolysis, the recently reported [10] values of $\Delta H_1^\ominus = -36.2$ and $\Delta H_2^\ominus = -72.4$ kJ mol^{-1}, determined at $I = 0.1$ mol dm^{-3}, were used for the enthalpies of hydroxylation of Hg^{II} instead of the values previously used.[3] Values for the protonation constants and enthalpies of protonation of the more basic ligands used in this investigation are shown in Table 1. The error, introduced by the fact that the data given in Table 1 for the enthalpy of protonation of ide were determined at an ionic strength other than 0.5 mol dm^{-3}, is second order and can be neglected.

TABLE 1

Protonation constants and enthalpies of protonation at $I = 0.5$ mol dm^{-3} for the more basic ligands used

Ligand	log β (pK_a)	Ref.	$\Delta H^\ominus$ kJ mol^{-1}	Ref.
py	5.45	10	−20.09	*a*
imH	7.20	*a*	−38.1	*a*
ide	8.95	*b*	−42.4 [c]	*d*
pip	10.88	*a*	−55.0	*a*

[a] This work. [b] J. F. Fisher and J. L. Hall, *Analyt. Chem.*, 1967, **39**, 1550. [d] V. E. Bower, R. A. Robinson, and R. G. Bates, *J. Res. Nat. Bur. Stand., Sect. A*, 1962, **66**, 71. [c] $I = 0$ mol dm^{-3}.

RESULTS

The experimental data for the potentiometric titrations and the calorimetric titrations are given in Supplementary Publication No. SUP 22153 (8 pp.).* Any special features encountered with the various systems will be discussed separately. Values for the thermodynamic properties of complex formation are listed in Table 2. The estimated error limits are three times the standard deviations given by the LETAGROP ETITR and KALLE programs.

Pyridine, Imidazole, and Piperidine.—The pK_a of the ligands imidazole and piperidine were determined at $I = 0.5$ mol dm^{-3} using $Na[ClO_4]$ and $K[NO_3]$ as the respective background electrolytes. For imH, a value of 7.20 was obtained which can be compared with the literature [11] values of 6.993 at $I = 0$ and 7.06 at $I = 0.3$ mol dm^{-3}. For pip, a value of 10.88 ± 0.04 was obtained which can be compared with previous [11] values of 11.12 ($I = 0$) and 11.6 (I not reported). Results from the calorimetric titrations for these systems, calculated using pK_a values from Table 1, are given in Table 2. For py and imH, the ionic strength was made up to 0.5 mol dm^{-3} using $Na[ClO_4]$; for pip, $K[NO_3]$ was used. Literature values are included in Table 2 for comparison.

Silver(I) *and 2,2′-Iminodiethanol.*—In order to avoid precipitation of Ag_2O by the strongly basic ligand, the ionic strength was made up to 0.5 mol dm^{-3} with ide·$HClO_4$. Stability constants of log β_1 2.69 and log β_2 5.48, measured at $I = 0.5$ mol dm^{-3},[12] were used in the calculation of the thermodynamic properties of complex formation (Table 2). No literature values are available for comparison.

Mercury(II) *and Pyridine.*—Pyridinium perchlorate was used to set the ionic strength at 0.5 mol dm^{-3} in order to minimise hydrolysis of the mercury(II) ions. The stability constants for the Hg^{2+} + py system, *i.e.* log β_1 5.1 and log β_2 10.0 at $I = 0.5$ mol dm^{-3},[13] are close in value to the pK_a of py, *i.e.* 5.45, with the result that low concentrations of Hg^{2+} ions in the presence of a pyridinium perchlorate background electrolyte have, to a large extent, already reacted with pyridine arising from dissociation of the pyridinium ions. Accordingly, a calorimetric titration was carried out by titrating an acidic solution of $Hg[ClO_4]_2$ into an 0.500 mol dm^{-3} solution of pyridinium perchlorate. Appreciable hydrolysis of the metal ion occurs if excess of pyridine is added to the titrate, resulting in less evolution of heat. Sjöberg [14] reported that, in the Hg^{2+}–$[OH]^-$–imH system, the stability constant of the $[Hg(OH)(imH)]^+$ complex is considerably larger than would be expected on statistical grounds. This also applies to the complex $[Hg(OH)(py)]^+$.

Mercury(II) *and Imidazole.*—There is a particularly wide scatter in the stability constants in the literature for this system. Brooks and Davidson [15] reported a value of log β_2 16.74 at 300.15 K and $I = 0.15$ mol dm^{-3} ($Na[ClO_4]$) and Smith [16] reported values of log β_1 3.57 and log β_2 6.95 at 298.15 K and $I = 0.058$ mol dm^{-3} (KCl). Recently, Sjöberg [14] determined values of log β_1 9.18 ± 0.12 and log β_2 18.19 ± 0.02 at 298.15 K and $I = 3.0$ mol dm^{-3}. A value of 21.86 was also obtained for the partly hydrolysed complex $[Hg(OH)(imH)]^+$.

It has been shown [15] that the equilibrium constant for the competition reaction (1) lies between 1 and 10^4,

$$Hg^{2+} + 2[imH_2]^+ \rightleftharpoons [Hg(imH)_2]^{2+} + 2H^+ \qquad (1)$$

i.e. within the range permitting simultaneous determination of equilibrium constants and enthalpy changes by titration calorimetry if a solution of mercury(II) ions is titrated with a solution containing imidazolium ions. Using the pK_a and $\Delta H^\ominus$ for protonation of imidazole given in Tables 1 and 2 respectively, the stability constants for this system were determined by this technique to be log β_1 9.64 ± 0.45 and log β_2 18.18 ± 0.21, in fair agreement with the values of Sjöberg.[14] Since the latter values (determined potentiometrically) are more precise, they were used to calculate values of $\Delta H^\ominus$ from the calorimetric results.

The reaction was carried out by addition of a solution of imidazolium perchlorate to an acidic solution of mercury(II) perchlorate. Since the program LETAGROP KALLE cannot deal with calculations involving prereacted components in the titrant solution, the data in Table II of SUP 22153 for this system were treated as a number of separate

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[9] R. Arnek, *Arkiv. Kemi*, 1970, **32**, 81.

[10] R. J. Bruehlman and F. N. Verhoer, *J. Amer. Chem. Soc.*, 1956, **78**, 5844.

[11] 'Handbook of Biochemistry,' 2nd edn., The Chemical Rubber Company, Cleveland, Ohio, U.S.A., pp. J58—173.

[12] J. Bjerrum and S. Refn, *Suomen Kem.*, 1956, **29**, B68.

[13] J. Bjerrum, *Chem. Rev.*, 1950, **46**, 381.

[14] S. Sjöberg, Doctoral Thesis, University of Umeå, 1976.

[15] P. Brooks and N. Davidson, *J. Amer. Chem. Soc.*, 1960, **82**, 2118.

[16] J. C. Smith, Dissertation, Kansas State University, 1961.

one-point titrations in which the ' titrate ' as a whole is added to increasing amounts of the ' titrant '. The values of $\Delta H_i^{\ominus}$ obtained appear in Table 2.

Mercury(II) *and 2,2′-Iminodiethanol*.—The hydrogen-perchlorate salt of ide was used to adjust the ionic strength to 0.5 mol dm^{-3}, and reported [13] stability constants of log β_1 7.84 and log β_2 15.66 at $I = 0.5$ mol dm^{-3} were used in the calculation of enthalpy changes from the calorimetric data (Table 2).

Mercury(II) *and Piperidine*.—Calorimetric titrations were carried out in the presence of 0.47 mol dm^{-3} piperidinium perchlorate in the titrate for buffering purposes, and the ionic strength was made up to 0.5 mol dm^{-3} with $Na[ClO_4]$. Stability constants of log β_1 8.70 and log β_2 17.44, determined at $I = 0.5$ mol dm^{-3},[13] were used for the calculation of the $\Delta H_i^{\ominus}$ (Table 2).

TABLE 2

Stability constants, β_i, together with the free energies $\Delta G_i^{\ominus}$, enthalpies $\Delta H_i^{\ominus}$, and entropies (expressed as the entropy contributions to the free energy of complex formation, $T\Delta S_i^{\ominus}$) of complex formation, of the metal M with the ligand L at 298.15 K and $I = 0.5$ mol dm^{-3}

Cation M	Ligand L	Complex	log β_i	$\Delta G_i^{\ominus}$	$\Delta H_i^{\ominus}$	$T\Delta S_i^{\ominus}$
					kJ mol^{-1}	
H^+	py	$[HL]^+$	5.45 [a]	−31.11 [a]	−20.09 ± 0.2 (−19.59 at $I = 0$) [a]	11.02 ± 0.2
	imH	$[HL]^+$	7.20 ± 0.05	−41.10 ± 0.28	−38.10 ± 0.12 (−37.78 at $I = 0.3$) [b]	3.0 ± 0.30
	pip	$[HL]^+$	10.88 ± 0.04	−62.10 ± 0.23	−55.0 ± 0.15 (−53.97 at $I = 0$) [a]	7.1 ± 0.27
Ag^+	ide	$[AgL]^+$	2.69	−15.35	−21.5 ± 1.8	−6.2 ± 1.8
		$[AgL_2]^+$	5.48	−31.28	−49.1 ± 1.2	−17.8 ± 1.2
Hg^{2+}	py	$[HgL]^{2+}$	5.1	−29.11	−36 ± 5	−7 ± 5
		$[HgL_2]^{2+}$	10.0	−57.1	−69 ± 34	−12 ± 34
	imH	$[HgL]^{2+}$	9.18	−52.4	−75 ± 5	−23 ± 5
		$[HgL_2]^{2+}$	18.18	−103.8	−107.1 ± 0.1	−3.3 ± 0.1
		$[Hg(OH)L]^+$	21.86	−124.8	−113.8 ± 1.5	11.0 ± 1.5
	ide	$[HgL]^{2+}$	7.84	−44.75	−80 ± 24	−35 ± 24
		$[HgL_2]^{2+}$	15.66	−89.39	−115 ± 15	−26 ± 15
	pip	$[HgL]^{2+}$	8.70	−49.66	−45 ± 15	7 ± 15
		$[HgL_2]^{2+}$	17.44	−99.55	−74 ± 9	26 ± 9
Cd^{2+}	imH	$[CdL]^{2+}$	2.76 ± 0.03	−15.8 ± 0.1	−20.4 ± 0.5	−4.6 ± 0.5
		$[CdL_2]^{2+}$	4.87 ± 0.03	−27.8 ± 0.2	−40.7 ± 1.6	−12.9 ± 1.6
		$[CdL_3]^{2+}$	6.32 ± 0.06	−36.1 ± 0.3		
		$[CdL_4]^{2+}$	7.49 ± 0.06	−42.8 ± 0.3		
	ide	$[CdL]^{2+}$	2.40	−13.7	−9.3 ± 1.2	4.4 ± 1.2
		$[CdL_2]^{2+}$	4.52	−25.80	−18.0 ± 1.2	7.8 ± 1.2

[a] Ref. 11. [b] Ref. 22.

No stability constants have been reported for the mixed complex species $[Hg(OH)(py)]^+$, $[Hg(OH)(ide)]^+$, or $[Hg(OH)(pip)]^+$. If these complexes are found to have stabilities substantially greater than expected on statistical grounds, then significant hydrolysis of the $[HgL]^{2+}$ complexes may have occurred in these measurements, resulting in a positive contribution to the calculated value for $\Delta H^{\ominus}$.

Cadmium(II) *and Imidazole*.—The stability constants for this system were measured by glass-electrode potentiometry at $I = 0.5$ mol dm^{-3} using $Na[ClO_4]$. The results are shown in Table 2. They can be compared with values of log β_2 5.07, log β_3 6.46, and log β_4 7.48,[17] and log β_1 2.80, log β_2 4.90, log β_3 6.45, and log β_4 7.58,[18] both sets at $I = 0.15$ mol dm^{-3}. The reasonable agreement obtained with the literature values shows, as argued previously,[5] that the effect of a change in ionic strength from *ca.* 0.1 to 0.5 mol dm^{-3} is small when no change of charge is involved in the reaction. The stability constants in Table 2 were used to calculate values of $\Delta H_i^{\ominus}$ from the calorimetric titration data, also obtained at $I = 0.5$ mol dm^{-3} ($Na[ClO_4]$). The results are listed in Table 2.

Cadmium(II) *and 2,2′-Iminodiethanol*.—In order to avoid precipitation of $Cd[OH]_2$, the ionic strength was made up to 0.5 mol dm^{-3} using ide·$HClO_4$. Stability constants from the literature [19] were used in the calculation of $\Delta H_i^{\ominus}$ from the calorimetric data (Table 2).

DISCUSSION

Values of $\Delta G_i^{\ominus}$ obtained from the stability constants β_i by use of relation (2) are plotted (together with

$$\Delta G_i^{\ominus} = -RT\ln\beta_i \qquad (2)$$

values determined previously,[3,5] and values taken from the literature [20,21]) in Figures 6 and 7 for the pairs of metal ions Ag^I and Hg^{II} and Ag^I and Cd^{II} respectively. Points plotted as squares refer to $\Delta G_1^{\ominus}$ and circles to $\Delta G_2^{\ominus}$.

By analogy with Figures 1—5, lines are drawn connecting the points corresponding to ' soft ', N-, and O-donors respectively. It is of interest that all three types of l.f.e.r.s encountered in Figures 1—5 are apparent in both Figures 6 and 7. This is because the hardness of Hg^{II} and Cd^{II} is such that complexes can form with ' soft ', N-, and O-donor ligands. There are more intermediate cases apparent in Figures 6 and 7, particularly between the N-donor and ' soft '-donor lines, than was apparent in Figures 1—5. Again it is noted

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[17] N. C. Li, J. M. White, and E. Doody, *J. Amer. Chem. Soc.*, 1954, **76**, 6219.

[18] C. Tanford and M. L. Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 434.

[19] P. K. Migal' and A. N. Pushnyak, *Russ. J. Inorg. Chem.*, 1960, **5**, 293.

[20] L. G. Sillén and A. E. Martell, ' Stability Constants of Metal–Ion Complexes,' *Special Publ.*, The Chemical Society, London, 1964, no. 17.

[21] L. G. Sillén and A. E. Martell, ' Stability Constants of Metal–Ion Complexes, ' *Special Publ.*, The Chemical Society, London, 1971, no. 25.

that most, but not all, of the l.f.e.r.s shown in Figures 1—7 pass close to the origin. This has been explained[3] in terms of a cancellation of enthalpy and entropy effects accompanying desolvation of metal ions on complex formation in aqueous solution. Cadmium seems to be an exception to this rule.

Before an attempt can be made to rationalise the data in Figures 6 and 7 it is necessary to establish whether the

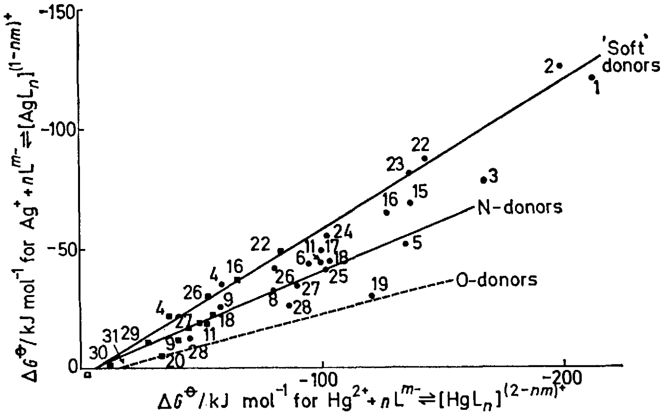

FIGURE 6 Linear free-energy relations for corresponding complex-formation reactions of Ag^I and Hg^{II}. L as in previous Figures except for selenourea (23), ethanethiosulphonate (24), $NH_2CH_2CH_2OMe$ (25), tris(3-sulphophenyl)arsine (26), ide (27), $[N_3]^-$ (28), aniline (29), F^- (30), and $[NO_3]^-$ (31)

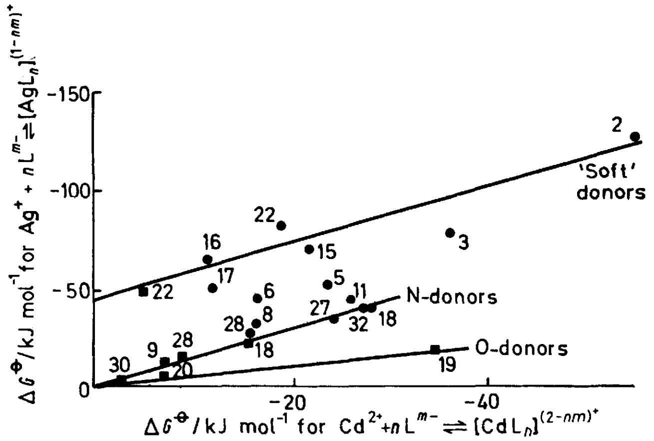

FIGURE 7 Linear free-energy relations for corresponding complex-formation reactions of Ag^I and Cd^{II}. L as in previous Figures except for NH_2Me (32)

patterns observed in the free energies of complex formation result primarily from enthalpy or from entropy effects, or whether they are the result of complicated self-compensating enthalpy and entropy effects. Figure 8 shows the $\Delta H_2^{\ominus}$ results for the pair Ag^I and Hg^{II}, and Figure 9 shows those for the pair Ag^I and Cd^{II}. The literature results used were taken from Christensen *et al.*[22] In Figure 8 it can be seen that the division of the free-energy relations into separate l.f.e.r.s for the ' soft ' and N-donor ligands is closely mirrored by separate linear enthalpy relations (l.e.r.s) for these two classes of ligands. A similar behaviour can be seen for the Ag^I and Cd^{II} pair in Figure 9. Less information is available for $\Delta H_1^{\ominus}$ for the ML complexes but a similar pattern can be discerned.

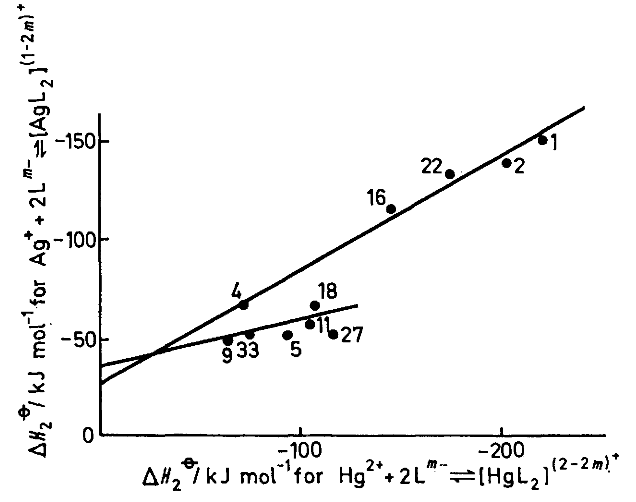

FIGURE 8 Linear enthalpy relations for corresponding complex-formation reactions of Ag^I and Hg^{II}. L as in previous Figures except for pip (33)

Turning to the entropies of complex formation, it has been pointed out in Part 1 of this series[3] that, for neutral ligands L of intermediate size, the entropies of complex formation for the metal ions Ag^I and Hg^{II} should be related by expression (3). This implies that, under the

$$T\Delta S_2^{\ominus}(\mathrm{AgL_2}^+) - T\Delta S_2^{\ominus}(\mathrm{HgL_2}^{2+}) = -37.1\ \mathrm{kJ\ mol^{-1}} \quad (3)$$

above restrictions on L, a plot of $T\Delta S_2^{\ominus}(\mathrm{AgL_2})$ against $T\Delta S_2^{\ominus}(\mathrm{HgL_2})$ for the pair of metal ions Ag^I and Hg^{II} should be linear with unit gradient and an intercept of

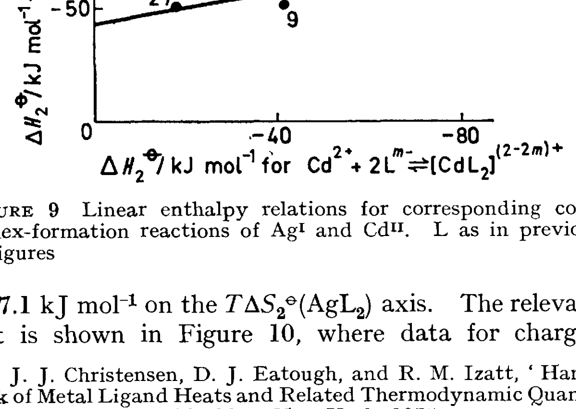

FIGURE 9 Linear enthalpy relations for corresponding complex-formation reactions of Ag^I and Cd^{II}. L as in previous Figures

-37.1 kJ mol^{-1} on the $T\Delta S_2^{\ominus}(\mathrm{AgL_2})$ axis. The relevant plot is shown in Figure 10, where data for charged

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[22] J. J. Christensen, D. J. Eatough, and R. M. Izatt, ' Handbook of Metal Ligand Heats and Related Thermodynamic Quantities,' 2nd edn., Marcel Dekker, New York, 1975.

ligands have also been included. Error ellipses have been drawn around the points, where the length of the principal axes represents 3σ, so the elliptical area represents a 95% probability region. Where information on error limits was not available, an arbitrary value of $3\sigma = 8$ kJ mol^{-1} was taken to be representative of the usual experimental uncertainty associated with measurements of $T\Delta S^{\ominus}$, and is indicated by broken lines in Figure 10. The point corresponding to the complex $[Hg(py)_2]^{2+}$ has been omitted from Figure 10 owing to the very large experimental uncertainty associated with $T\Delta S_2^{\ominus}$ for this species.

Unfortunately, the magnitude of the experimental uncertainties makes it difficult to assign a ' best ' straight line to the data. However, it can be seen that all the data, with the exception of ide and piperidine, lie on the indicated linear entropy relation (l.s.r.) to within the estimated experimental error. It should be noted that the very small ligands NH_3 and $[CN]^-$ deviate significantly from the l.s.r. and have not been included in Figure 10. The model of Powell, Latimer, and Cobble,[23-26] from which equation (3) is derived, requires that the ' organic '-type ligand should be sufficiently large to shield the metal ion from the solvent. In the case of ide, it can be seen that the point corresponding to this ligand on the $\Delta H^{\ominus}$–$\Delta H^{\ominus}$ relation in Figure 8 is displaced in a direction which suggests an anomalously negative value of $\Delta H_2^{\ominus}$ with the metal ion Hg^{II}. This indicates that ide may form a chelate complex with Hg^{II} involving five-membered ring systems. This would result in increased stability owing not only to the formation of Hg–OH bonds but also to a reduction in steric hindrance between the ethanolic group and water molecules of hydration on the metal ion.[27] This presumably does not happen with Ag^I owing to its greater tendency to form linear complexes. The deviation of the point for ide in Figure 10 is presumably related to entropy effects associated with the formation of the chelate rings. An analogous deviation from the $\Delta H^{\ominus}$–$\Delta H^{\ominus}$ relation for ' soft ' donors is not observed for the ligand thiodiglycol. Molecular models show quite clearly that the much larger size of the sulphur donor atom precludes chelation in this instance. Thus, for thiodiglycol no deviation is seen in the $T\Delta S^{\ominus}$–$T\Delta S^{\ominus}$ plot of Figure 10.

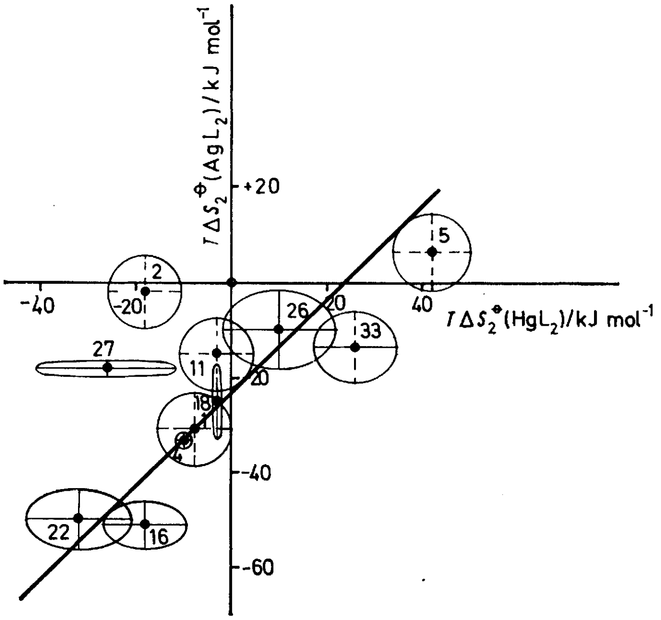

FIGURE 10 Linear entropy relation for corresponding complex-formation reactions of Ag^I and Hg^{II}

It can be seen from Figure 10 that the l.s.r. seems to hold irrespective of the hardness or softness of the ligand donor atom, and, in fact, holds also for the larger charged ligands, like 4-(diphenylphosphino)benzenesulphonate and tris(3-sulphophenyl)arsine, as well as for the sulphite ion. As predicted by the Powell–Latimer–Cobble model, the l.s.r. in Figure 10 has a gradient close to unity, but is displaced upward from the predicted intercept by *ca.* 15 kJ mol^{-1}. This must be attributed to the partial breakdown of the condition that the central metal ion be completely surrounded by an organic-type ' sheath ', which cannot be the case for ML_2 complexes, leading to more negative values for the entropies of formation of the complex involving Hg^{II} which is more strongly hydrated in this case. There are insufficient entropy data to allow a conclusion to be drawn in the case of Ag^I–Cd^{II}, but the available data indicate a pattern similar to Figure 10 with a somewhat larger deviation, in the same direction, from the intercept predicted by the model.

The l.f.e.r.s of Figure 6 can now be understood as resulting primarily from two separate l.e.r.s, one for ' soft ' and one for N-donors. (It is expected that a separate enthalpy relation also exists which incorporates the negatively charged O-donors.) The entropy contribution, $T\Delta S^{\ominus}$, to the free energies of complex formation is relatively small here, *i.e.*, for the relatively soft metal ions chosen for this study, the complexes formed are predominantly enthalpy stabilised. (Figure 10 has been plotted on a scale almost twice as large as Figure 8.)

In concluding that the separate l.f.e.r.s given by the ' soft ', N-, and O-donor ligands for the pairs of metal ions Ag^I and Hg^{II} and Ag^I and Cd^{II} represent primarily an enthalpy effect, it might be noted that, whereas the enthalpies of formation of halogeno-complexes of a soft metal ion such as Hg^{II} decrease in the order $I^- > Br^- > Cl^-$ in aqueous solution, the gas-phase enthalpies decrease in the reverse order. Therefore, it may be erroneous to relate enthalpies in aqueous solution too closely to enthalpies in the gas phase, and hence to electronic-bonding effects. However, it does seem that the division into separate l.f.e.r.s is primarily a bonding effect, which may be related to the different electrostatic and covalent contributions to the metal–ligand bond.

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[23] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, 1951, **19**, 1139.

[24] J. W. Cobble, *J. Chem. Phys.*, 1953, **21**, 1443.

[25] J. W. Cobble, *J. Chem. Phys.*, 1953, **21**, 1446.

[26] J. W. Cobble, *J. Chem. Phys.*, 1953, **21**, 1451.

[27] R. D. Hancock and F. Marsicano, *J.C.S. Dalton*, 1976, 1096.

Indeed, Figures 1—7 can be quite convincingly rationalised in terms of Pearson's hard and soft acid and base principle, where ligands lying on the same l.f.e.r. are of similar softness albeit different intrinsic strength. The intermediate cases, such as, for example, the negatively charged S-donors and the halides, would be expected to be harder than the neutral soft donors and accordingly occupy a position intermediate between the lines of the ' soft ' and N-donors. Similarly the position of azide in Figure 6 indicates that, as expected, this ion is harder than NH_3 because of its negative charge.

We are now using l.f.e.r.s similar to those in Figures 1—7 in an attempt to quantify the hard and soft acid and base principle, and to improve recent attempts to use two- and four-parameter equations to predict stability constants in aqueous solution. There seems to be a general feeling that enthalpy data are more ' fundamental ' than free energies and should therefore be used in preference to free energies when attempting to correlate the properties of complexes in aqueous solution. The significance of the parallelism between free-energy and enthalpy behaviour shown in this study is that it is probably not necessary to restrict attention to enthalpy data only. On the contrary, self-cancellation effects between enthalpy and entropy changes in aqueous solution sometimes lead to apparently simpler behaviour for free energies, such as, for example, the tendency of l.f.e.r.s to pass through, or close to, the origin.

It has been argued recently [28] that structural changes in the solvent can have no effect on the free-energy changes of solution-phase reactions, whereas they can affect the corresponding enthalpy and entropy changes to an equal and opposite extent. It seems that desolvation effects can be viewed to a certain extent, at least for outer-sphere water, as a structural change in the solvent, which implies that such effects would not affect [5] the free-energy change on complex formation. This would make the use of free-energy data more appropriate for parametric modelling.

Since completion of this study, it is becoming clear that the existence of relatively simple l.e.r.s, as for the pair of large metal ions Ag^{I} and Hg^{II}, is not necessarily general for other smaller metal ions. This will be dealt with in a future paper.

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[7/916 *Received*, 26*th May*, 1977]

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[28] A. Ben-Naim, *Biopolymers*, 1975, **14**, 1337.