Flow Microcalorimetry in Stepwise Equilibria of Metal Complexes. Reactions of *NN'*- and *NN*-Diethylethylenediamine with Hydrogen and Copper(II) Ions

By **Claudio Bianchini, Luigi Fabbrizzi, and Piero Paoletti,*** Istituto di Chimica Generale dell'Università di Firenze and Laboratorio del C.N.R., Via I. Nardi 39, 50132 Florence, Italy

Enthalpy values associated with the stepwise reactions of hydrogen and copper(II) ions with the two isomeric diamines *NN'*- and *NN*-diethylethylenediamine have been determined by flow microcalorimetry at 25 °C and $I = 0{\cdot}5$M ($NaClO_4$). Combination with the reported $\Delta G^{\ominus}$ values gives appropriate $\Delta S^{\ominus}$ values. Comparison with the results for ethylenediamine shows that ethyl substitution causes a decrease in exothermicity of the reactions of protonation and complex formation and leads to a larger entropy change. In general, reactions with the symmetrical ligand are more exothermic than those of the asymmetrical one. The method of measuring and calculating enthalpies of stepwise reaction from flow-microcalorimetric data is described in detail.

THE commercial availability of calorimeters and their introduction to usage in inorganic chemistry have made possible the availability of a large number of enthalpy values for formation of metal complexes in solution.[1] Separation of the $\Delta H^{\ominus}$, $\Delta S^{\ominus}$, and $\Delta G^{\ominus}$ parameters allows hypotheses about the nature of solution reactions, particularly the energies of co-ordinate bonds and the interaction of complex species with the solvent.

Calorimetric studies of complex formation between metal ions and *N*- and *C*-substituted diamines have recently been reported.[2-4] *N*-Methyl substitution influences remarkably the thermodynamics of metal-complex formation,[3] while *C*-methyl substitution has a less noticeable effect.[4] Particularly, complex formation of Cu^{II} (ref. 3) and Ni^{II} (ref. 5) with the symmetric diamine *NN'*-dimethylethylenediamine (dmen) is accompanied by a more exothermic enthalpy than with the corresponding asymmetrical isomer *NN*-dimethylethylenediamine (2-dimethylaminoethylamine, dmae).

Until now no calorimetric data have been reported for complex formation with *N*-ethyl-substituted ethylenediamines. This paper reports a calorimetric study of protonation of the two ligands *NN'*-diethylethylenediamine (deen) and *NN*-diethylethylenediamine (deae) and their complex formation with Cu^{II} ion. The heats involved in these reactions have been measured by flow microcalorimetry. In the past flow microcalorimetry has been used only in the study of biochemical equilibria.[6] It seems particularly suitable for the study of complex formation in solution because of the ease of use and the comparatively small amounts of time and substances required for each experiment. Reported here are descriptions of the experimental techniques and the method of calculating the enthalpy, $\Delta H^{\ominus}$, for stepwise reactions.

EXPERIMENTAL

Calorimetric Measurements.—Apparatus. Calorimetric measurements were carried out using a LKB 10700—1 flow microcalorimeter utilising the 'mixing cell.' In order to minimise experimental noise the solutions were passed from the mixing cell into the second cell ('flow through') before being pumped out from the calorimeter. This technique can only be used for fast reactions or those for which reaction is complete within the retention time (*ca.* 2 min) inside the calorimetric cell. The thermostat of the calorimeter was maintained at 25·00 °C. Water at 18·00 ± 0·05 °C was passed through the cooling coils of the air-bath and room temperature was kept at 22·0 ± 0·5 °C. Reagent solutions were pumped through the calorimeter by two LKB 10200 Perspex peristaltic pumps (see the Figure). The flow rate of each pump was *ca.* $5\ \mu l\ s^{-1}$ and was determined exactly before and after each experiment. Silicon tubing (diameter 1·15 mm) was used for acid and neutral solutions, Tygon tubing (1·10 mm) for sodium hydroxide solutions. Thermocouple signals were amplified by a Keithley 150 B microvoltmeter before being recorded on a digital voltmeter (five digits).

The heat flow, Φ, associated with a reaction may be obtained from equation (1), where h is a constant and ΔE

$$\Phi = h\Delta E \qquad (1)$$

the variation of potential across the thermocouple. The constant h was determined for each experiment using an electrical calibration which produced a known heat flow (heater resistance, $R = 49{\cdot}335\ \Omega$). The values of h depend

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[1] J. J. Christensen and R. M. Izatt, 'Handbook of Metal Ligand Heats,' Marcel Dekker, New York, 1970.

[2] P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chim. Acta Rev.*, 1973, **7**, 43 and refs. therein.

[3] R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J.C.S. Dalton*, 1972, 740.

[4] H. K. J. Powell and N. F. Curtis, *J. Chem. Soc.* (*A*), 1967, 1441.

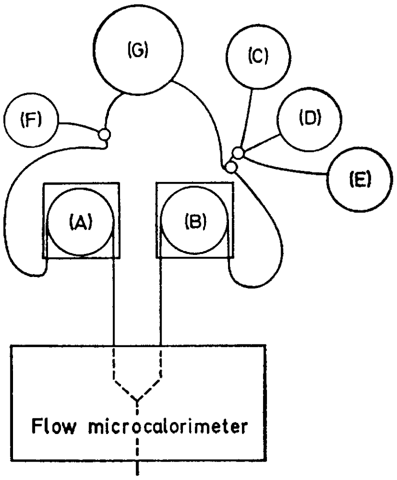
[5] R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, unpublished work.

[6] P. Monk and I. Wadsö, *Acta Chem. Scand.*, 1968, **22**, 1842; 1969, **23**, 29; A. E. Beezer and H. J. V. Tyrrell, *Science Tools*, 1972, **19**, 13.

on the flow rate and the heat capacity of the solution (and therefore also on the ionic strength). In order to standardise the apparatus the reaction of formation of water was carried out by pumping through peristaltic pumps (A) and (B) solutions of HCl (1×10^{-2}M) and KOH (2×10^{-2}M).* Reaction heat flows were corrected for dilution of the reagents by measuring separately the dilution heat flows of the HCl and KOH solutions into decarbonated water at a measured constant flow rate. The heat flow (mcal s^{-1}), corrected for dilution, divided by the flow rate of HCl (μmol s^{-1}) gives the enthalpy of reaction, $\Delta H^{\ominus}$, in kcal mol^{-1}. The obtained value ($-13{\cdot}39 \pm 0{\cdot}02$ kcal mol^{-1}) refers to reaction (2). If this value is corrected to infinite dilution,

$$\mathrm{HCl}\ (1 \times 10^{-2}\mathrm{M}) + \mathrm{KOH}\ (2 \times 10^{-2}) \longrightarrow \mathrm{H_2O} + \mathrm{HCl}\ (1 \times 10^{-2}) \quad (2)$$

using the reported heats of dilution of HCl (10^{-2}), KOH (2×10^{-2}), and KCl (10^{-2}M) in the literature ($0{\cdot}05$ kcal mol^{-1} on the whole), we obtain a value ($-13{\cdot}34$ kcal mol^{-1}) in excellent agreement with the data reported.[7]



Block diagram of the microcalorimetic apparatus. The protonation measurements were carried out by pumping through peristaltic pumps (A) and (B) solutions of the amine hydrochloride (F) and standard NaOH [bottles (C)—(E)]. In the study of metal-complex formation, the bottle (F) contained also an appropriate amount of the metal salt. Bottle (G) contained $0{\cdot}5$M-$NaClO_4$

Determination of the heats of ligand protonation and complex formation with Cu^{II}. In the Figure the pump (B) [poly(vinyl chloride)–Tygon tubing] was connected by three-way stopcocks to the three bottles (C)—(E) containing standard NaOH solution (*ca.* 1×10^{-2}, 2×10^{-2}, and 3×10^{-2}M). For the protonation measurements, pump (A) was connected to a bottle (F) containing a solution of the amine hydrochloride (*ca.* $1{\cdot}5 \times 10^{-2}$M) and excess of perchloric acid. For copper(II) complex formation, the bottle (F) contained a solution of the amine hydrochloride, excess of acid, and $Cu(ClO_4)_2$. All the solutions were made up to $I = 0{\cdot}5$M with $NaClO_4$. Both pumps (A) and (B) are connected by stopcocks to a solution of $0{\cdot}5$M-$NaClO_4$ in bottle (G) in order to perform the dilution measurements. Pump speeds were kept at *ca.* $5{\cdot}5$ μl s^{-1}. The heat flow, Φ, recorded (energy divided by time) was the sum of the effects due to the amine hydrochloride deprotonation ($H_2L^{2+} \longrightarrow HL^+ + H^+ \longrightarrow L + H^+$), water formation ($H^+ + OH^-$), and metal-complex formation (Cu + L,*etc.*). Determination of the molar enthalpies of these reactions requires the exact knowledge of the flow rates (moles divided by time) of each species present in equilibrium before and after the reaction, *i.e.* before and after the mixing of the solutions pumped by (A) and (B).

Let us consider the more general case of complex formation. The molar flow rate of a complex species of general formula $M_pH_qL_r$ (M = metal, H = hydrogen, and L = ligand; charges have been omitted for clarity) is expressed by equation (3), where $v_{M_pH_qL_r}$, v_M, v_H, and v_L denote the

$$\frac{v_{M_pH_qL_r}}{R} = \beta_{pqr}\left(\frac{v_M}{R}\right)^p\left(\frac{v_H}{R}\right)^q\left(\frac{v_L}{R}\right)^r \quad (3)$$

molar flow rates of the species $M_pH_qL_r$, M, H, and L, respectively, at equilibrium. The molar flow rates v are expressed in this paper in μmol s^{-1}; β_{pqr} is the formation constant of the species under consideration,[8] and R represents the total flow rate expressed in μl s^{-1} obtained by summing the speeds of the two pumps (A) and (B). Only R and β_{pqr} are known. The values of v_M, v_H, and v_L can be calculated from the three mass-balance equations (4)—(6),

$$\frac{V_M}{R} = \frac{v_M}{R} + \sum_p \beta_{pqr}\left(\frac{v_M}{R}\right)^p\left(\frac{v_H}{R}\right)^q\left(\frac{v_L}{R}\right)^r \quad (4)$$

$$\frac{V_H}{R} = \frac{v_H}{R} + \sum_q \beta_{pqr}\left(\frac{v_M}{R}\right)^p\left(\frac{v_H}{R}\right)^q\left(\frac{v_L}{R}\right)^r \quad (5)$$

$$\frac{V_L}{R} = \frac{v_L}{R} + \sum_r \beta_{pqr}\left(\frac{v_M}{R}\right)^p\left(\frac{v_H}{R}\right)^q\left(\frac{v_L}{R}\right)^r \quad (6)$$

where V_M, V_H, and V_L are the *total flow rates* of the metal, hydrogen, and ligand, respectively: these values (μmol s^{-1}) are obtained by multiplying the concentration of the solution (μmol μl^{-1}) by the appropriate pump speed (μl s^{-1}). It is to be noted that V/R has dimensions of molar concentration (μmol μl^{-1}).

The set of three non-linear equations in the three unknowns v_M, v_H, and v_L are solved by the Newton–Raphson iterative method.[9] For protonation ($V_M = 0$) the system is reduced to two equations. The values of v_M, v_H, and v_L so obtained are substituted in equation (3) and $v_{M_pH_qL_r}$ obtained. The knowledge of $v_{M_pH_qL_r}$ for each species present at equilibrium before and after mixing allows the recorded heat flow to be split into the various enthalpic contributions. Let us consider first the protonation reaction. The measured heat flow, Φ/mcal s^{-1}, is given by equation (7) where $\Phi_{dil.}$ represents the sum of the heat

$$\Phi = \Phi_{dil.} - V_{OH}\Delta H_w + \delta v_{OH}\Delta H_w + \Sigma\delta v_{H_qL}[\Delta H(L + qH)] \quad (7)$$

flows on dilution of the hydrochloride and standard NaOH solutions, ΔH_w is the enthalpy of formation of water ($H^+ + OH^-$) measured under the appropriate conditions of ionic strength [$I = 0{\cdot}5$M ($NaClO_4$) in this case], V_{OH} is the total flow rate of OH^-, δv_{OH} represents the variation in v_{OH} during the reaction, and δv_{H_qL} represents the variation in v_{H_qL} during the reaction. The term $V_{OH}\Delta H_w$ is introduced to simplify the calculation; in fact the increase in

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* 1M = 1 mol dm^{-3}, 1 cal = 4·184 J.

[7] T. Davies, S. S. Singer, and L. A. K. Staveley, *J. Chem. Soc.*, 1954, 2304; L. Sacconi, P. Paoletti, and M. Ciampolini, *Ricerca sci.*, 1959, **29**, 2412; J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, 1963, **67**, 2605; C. E. Wanderzee and J. A. Swanson, *ibid.*, p. 2608.

[8] E. Arenare, P. Paoletti, A. Dei, and A. Vacca, *J.C.S. Dalton*, 1972, 736.

[9] H. Margenau and G. M. Murphy, 'The Mathematics of Physics and Chemistry,' 2nd edn., Van Nostrand, New York, 1956, p. 492.

TABLE 1

Experimental details of microcalorimetric measurements at 25 °C in 0·5M-NaClO$_4$

	V_H [a,b] μmol s^{-1}	V_M [a] μmol s^{-1}	V_L [a] μmol s^{-1}	R [c] μl s^{-1}	Φ [d,e] μcal s^{-1}
(*a*) deen + H$^+$					
(i)	0·13292		0·06646	9·595	127·0, 127·1
(ii)	0·08711				
(i)	0·13292		0·06646	9·595	241·6, 242·3
(ii)	0·04096				
(i)	0·13292		0·06646	9·595	312·2, 313·4
(ii)	−0·00496				
(i)	0·13245		0·06223	9·610	126·1, 126·3
(ii)	0·08660				
(i)	0·13245		0·06223	9·610	240·8, 240·8
(ii)	0·040415				
(i)	0·13245		0·06223	9·610	311·8, 310·9
(ii)	0·00550				
(*b*) deac + H$^+$					
(i)	0·12105		0·06052	9·651	155·0, 154·3
(ii)	0·07478				
(i)	0·12105		0·06052	9·651	300·6, 303·7
(ii)	0·02816				
(i)	0·12015		0·06052	9·651	386·2, 385·1
(ii)	−0·01819				
(i)	0·15192		0·07596	9·599	152·6, 152·5
(ii)	0·10583				
(i)	0·15192		0·07596	9·599	299·3, 299·8
(ii)	0·05939				
(i)	0·15192		0·07596	9·599	432·2, 431·8
(ii)	0·01323				
(*c*) deen + Cu^{II}					
(i)	0·05506	0·01366	0·02748	10·210	268·0, 267·7
(ii)	0·009142				
(i)	0·05506	0·01366	0·02748	10·210	313·3, 333·4
(ii)	−0·03712				
(i)	0·05506	0·01366	0·02748	10·210	328·8, 330·8
(ii)	−0·08311				
(i)	0·08017	0·02177	0·04001	10·210	297·9, 297·0
(ii)	0·03426				
(i)	0·08017	0·02177	0·04001	10·210	511·2, 511·0
(ii)	−0·01200				
(i)	0·08017	0·02177	0·04001	10·210	515·6, 515·6
(ii)	−0·05799				
(i)	0·09669	0·04369	0·04819	10·210	306·8, 306·8
(ii)	0·05077				
(i)	0·09669	0·04369	0·04819	10·210	611·1, 611·4
(ii)	0·00451				
(i)	0·09669	0·04369	0·04819	10·210	860·5, 857·9
(ii)	−0·04148				
(*d*) deae + Cu^{II}					
(i)	0·06834	0·01386	0·03412	10·230	274·6, 274·2
(ii)	0·02242				
(i)	0·06834	0·01386	0·03412	10·230	400·0, 398·6
(ii)	−0·02383				
(i)	0·06834	0·01386	0·03412	10·230	408·0, 405·3
(ii)	−0·06982				
(i)	0·07104	0·01109	0·03592	10·261	254·6, 254·6
(ii)	0·02494				
(i)	0·07104	0·01109	0·03592	10·261	369·4, 369·4
(ii)	−0·02508				
(i)	0·07104	0·01109	0·03592	10·261	376·9, 376·5
(ii)	−0·06776				
(i)	0·12061	0·02751	0·06021	10·273	307·5, 308·7
(ii)	0·07451				
(i)	0·12061	0·02751	0·06021	10·273	575·5, 576·0
(ii)	0·02806				
(i)	0·12061	0·0275	0·06021	10·273	641·9, 744·0
(ii)	−0·01809				
(i)	0·08172	0·03855	0·04072	10·262	313·8, 314·7
(ii)	0·03562				
(i)	0·08172	0·03855	0·04072	10·262	613·1, 613·7
(ii)	−0·01083				
(i)	0·08172	0·03855	0·04072	10·262	780·7, 780·8
(ii)	−0·05699				

[a] Total or analytical flow rates of the acid, metal, and ligand; V_H takes into account the hydrogen ions from the diamine hydrochloride and those of the acid in excess. [b] The values refer to V_H before (ii) and after (i) mixing. The (ii) values were obtained by subtracting the analytical flow rate of OH$^-$ from the (i) values. Negative values are referred to OH$^-$. [c] Total flow rate [pump (A) + pump (B)]. [d] Heat flow corrected for dilution. [e] The values refer to duplicate measurements carried out consecutively.

flow rate of OH^- during the reaction is considered as the corresponding decrease in H^+ flow rate. This term takes into account the (endo) thermal effect involved in this ideal process. In the case of a diamine ($q = 1$ or 2) more than two measurements are required. The set of linear equations of type (7) was solved by a least-squares method.

For complex formation the heat flow of each reaction is given by (8) which may also be solved by the least-squares

$$\Phi = \Phi_{\text{dil.}} - V_{\text{OH}}\Delta H_{\text{w}} + \delta v_{\text{OH}}\Delta H_{\text{w}} + \Sigma\delta v_{\text{H}_q\text{L}}[\Delta H(\text{L} + q\text{H})] - \Sigma v_{\text{M}_p\text{H}_q\text{L}_r}[\Delta H(p\text{M} + q\text{H} + r\text{L})] \quad (8)$$

method. Calculations were made with a FORTRAN program written for an IBM 1130 computer. Table 1 gives experimental details of the calorimetric measurement of protonation and complex formation.

Materials.—The ligands *NN'*-diethylethylenediamine, deen (Fluka, pract.) and *NN*-diethylethylenediamine, deae (Fluka, pract.) were distilled. The middle fraction was used to prepare the appropriate hydrochloride. The hydrochloride was prepared by adding an excess of hydrochloric acid to a cooled and continuously stirred alcoholic solution of the diamine. The two hydrochlorides were recrystallised from aqueous ethanol, dried *in vacuo*, and analysed for C, H, N, and Cl (Volhard method). The analysis gave satisfactory results. Solutions of sodium hydroxide were prepared by washing solid NaOH with CO_2-free water under nitrogen and standardised against a dilute standard solution of potassium hydrogenphthalate. The acid solution was obtained by diluting an azeotropic HCl solution, the chloride concentration being gravimetrically determined (AgCl). The metal content of the copper(II) solution was electrolytically established.

RESULTS AND DISCUSSION

In Table 2 are reported the $\Delta H^\ominus$, $\Delta G^\ominus$, and $\Delta S^\ominus$ values for protonation of deen and deae together with the corresponding values for the homologous ethylenediamine (en), dmen, and dmae. Protonations of the two ethyl-substituted diamines, symmetrical and asymmetrical, are accompanied by enthalpies less exothermic than for protonation of en. In any case the entropy contributions more than compensate the smaller exothermic values so that the two ethyl-substituted diamines are more basic than en for both the first and second protonation steps. The same behaviour was observed for methyl-substituted diamines.[10] The symmetrical diamine deen has a heat of protonation larger than for the asymmetric diamine for both the first and second step. This type of behaviour has also been observed for the homologous dimethyl-substituted diamine.[10] Protonation of the diethyl-substituted diamines, symmetrical and asymmetrical, is more exothermic than for the corresponding dimethyl-substituted diamines. Furthermore, the more favourable entropy leads to an increase in basicity of the ethyl-substituted with respect to the methyl-substituted diamine.

TABLE 2

Thermodynamic functions for the protonation of substituted ethylenediamines at 25·0 °C and $I = 0{\cdot}5\text{M}$ [a]

Reaction		deen [b]	deae [b]	en [c]	dmen [c]	dmae [c]
$\text{L} + \text{H}^+ \rightleftharpoons \text{HL}^+$	$-\Delta G^\ominus$/kcal mol^{-1}	14·24 [d]	13·84 [e]	13·61	13·86	13·21
	$-\Delta H^\ominus$/kcal mol^{-1}	10·87(4)	10·06(5)	12·18	10·74	10·42
	$\Delta S^\ominus$/cal K^{-1} mol^{-1}	11·1(1)	12·6(1)	4·8	10·5	9·3
$\text{HL}^+ + \text{H}^+ \rightleftharpoons \text{H}_2\text{L}^{2+}$	$-\Delta G^\ominus$/kcal mol^{-1}	10·25	9·64	9·93	9·96	9·13
	$-\Delta H^\ominus$/kcal mol^{-1}	10·52(8)	10·01(8)	10·90	9·67	8·42
	$\Delta S^\ominus$/cal K^{-1} mol^{-1}	−0·1(1)	−1·1(1)	−3·3	0·9	2·4

[a] Numbers in parentheses are standard deviations in the last significant figure. [b] This work. [c] 0·5M-KNO_3, Values taken from ref. 10 and R. Barbucci, P. Paoletti, and A. Vacca, *J. Chem. Soc.* (*A*), 1970, 2202. [d] Ref. 9. [e] R. Näsänen and P. Meriläinen, *Suomen Kem.*, 1963, **B36**, 205.

Proton-transfer Reaction.—For the symmetric amines, reaction (9) is entirely controlled by electrostatic

$$\text{H}_2\text{L}^{2+} + \text{L} \longrightarrow 2\text{HL}^+ \qquad (9)$$

forces.[11,12] The variation in thermodynamic functions ΔQ ($Q = G^\ominus$, $H^\ominus$, or $S^\ominus$) associated with these reactions can be calculated from the difference $\Delta Q_1 - \Delta Q_2$. The value of $\Delta G^\ominus$, corrected for the statistical term $RT \ln 4 = T\Delta S_{\text{stat.}}$, furnishes the electrostatic work, $W_{\text{el.}}$, necessary to transfer the proton [11] from H_2L^{2+} to L [equation (10)],

$$-\Delta G^\ominus - T\Delta S_{\text{stat.}} = W_{\text{el.}} = \frac{Ne^2}{\varepsilon_{\text{eff.}}a_0} \qquad (10)$$

where N is Avogadro's constant, e the electron charge, a_0 the distance between the two furthest hydrogen atoms of the two amine groups completely elongated in the diamine, and $\varepsilon_{\text{eff.}}$ the effective dielectric constant.[11] From the enthalpy value of reaction (9) it is possible to

$$\Delta H^\ominus = -W_{\text{el.}}\left(1 + \frac{1}{\varepsilon_{\text{eff.}}}\frac{\delta\varepsilon_{\text{eff.}}}{\delta T}\right) \qquad (11)$$

obtain the value of $\delta\varepsilon_{\text{eff.}}/\delta T$, the thermal coefficient of the effective dielectric constant.[11]

In Table 3 are reported values of $\varepsilon_{\text{eff.}}$ and $\delta\varepsilon_{\text{eff.}}/\delta T$ obtained for the diamines, en, dmen, deen, and for piperazine (pip) (isomer of dmen), and 1,4-diazabicyclo[2.2.2]octane (dabo) (isomer of deen). The effective dielectric constant, $\varepsilon_{\text{eff.}}$, decreases in both types of isomeric diamines as the aliphatic part of the diamine increases in length. The decrease is more abrupt when the alkyl branches are ' frozen ' as in pip and dabo. This behaviour is expected: the alkyl groups reduce the degree of solvation of the diamine and this ' organic ' dielectric medium is less polarisable. However, the

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[10] R. Barbucci, P. Paoletti, A. Vacca, and A. Dei, *J. Chem. Soc.* (*A*), 1971, 310.

[11] G. Schwarzenbach, *Pure Appl. Chem.*, 1970, **24**, 307.

[12] L. Fabbrizzi, P. Paoletti, M. C. Zobrist ,and G. Schwarzenbach, *Helv. Chim. Acta*, 1973, **56**, 670.

behaviour of $\delta\varepsilon_{\text{eff.}}/\delta T$ is different for the two types of diamines: for the 'frozen' amines $\delta\varepsilon_{\text{eff.}}/\delta T$ decreases in absolute value as the length of the aliphatic branch increases. In fact the polarisation of an organic dielectric medium is less temperature dependent than that of a polar medium (in the fully solvated unsubstituted diamine). For the diamines dmen and deen the polarisation becomes more endothermic with the increase in aliphatic chain length. This behaviour is probably related to the possibility of the alkyl branches orientating themselves. Therefore, polarisation of the dielectric medium in this case requires (*i*) the organisation of solvent molecules and (*ii*) the 'freezing' of the alkyl groups into relatively fixed orientations: this type of polarisation is more endothermic (than in the absence of alkyl branches) and the endothermic effect must increase with the length of the aliphatic chain.

TABLE 3

Values of the electrostatic work, $W_{\text{el.}}$, the effective dielectric constant, $\varepsilon_{\text{eff.}}$, and its temperature coefficient, $\delta\varepsilon_{\text{eff.}}/\delta T$, for the proton-transfer reaction $H_2L^{2+} + L \rightleftharpoons HL^+ + HL^+$ at 25 °C [a]

L	$W_{\text{el.}}$/kcal mol^{-1}	$\varepsilon_{\text{eff.}}$	$\delta\varepsilon_{\text{eff.}}/\delta T$
en [b]	2·8	22	−0·039
dmen [b]	3·1	20	−0·046
deen [c]	3·2	19	−0·055
pip [d]	4·8	14	−0·017
dabo [d]	7·1	10	−0·014

[a] Values have been calculated as reported in the text from thermodynamic data taken from the appropriate references. [b] I = 0·5M (KNO$_3$), refs. 10 and 11. [c] I = 0·5M (NaClO$_4$), this work. [d] I = 0·1M (KCl), ref. 11 and P. Paoletti, J. H. Stern, and A. Vacca, *J. Phys. Chem.*, 1965, **69**, 3759.

Copper(II) *Complexes*.—In Table 4 are reported values of $\Delta H^{\ominus}$, $\Delta G^{\ominus}$, and $\Delta S^{\ominus}$ relative to the formation of simple complexes [CuL] and [CuL$_2$]. In Table 5 are listed the thermodynamic quantities for the hydrolysis $[CuL]^{2+} + OH^- \longrightarrow [Cu(OH)L]^+$ and olation reactions $2[CuL]^{2+} + 2OH^- \longrightarrow [Cu_2(OH)_2L_2]^{2+}$. The heats of formation of the complexes with the ethyl-substituted diamines are smaller than those for complex formation with the corresponding methyl-substituted diamines (see Table 4). The bis(diamine) complexes of Cu^{II} are probably distorted octahedral with the nitrogen atoms in equatorial positions and water molecules at the apical positions.[2] Molecular models show the existence of a remarkable repulsion between the two ligands in a molecule of the bis complex. This repulsion prevents the formation of stronger bonds. Increasing the bulkiness of the aliphatic chain creates greater repulsion and consequently a lower overall enthalpy of complex formation.

The lower exothermicity of reactions of the strongly hindered diamines deen and deae, both in the first and second step, could suggest that the ligands are unidentate. The heat effect due to the binding of an amine N atom in the absence of steric repulsions may be assumed to be *ca.* 6·3 kcal mol^{-1} (half the enthalpy of the Cu^{2+}–en reaction). The fact that the reactions Cu–deen and Cu–deae give 8·19 and 7·03 kcal mol^{-1}, respectively, shows that more than one nitrogen atom interacts with the copper ion.

TABLE 4

Thermodynamic functions for complex formation at 25·0 °C and I = 0·5M [a]

Reaction		deen [b]	deae [b]	en [c]	dmen [c]	dmae [c]
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	$-\Delta G^{\ominus}$/kcal mol^{-1}	12·23 [d]	11·36 [e]	24·44	13·79	12·66
	$-\Delta H^{\ominus}$/kcal mol^{-1}	8·19(4)	7·03(7)	12·56	11·10	9·82
	$\Delta S^{\ominus}$/cal K^{-1} mol^{-1}	13·4(2)	14·5(3)	6·3	9·0	9·5
$[CuL]^{2+} + L \rightleftharpoons [CuL_2]^{2+}$	$-\Delta G^{\ominus}$/kcal mol^{-1}	7·7 [d]	7·8 [e]	12·5	9·8	9·6
	$-\Delta H^{\ominus}$/kcal mol^{-1}	7·3(3)	6·2(3)	12·6	9·7	9·5
	$\Delta S^{\ominus}$/cal K^{-1} mol^{-1}	2(1)	5(1)	−0·5	0·3	0·4

[a] Numbers in parentheses are standard deviations in the last significant figure. [b] This work. [c] 0·5M-KNO$_3$, Values taken from ref. 3. [d] 0·5M-NaClO$_4$, Values taken from R. Näsänen and P. Meriläinen, *Suomen Kem.*, 1963, **B36**, 205; 1964, **B37**, 54. [e] 0·5M-NaClO$_4$, Values taken from R. Näsänen, P. Meriläinen, and M. Koskinen, *Suomen Kem.*, 1963, **B36**, 9; R. Näsänen and P. Meriläinen, *ibid.*, p. 97.

TABLE 5

Thermodynamic functions for hydrolysis and olation of [CuL]$^{2+}$ at 25·0 °C and I = 0·5M [a]

Hydrolysis		deen [b]	deae [b]	dmen [c]	dmae [c]
$[CuL]^{2+} + OH^- \rightleftharpoons [Cu(OH)L]^+$	$-\Delta G^{\ominus}$/kcal mol^{-1}	1·1 [d]	6·4 [e]		
	$-\Delta H^{\ominus}$/kcal mol^{-1}	5·4(7)	6·2(5)		
	$\Delta S^{\ominus}$/cal K^{-1} mol^{-1}	7(1)	7(1)		
Olation					
$2[CuL]^{2+} + 2OH^- \rightleftharpoons [Cu(OH)_2L_2]^{2+}$	$-\Delta G^{\ominus}$/kcal mol^{-1}	0·8 [d]	5·4 [e]	20·5	21·0
	$-\Delta H^{\ominus}$/kcal mol^{-1}	11·4(4)	12·5(7)	11·2	11·2
	$\Delta S^{\ominus}$/cal K^{-1} mol^{-1}	27(1)	26(1)	31(1)	33(1)

[a] Numbers in parentheses are standard deviations in the last significant figure. [b] This work. [c] 0·5M-KNO$_3$, Values taken from ref. 3. [d] R. Näsänen and P. Meriläinen, *Suomen Kem.*, 1963, **B36**, 205; 1964, **B37**, 54. [e] R. Näsänen and P. Meriliänen, *Suomen Kem.*, 1964, **B37**, 41.

Complex formation between copper(II) and the symmetrical ligand deen is accompanied by an enthalpy more exothermic than that for copper(II) and the asymmetrical deae. Similar behaviour has been observed for methyl-substituted diamines.[3] Complex formation between a metal ion and a bidentate amine ligand causes liberation of water molecules from the hydrated ion and gives rise to a positive entropy, ΔS, value. The released water molecules are in fact transferred from the first and second co-ordination spheres of the metal ion. Presence of hydrophobic alkyl groups on the nitrogen atoms of the amine causes a larger desolvation of the aqueous metal ion and consequently the liberation of more water molecules from the co-ordination sphere.[2] The extent to which this occurs is dependent on the bulkiness of the alkyl substituents; the value of ΔS is larger for reaction of ethyl than for methyl-substituted diamines. For the same ligand, symmetrical and asymmetrical, the ΔS value is larger for the asymmetrical case. Since liberation of water molecules is an endothermic process, the smaller exothermic values for the reactions of copper(II) with *N*-alkyl-substituted diamines must be attributed not only to the formation of weaker co-ordinate bonds but also to greater desolvation. It should be noticed that the high values of ΔS_1 observed in the reactions of deen and deae confirm the bidenticity of these ligands in aqueous solution. In fact the full co-ordination of the diamine causes the release of a larger number of water molecules and this is reflected in the ΔS values.

The enthalpy values for reactions of the simple complexes of Cu^{II} and OH^-, hydrolysis and olation, are comparable for the two amines (symmetrical and asymmetrical). For each complex the heat of olation is about twice the heat of hydrolysis. It is to be noted, however, that the corresponding ΔS values do not have the same ratio. A direct comparison of ΔS values should not be made in this manner because of the non-equivalence of their methods of derivation. The constants of olation and hydrolysis have different dimensions ($mol^3\ l^{-3}$ and $mol\ l^{-1}$ respectively) and therefore their values, and those of the derived functions ΔG and ΔS, depend on the choice of the standard state.

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