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THE THERMODYNAMICS OF METAL-COMPLEX AND ION-PAIR FORMATION

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CONTENTS

ABBREVIATIONS

BATA	2,2′-oxybis[ethyliminodi-(acetic acid)]
BSTA	2,2′-thiobis[ethyliminodi-(acetic acid)]
DCTA	*trans*-cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
dien	diethylenetriamine
dip	dipyridyl
Dop	diethyl-β-oxyethyl phosphine
DTPA	diethylenetriaminepentaacetic acid
EDTA	ethylenediaminetetraacetic acid
EGTA	2,2′-ethylenedioxybis-[ethyliminodi(acetic acid)]
en	ethylenediamine
HDTA	hexamethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
IDA	iminodiacetate
mIDA	methyl iminodiacetate
NTA	nitrilotriacetate
ODTA	octamethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
PDTA	propylene-1,2-diaminetetraacetic acid
penten	*N*,*N*,*N*′,*N*′-tetra-(2-aminoethyl)-ethylenediamine
PETA	pentamethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
phen	1.10-phenanthroline
TETA	tetramethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
tetren	tetraethylenepentamine
TMTA	trimethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
tren	2,2′,2″-triaminotriethylamine
trien	triethylenetetramine

A. INTRODUCTION

During the past ten years there has been an increasing interest in the direct calorimetric measurement of the enthalpy changes accompanying metal-complex and ion-pair formation in solution[1]. In the past, some relationships involving free energy changes and properties of the ions taking part in the complex formation reactions have been demonstrated but it is clear that such correlations are of very limited applicability. It is best to regard the free energy changes as being a consequence of changes in enthalpy and entropy terms,

$$\Delta G = \Delta H - T\Delta S.$$

The paucity of reliable calorimetric enthalpy data has in many cases made it impossible to discuss important factors such as changes in hydration of the ions, the nature of the metal ligand bonding, and structure relationships. The enthalpy change is the property most directly related to the changes in numbers and strengths of bonds as the system passes from reactants to products. The entropy change is a measure of the change of randomness, and the driving force in this process is the tendency of the system to go to the most probable, that is the most random, state.

It is the purpose of this review to outline some of the recent advances made in the measurement and interpretation of the thermodynamic functions accompanying ion-pair and complex formation. Following an outline of recent experimental developments, the nature of ΔH and ΔS will be discussed in the light of recent calorimetric data for some specific systems.

B. THE STABILITY CONSTANT

The elucidation of the nature and concentrations of the species present in electrolyte solutions is a difficult problem and requires as many independent lines of attack as possible. During the past ten years the application of new physical-chemical methods has produced significant contributions particularly in respect to the determination of the sites of binding between the metal ions and ligand molecules.

Nuclear magnetic resonance spectroscopy offers attractive possibilities for the study of the structures of metal complexes in solution and for estimating their stability constants. The magnitude of the chemical shifts of nuclear resonance in solution are determined by the electron distribution in the molecule or ion containing the nucleus and by the fields set up in the molecule by molecules or ions with which it interacts. Separate resonance bands are observed with magnetically distinct nuclei but a sufficiently rapid chemical exchange between them will result in a single resonance of some intermediate value of chemical shift. Studies of proton chemical shifts of aqueous solutions of acids have yielded dissociation data[2], and measurements on the H_2O–SO_3 system have been used to calculate the degree of ionization of water in solutions containing excess of sulphuric acid[3].

Chemical shifts associated with atoms other than hydrogen have also been used as an indication of complex formation. Thus measurements of the concentration dependencies of the changes in the nuclear magnetic resonance frequency for the $^{205}Tl^{III}$ nucleus in the presence of halide ions have been interpreted in terms of the formation of a variety of thallic halide complexes[4]. Similarly Richards[5] found that the thallium resonance line shifted with increasing concentration of thallous hydroxide owing to the change in the concentrations of the species in equilibrium, Tl^+, OH^- and TlOH. A detailed study gave K_1(TlOH) = 5, in agreement with the solubility (6.7)[6], spectrophotometric (5)[7] and kinetic (7)[8] estimates. The presence of solutes in water also increases the rate of proton relaxation, the effect being greatest for paramagnetic and least for diamagnetic species. The interconversion of diamagnetic and paramagnetic species in solution can therefore be readily detected, and Blackie and Gold have applied spin–lattice relaxation measurements of this kind to the problem of identifying the complexes present in solutions of nickel(II) cyanide[9]. Information about the stability of $Ni(CN)_6{}^{4-}$ ion was obtained by competing for the cyanide ion with other metal ions which had affinities for cyanide comparable with that of nickel(II) ion[10].

The measurement of proton chemical shift provides a powerful method for studying protonation schemes in metal chelates. Although the protons are not bonded directly to the metal ions in the chelate, they may be sufficiently close to the potential coordination sites to act as effective monitors of the electronic environment in the vicinity of these sites. The protonation of some metal–EDTA complexes was studied by Sawyer and co-workers[11], and Reilley and his associates have applied the method to the determination of the protonation schemes of a large number of polyamine and aminopolycarboxylate ligands[12]. Substituent shielding constants, obtained from a study of methylenic proton chemical shifts of model compounds as a function of pH, were used to determine the distribution of protons among the various sites on the ligand. The non-labile methylenic protons are deshielded by the protonation of a nearby site by an amount which depends upon the nature of the basic site, its proximity to the proton under consideration, and the fraction of the time it is protonated[12].

NMR studies of metal complexes as a function of pH yield information about the pH at which metal–ligand bonding occurs and the ligand atom which participates in the bond. The presence or absence of various splitting patterns can be used to estimate the lability of individual metal–ligand bonds. If a rapid exchange takes place with relatively short bond lifetimes, simple NMR spectra are obtained with a single averaged proton resonance line. When the exchange rate for the bond decreases, line broadening is first observed and, as the bonding becomes non-labile, separate resonances are found for the free ligand and the coordinated ligand[11,13,14]. A number of metal aminocarboxylate complexes have been studied by this method[13,14,15,16].

Covalent interaction of ions in solution give rise to new Raman lines characteristic of the complexes formed and the integrated intensities of the lines for a given species appear to be proportional to its concentration. A study of Raman spectra, therefore, will afford more direct evidence of specific interactions in electrolyte solutions than can be obtained by the more classical methods. Dissociation constants of nitric[17], perchloric[18] and sulphuric[17] acids have been obtained by this method and the values are in reasonable agreement with those calculated from nuclear magnetic resonance spectra[19]. Raman spectra of a number of metal-ion perchlorate[20] and sulphate[21] solutions have been examined for evidence of complex formation, and although the perchlorates of Cd^{II}, Hg^{I}, Hg^{II}, La^{III}, Tb^{I}, Mg^{II} and Mn^{II} exhibited Raman lines in addition to those expected from the perchlorate ion, these were extremely weak and could not be attributed with certainty to ion-pair or complex formation. Of the sulphates, only indium(III) showed Raman evidence of complex formation Four new polarised lines in the Raman spectrum were attributed to the formation[21] of either $InSO_4^+$ or $In(SO_4)_2^-$. Thus in most of the metal sulphates for which conductivity and solubility measurements indicate quite extensive association, the ions appear to be separated by one or more solvent molecules. In metal nitrate solutions, on the other hand, Raman studies indicate that association occurs through close-contact ion-pairing with an oxygen atom of the nitrate ion participating in the bond with the metal ion[22]. Halide complexes of metal ions have also been studied by Raman spectroscopy[23,24] and, in the case of bismuth(III) chloride and bromide, the method was used in an attempt to identify the complex species present with high ligand numbers[25]. Precise solubility measurements by Haight and his co-workers[26,27] had previously indicated that the important species present in the bromide solutions were $n = 1, 2, 4, 6$ and 8 for $BiBr_n^{3-n}$ and $n = 4$ and 6 for the two $BiCl_n^{3-n}$ species involved in the highest equilibrium in chloride solutions. They suggested that the complex species having $n = 3$ or 5 were either absent or present only in extremely low concentrations whereas previous workers had used the results of spectrophotometric[28] and potentiometric[29] measurements to establish the existence of all species having $n = 1$–5. From the results of the Raman studies, Oertel and Plane[25] identified the species $BiCl_4^-$, $BiCl_5^{2-}$ and $BiCl_6^{3-}$ and determined their frequencies; in addition, chloride species with $n = 3$, 2 and possibly 1 were found. These studies of the bismuth halide complexes indicate the desirability of using as many different experimental approaches as possible in attempting to characterise the complex species present in solution. Frequently, one method can be used to determine the stoichiometry of the species present whilst another method is best suited for the determination of reliable stability constants.

The use of the well-established methods for the determination of stability constants has continued during the past decade, and the data in the literature up to about 1963 have been summarized in a valuable revised compilation by Sillen and Martell[30]. The comparatively recent development of cation-sensitive electrodes[31] has opened up new possibilities for direct potentiometric determination of the concentrations of uncomplexed ions in solution. Sodium and potassium ion-responsive electrodes have been particularly well-characterised, largely due to the efforts of Eisenman[31] who has examined the theoretical aspects of the behaviour of these electrodes. The direct measurement of the activities of alkali metal ions in solutions containing anions of weak acids with which they form complexes offers substantial advantages over the indirect pH shift method for determining the stability constants. A number of relatively weak sodium complexes which could not be detected by the latter method have been characterised using the sodium-sensitive glass electrode[32,33].

Another class of cation-selective electrodes which offer attractive possibilities for the study of complex formation in aqueous solutions are the liquid–liquid membrane electrodes. Rechnitz and his co-workers have used the copper[34] and calcium[35] electrodes to study a number of complexes involving nitrogen and oxygen coordination and have shown that the calculated stability constants are in good agreement with those obtained by the pH-shift method.

The cation-sensitive electrodes are still being developed and improved and they do not as yet offer the stability and reproducibility of more conventional electrodes. However, with careful attention to pretreatment of the electrodes[36,37] it is expected that they will find increasing application in the study of metal complexes in solution Another important application, resulting from their specificity, is the measurement of ion activities as a function of ionic strength in the presence of added electrolytes and in the absence of complexing. The possibilities of studies in mixed electrolytes at relatively high ionic strengths such as those pertaining to biological fluids and in seawater, will enable activity effects to be estimated with a precision hitherto impossible. Potassium-ion activities, measured in potassium chloride solutions[38] by means of a cation-selective glass electrode are in striking agreement up to ionic strengths as high as 0 1M with the mean activities calculated from the Debye–Hückel equation using the ion-size parameters proposed by Klotz[39].

Since 1960, the curve-fitting methods for the calculation of stability constants, of great value in systems containing a large number of complex species, have been supplemented by computer methods designed for the systematic trial of all possible combinations of ionic interactions[40]. It is usually essential to study such systems at constant ionic strength so that activity coefficients can be assumed constant. For studies of complexing in solutions of low ionic strengths, the calculation of activity coefficients can be made by successive approximation procedures with great facility using electronic computers[1]. Best values of the parameters to be used in the activity-coefficient equations can, in many cases, be calculated from the experimental results. With the current interest in metal complexes of amino acids and peptides, a frequently observed combination of species in dilute solution is MA and MHA. Although it is not possible to solve simultaneously for the stability constants of these complexes the problem may be resolved by means of a trial-and-error re-iterative computer procedure involving the total ionic strength of the solution[1]. The study of protonated and of mixed-ligand complexes in solution is receiving increasing attention especially in the elucidation of the complex species present in systems of biological interest. A number of graphical methods of analysing pH-titration data for such systems have been proposed but they have not yet been widely used. The surface potentiometric method originated by Lefebvre[41] has been applied in studies of copper glycine complexes[42], copper–sulphosalicyclic acid, ammonia mixed complexes[43] and nickel–glycine–alanine mixed complexes[44]. It is essentially a graphical method for the determination of the free ligand and free metal-ion concentrations. Since the surface potentiometric method involves the measurement of gradients of curves, its use should be limited to the identification of the complex species present; subsequent calculations of the stability constant values should be refined by computer methods. A general computer program for the calculation of the stability constants of mixed complexes of copper and nickel with ethylenediamine, histamine and serine was developed by Perrin and his co-workers[45,46]. Osterberg[47] has applied Sillen's[48] curve-fitting method to systems in which species of the general formula M_pH_qA are assumed to be present. A number of metal complexes with *o*-phosphorylated peptides were characterised by this method which is particularly useful for systems in which the number of species is limited to the type MA and MHA.

The question as to whether to study a system at some constant ionic strength by the addition of "neutral" electrolyte or whether to work at low ionic strengths in an attempt to compute the activity corrections, has been discussed in some detail[1] The constant ionic medium is invaluable where a number of complicated equilibria are involved and different schools have tended to choose different ionic strengths for their studies of metal-complex formation. The derived thermodynamic functions are, however, directly comparable for different systems only when obtained at the same ionic strength and for this reason, there continues to be an interest in the calculation of activity coefficients in order that thermodynamic equilibrium constants can be obtained. The derivation of the thermodynamic constants is made possible by a suitable choice of the concentrations of the reactants so that the number of complexes is limited to one or two. Where there is doubt as to the stoichiometry of the species present, these can usually be identified by making preliminary measurements at a constant ionic strength. This method was used to identify the complex species present in some bivalent metal succinate solutions in which it was known that either ML_2 or MHL was present in addition to ML[49]. By making additional potentiometric measurements at low concentrations, it was then possible to calculate, by successive approximations, values for the activity coefficients and the thermodynamic association constants for the formation of ML and MHL found to be present under the particular experimental conditions.

Selection of the best values of the parameters a and C in a form of the Debye–Hückel equation such as

$$\log f_z = \frac{-Az^2I^{\frac{1}{2}}}{1+BaI^{\frac{1}{2}}} + CI,$$

may conveniently be made by carrying through the complete successive approximation procedures with various parameter values and choosing those which best fit the experimental data. In this equation, f_z is the activity coefficient of a z-valent ion, A and B are constants of the Debye–Hückel theory, and a and C are parameters. Computations, with the aid of an electronic computer, have been made for a number of dicarboxylate and amino acid complexes[49–52]. For magnesium sulphate, it was possible to calculate unique parameter values for the calculation of activity coefficients[1].

C. THE ENTHALPY CHANGES

Enthalpy changes accompanying complex formation may be obtained from studies of the association constants as a function of temperature but the uncertainties in the ΔH values derived from data over a small temperature range are considerable. When precise determinations of K values are made over a wide range of temperature, the resulting enthalpy changes are much more reliable[53] and moreover can yield approximate values for the heat-capacity changes. Under these circumstances, the agreement between the results of calorimetric and temperature-coefficient methods is usually satisfactory[54] but in general, the former method is to be preferred.

There is an increasing interest in the direct calorimetric determination of enthalpy changes, and a number of new calorimeters have been developed for the measurement of small heat changes in solution[1]. Improvements in thermistor design make this a very popular temperature sensor expecially in twin differential calorimeters, and temperature changes can be measured with an accuracy[55–57] of at least $3–5 \times 10^{-5}$°C. Long-term stability is not required for measurement of the heat changes associated with the formation of metal complexes, and a very simple Wheatstone Bridge, energised by means of a mercury cell, can be used in a differential arrangement. The recent development of quartz thermometers offers attractive advantages to the calorimetrist in that both absolute single, and differential measurements of temperature can be made with great ease.

While not as popular as the differential calorimeters described above, the isothermal fusion calorimeter has been used recently for the study of some alkaline earth complexes of diethylenetriaminepentaacetic acid (DTPA)[58]. Diphenyl ether was selected as the working substance, and the calorimeter was constructed specifically for precise measurement of the small quantities of heat involved.

There has been a resurgence of interest in thermometric titration procedures[59,60], particularly for analytical applications, due largely to the work of J. J. Christensen, R. M. Izatt, and their co-workers[56,61]. The temperature of the calorimeter contents, measured by a low heat capacity, fast-response thermistor, is continuously monitored during the controlled addition of reagent. Although the method does not have quite the precision of conventional single addition calorimetry, the amount of data obtained is considerably greater. Each thermometric titration curve is equivalent to a large number of separate determinations made by conventional solution-reaction calorimetry. For certain classes of reactions with $\log K$ values between 0.5 and 3.0 and with enthalpy changes larger than about 1 kcal.mole^{-1}, data obtained from a single thermometric titration can yield both ΔG and ΔH values. For the second dissociation of sulphuric acid[61], and the stepwise formation of silver pyridine complexes[62] the results obtained by this method are in good accord with the values obtained by potentiometry and by conventional calorimetry; it is clear, however, that care must be taken in the computational procedure used to analyze the data[63].

Determinations of the heats of complex formation are usually made by measuring the temperature changes on dilution of small volumes of a relatively concentrated solution of the ligand with (i) a larger volume of a solution containing the metal ion and (ii) a similar volume of the background electrolyte having the same ionic strength. When the ligand is an anion of a weak acid, it may be necessary to take into account heat changes accompanying the variation of the concentration of protonated species as well as that due to complex formation[64,65]. The method requires precise measurement of the pH values of the solutions in the calorimeter and it is possible to incorporate glass and reference electrodes in the differential calorimeters[66].

For a number of ion-association reactions which have been studied over a wide range of temperature, it is observed[1] that K has a minimum at a certain temperature T^*, given by

$$T^* = \gamma \left[1 + \frac{\Delta G_c}{\Delta G_e}\right] \tag{1}$$

In Eqn. (1), γ is a temperature characteristic of the solvent (219 °K for water), ΔG_e and ΔG_c are the temperature-dependent and temperature-independent components of the free energy change, the former representing the electrostatic contributions, and the latter the covalent contributions. It is seen from Eqn. (1) that T^* depends upon the ratio of covalent to electrostatic free energies of interaction. If T^* lies above the freezing point of the solvent, $\log K$ decreases over the whole accessible temperature range corresponding to an exothermic enthalpy of interaction and a major contribution from covalent forces. Conversely, a T^* below the freezing point of the solvent will lead to an endothermic ΔH reflecting an essentially electrostatic interaction.

The electrostatic components, ΔG_e and ΔH_e may be calculated from the Eqns.[67]

$$\Delta G_e = \gamma(\Delta S + \Delta n R \ln 55.5)$$

and

$$\Delta H_e = (T-\gamma)(\Delta S + \Delta n R \ln 55.5)$$

where Δn is the decrease in the number of solute particles in the ion association reaction. The temperature-independent part of the enthalpy, ΔH_c, reflecting both the covalent interactions and structural changes, is given by the difference ($\Delta H - \Delta H_e$) and values have been calculated for a number of closely related complexes involving nitrogen and carboxylate oxygen ligand atoms[67] and for halide and pseudo halide complexes[71].

D THE ENTROPY CHANGES

There is now a substantial body of precise entropy data which can be used to discuss, in more detail, the ion association reactions. In the case of mononuclear complexes containing only one ligand molecule bound to each metal ion, the entropy of association,

$$\Delta S = \Delta S_g + \Delta S_h\,(\mathrm{ML}) - \Delta S_h\,(\mathrm{M}) - \Delta S_h\,(\mathrm{L}) \tag{2}$$

in which ΔS_g is the entropy change for the hypothetical reaction in the gas phase and ΔS_h is the hydration entropy of the species contained in parentheses. For the formation of 1:1 complexes between a polyatomic anion, L^{y-} and a series of cations, M^{x+}, it is useful to remove the variable $S^0\,(\mathrm{M}^{x+})$ [$= S_g\,(M^{x+}) + S_h\,(\mathrm{M}^{x+})$] and to write[65]

$$\Delta S + S^0\,(\mathrm{M}^{x+}) = \underbrace{[S_g\,(\mathrm{ML}^{(x-y)+}) - S_g\,(\mathrm{L}^{y-})]}_{\mathrm{I}} + \underbrace{[\Delta S_h\,(\mathrm{ML}^{(x-y)+}) - \Delta S_h(\mathrm{L}^{y-})]}_{\mathrm{II}} \tag{3}$$

In Eqn. (3), term I reflects the change in configurational and librational entropy of the ligand molecule when it enters into complex formation. The increase in translational entropy will be small, and, since the ligand loses freedom — especially if bonded to the metal through more than one binding site — the term I will be negative. The negative hydration entropy of the ion L^{y-} will be greater than that of the lower-charged $\mathrm{ML}^{(x-y)+}$, resulting in a positive term II in Eqn. (3).

Recently, careful thermodynamic studies have been made of a number of metal-complex formation reactions. The remainder of this review will be concerned with a discussion of those systems for which accurate association constants over a wide range of temperature have been measured, or calorimetric enthalpy changes have been obtained.

TABLE 1

METAL COMPLEXES WITH OXYGEN-COORDINATING LIGANDS

Reaction	ΔH_C (*kcal.mole*$^{-1}$)	ΔH_T (*kcal mole*$^{-1}$)	$-\Delta G$ (*kcal mole*$^{-1}$)	ΔS (*cal deg*$^{-1}$. *mole*$^{-1}$)	ΔS_{hyd} (*MA*) (*cal deg*$^{-1}$ *mole*$^{-1}$)	*Ref.*
L^{2-} = *Oxalate (ionic strength → 0)*						
$Mn^{2+}+L^{2-}$	—	1.42	5.41	22.9	−54.8	50
$Co^{2+}+L^{2-}$	—	0.59	6.54	23.9	−55.8	50
$Ni^{2+}+L^{2-}$	—	0.15	7.05	24.2	−56.1	50
$Cu^{2+}+L^{2-}$	−0.05	—	8.49	28.3	−52.5	50
L^{2-} = *Malonate (ionic strength → 0)*						
$Mn^{2+}+L^{2-}$	3.68	3.53	4.48	27.4	−57.5	53,68
$Co^{2+}+L^{2-}$	2.90	2.57	5.13	27.0	−59.8	53,68
$Ni^{2+}+L^{2-}$	1.88	1.77	5.60	25.0	−62.8	53,68
$Cu^{2+}+L^{2-}$	2.85	—	7.69	35.4	−52.6	68
$Zn^{2+}+L^{2-}$	3.13	3.06	5.22	28.0	−61.6	68
L^{2-} = *Succinate (ionic strength → 0)*						
$Mn^{2+}+L^{2-}$	3.02	2.95	3.09	20.5	−64.2	69
$Co^{2+}+L^{2-}$	3.15	2.81	3.02	20.7	−65.9	69
$Ni^{2+}+L^{2-}$	2.46	2.23	3.20	19.0	−68.7	69
$Cu^{2+}+L^{2-}$	4.56	—	4.42	30.1	−55.5	69
$Zn^{2+}+L^{2-}$	4.39	—	3.36	26.0	−64.3	69
L^{-} = *Acetate (ionic strength = 3.0M)*						
$Cu^{2+}+L^{-}$	1.04		2.56	12.1		70
$CuL^{+}+L^{-}$	0.41		1.69	7.1		70
CuL_2+L^{-}	0.07		0.64	2.4		70
$Zn^{2+}+L^{-}$	2.04		1.29	11.2		70
$ZnL^{+}+L^{-}$	3.22		0.54	12.5		70
ZnL_2+L^{-}	1.15		0.69	6.1		70
$Cd^{2+}+L^{-}$	1.46		1.78	10.9		70
$CdL^{+}+L^{-}$	0.84		1.33	7.3		70
CdL_2+L^{-}	0.41		0.19	2.0		70
$Pb^{2+}+L^{-}$	−0.06		3.18	10.5		70
$PbL^{+}+L^{-}$	−0.09		1.73	5.5		70
PbL_2+L^{-}	−0.96		−0.02	−3.3		70

E. EXPERIMENTAL DATA

(i) *Metal complexes with oxygen coordinating ligands*

Thermodynamic functions for the formation of divalent metal carboxylates are given in Table 1. ΔH_T and ΔH_C refer to temperature coefficient and calorimetric data respectively; the entropy changes have been calculated from ΔH_C where available. The good agreement between ΔH_T and ΔH_C indicates that reliable thermodynamic data can be obtained where a sufficiently large temperature range is used.

The heats of formation of the metal–carboxylate complexes are predominantly endothermic since, as discussed above, coulombic forces between the charged centers will vary with temperature in the same way as the macroscopic dielectric constant of water. In spite of this unfavourable enthalpy change, the complexes are stabilized by the relatively large positive entropy changes due to the liberation of water molecules from the ions accompanying complex formation. For the singly charged acetate ion, the ΔS for the first step in the association reactions is considerably less than that for the doubly charged dicarboxylates. The entropies of hydration of the dicarboxylate complexes follow the order oxalate $>$ malonate $>$ succinate and may reflect an increasing polarity of the complexes associated with reduced stability.

The crystal fields produced by oxygen-coordinating ligands are quite similar to those of the water molecules, and so ΔH will not be much affected by ligand field stabilization. Nevertheless, for the most stable oxalate complexes, the enthalpies of formation vary in the expected direction. With the exception of manganese and cobalt succinates, the stability constants for all the dicarboxylate complexes follow the Irving–Williams order but this cannot be explained solely on the basis of crystal field stabilization by assuming that $-\Delta G$ depends only upon $-\Delta H$. Both copper monomalonate and monosuccinate complexes are formed with abnormally large endothermic heat changes. In the case of copper(II), additional stabilization is possible due to tetragonal distortion of the octahedral symmetry as a result of the Jahn–Teller effect. The resulting four short bonds in the xy plane and two long bonds in the z direction may affect the thermodynamic functions in two ways[1]: (i) The increased covalent nature of the shortened M–ligand bonds in the xy plane will result in a more exothermic heat of formation; (ii) the accompanying closer contact of metal ion and charged coordinating sites in the ligand will lead to a more positive entropy of formation through increased release of coordinated solvent molecules At the limit of distortion a change of coordination from six in the aquo ion to four in the complex will also result in a more positive entropy of formation, but in this case an increased endothermicity will be expected due to the breaking of metal–water bonds.

For both copper monomalonate and monosuccinate, abnormally large entropies of formation are accompanied by large endothermic heat changes rather than the exothermic changes required by (i) above. The data are consistent with the hypothesis that a larger number of water molecules are released in the process of complex formation with a change of coordination number of the copper(II). The increasing endothermicity of copper oxalate $<$ malonate $<$ succinate may reflect the increasing strain introduced in the ligand molecules in bringing the coordinating groups into bonding in the xy plane. In the ensuing discussion, it will be seen that the features noted above in the thermodynamic functions for the formation of copper complexes with charged multidentate ligands are of a rather general nature.

In contrast to the cadmium halide and pseudo halide systems, the cadmium acetate complexes are stabilized by favorable entropy rather than enthalpy changes. This is consistent with the predominantly Coulombic interactions involving the carboxyl group. The order of the stabilities of the acetate complexes of different metal ions is, however, determined largely by the enthalpy changes. The comparatively large and positive values of ΔH_2 and ΔS_2 (Table 1) for the formation of ZnL_2 from ZnL^+ are consistent with the tendency of Zn^{II} to form tetrahedral complexes[72] and similar effects are evident in the association of this metal ion with other types of ligand molecules[1].

(*ii*) *Halide and pseudo-halide complexes*

Metal complexes with simple ionic ligands form particularly suitable systems for which to discuss the thermodynamic functions Reliable values of the aqueous entropies of the ligand ions are usually available and it is possible to calculate the hydration entropies of the complexes by means of Eqn. (2)[73,74].

TABLE 2

THERMODYNAMIC FUNCTIONS FOR THE FORMATION OF METAL HALIDE AND PSEUDO-HALIDE COMPLEXES AT 25°

Reaction	*Ionic strength (M)*	*$-\Delta G$ (kcal mole^{-1})*	*ΔH (kcal mole^{-1})*	*ΔS (cal deg^{-1}. mole^{-1})*	*Ref*
Halides					
$Cd^{2+}+F^-$	3.0	0.63	1.23	6.2	76
$Cd^{2+}+Cl^-$	3.0	2.16	−0.10	6.9	76
$CdCl^++Cl^-$	3.0	0.88	0.02	3.0	76
$CdCl_2+Cl^-$	3.0	0.25	1.85	7.0	76
$Cd^{2+}+Br^-$	3.0	2.40	−0.98	4.7	76
$CdBr^++Br^-$	3.0	0.80	−0.57	0.8	76
$CdBr_2+Br^-$	3.0	1.34	+1.72	10.2	76
$CdBr_3^-+Br^-$	3.0	0.51	+0.30	2.7	76
$Cd^{2+}+I^-$	3.0	2.84	−2.26	2.0	76
CdI^++I^-	3.0	0.95	−0.20	2.5	76
CdI_2+I^-	3.0	2.91	−0.73	7.3	76
$CdI_3^-+I^-$	3.0	2.19	−3.81	−5.5	76
$Hg^{2+}+Cl^-$	0.50	9.2	−5.5	12.4	77
$HgCl^++Cl^-$	0.50	8.8	−7.3	5.3	77
$Hg^{2+}+Br^-$	0.50	12.3	−10.2	7.1	77
$HgBr^++Br^-$	0.50	11.3	−11.0	1.1	77
$Hg^{2+}+I^-$	0.50	17.5	−18.0	−1.5	77
HgI^++I^-	0.50	15.0	−16.2	−4.2	77
$Mg^{2+}+F^-$	1.0	1.80	3.2	16.8	78
$Ca^{2+}+F^-$	1.0	0.86	3.5	15.0	78
$Sr^{2+}+F^-$	1.0	0.20	~4	~14	78
$Ba^{2+}+F^-$	1.0	~−0.3	~0	~ 0	78

(Table 2 continued)

Reaction	*Ionic strength (M)*	$-\Delta G$ *(kcal mole^{-1})*	ΔH *(kcal mole^{-1})*	ΔS *(cal deg^{-1}. mole^{-1})*	*Ref*
$Tl^{+}+Cl^{-}$	$\to 0$	0.93	−1.43	1.7	76
$Tl^{+}+Br^{-}$	$\to 0$	1.2	−2.45	−4.2	79
$Tl^{3+}+Cl^{-}$	3.0	9.74	−5.45	14.5	80
$TlCl^{2+}+Cl^{-}$	3.0	7.39	−4.40	10.1	80
$TlCl_2^{+}+Cl^{-}$	3.0	3.46	−1.1	8.0	80
$TlCl_3+Cl^{-}$	3.0	2.95	−0.3	8.9	80
Cyanides					
$CH_3Hg^{+}+CN^{-}$	0.1	18.8	−22.1	−11.4	84
$Cu^{+}+2CN^{-}$	$\to 0$	32.7	−29.1	+12	81
$Cu(CN)_2^{-}+CN^{-}$	$\to 0$	7.23	−11.1	−13.4	81
$Cu(CN)_3^{2-}+CN^{-}$	$\to 0$	2.0	−11.2	−31	81
$Ag^{+}+2CN^{-}$	$\to 0$	27.89	−33.0	−16	81
$Ag(CN)_2^{-}+CN^{-}$	$\to 0$	2.11	− 0.6	+5	81
$Zn^{2+}+2CN^{-}$	$\to 0$	15.10	−10.8	+14.4	83
$Zn(CN)_2+CN^{-}$	$\to 0$	6.80	− 8.4	− 5.4	83
$Zn(CN)_3^{-}+CN^{-}$	$\to 0$	4.87	− 8.6	−12.4	83
$Cd^{2+}+4CN^{-}$	$\to 0$	26.77	−27.8	− 1.0	83
*Thiocyanates**					
$Mn^{2+}+NCS^{-}$	$\to 0$	1.68	−0.9	2.5	82
$Co^{2+}+NCS^{-}$	$\to 0$	2.35	−1.6	2.2	82
$Ni^{2+}+NCS^{-}$	$\to 0$	2.40	−2.3	0.5	82
$Cu^{2+}+NCS^{-}$	$\to 0$	3.18	−3.0	0.6	82
$Zn^{2+}+NCS^{-}$	$\to 0$	2.53	0.2	9	82
$Cd^{2+}+NCS^{-}$	$\to 0$	3.42	−0.7	9	82
$Pb^{2+}+NCS^{-}$	$\to 0$	1.49	0.3	6	82

* With the possible exception of Cd^{2+} and Pb^{2+}, bonding is through the nitrogen atom

ΔS_g terms contain both rotational and translational contributions

$$\Delta S_g = S_{\text{trans}}(\text{ML}) - S_{\text{trans}}(\text{M}) - S_{\text{trans}}(\text{L}) - S_{\text{rot}}(\text{L}) + S_{\text{rot}}(\text{ML})$$

which can be calculated statistically[1].

As discussed above, the sensitivity of the electrostatic interaction energy to changes in temperature, through the temperature differential of the solvent dielectric constant, leads to the expectation of endothermic enthalpies of formation of complexes for which this model is appropriate. Such interactions would involve "hard" ligands[75] and metal ions of *A*-character and the driving force will be the positive entropy accompanying solvent release from the co-spheres of the ions (term II in Eqn. (3)). Increasingly covalent interactions between 'soft" entities will result in more exothermic enthalpies of formation. In the series of anions under discussion, the ability for covalent bonding, or softness, increases in the inverse order of the electronegativities,

$F^- \ll Cl^- < Br^- < I^-$

and the thermodynamic functions are given in Table 2 The striking increase in exothermicity for the formation of 1:1 complexes as the ligand is changed from fluoride to iodide is seen for each of the metal ions. For the very hard fluoride ion, the complexes are stabilised entirely by the entropy changes accompanying the breakdown of the "iceberg" structure of coordinated solvent molecules around the ions. The concomitant endothermicity reflects both the electrostatic nature of the interactions and the energy required to break the ion–water bonds. For the alkaline earth monofluorides, the value of $\Delta S(MgF^+)$ is unusually close to that for CaF^+ and the calculated $\Delta S_h(MgF^+)$ is therefore more negative than that for the other members. This may reflect the greater retention of the hydration co-sphere of the Mg^{II} ion in MgF^+ than is the case for the other alkaline earth monofluorides[78]. A similar suggestion was made for the acetate and formate complexes of magnesium, based upon thermodynamic functions derived from potentiometric studies[85]. It is interesting to note that the low charge density and comparative softness of the Ba^{II} ion allows of only a very weak interaction with hard fluoride ion. Although the thermodynamic data for this interaction do not have the precision of those for the corresponding Mg^{II} and Ca^{II} species, it is seen that both ΔH and ΔS values are approximately zero again indicating a greater retention of solvent structure of the free ion in the complex. The less effective bonding of ligand molecules to the large Ba^{II} ion is manifested in the thermodynamic data for other complexing systems.

As the *B*-character or softness of the metal ion is increased, the enthalpy of formation of halide complexes becomes more favourable. It is seen in Table 2 that the enthalpies of formation of $CdCl^+$ and TlCl are already slightly negative indicating a greater covalency than for the monofluoride complexes. With the typically soft Hg^{II} and Tl^{III}, the monochloride complexes are formed with appreciable exothermic enthalpy changes. The structure-breaking properties of the halide ions increase in the order $Cl^- < Br^- < I^-$ and it is seen that the values of the association entropies for all the monohalide complexes decrease along the series $F^- > Cl^- > Br^- > I^-$ owing to the decreasing strength of interaction between ligand and solvent. In the case of the large iodide ion, the ΔS value is unfavourably negative in some instances (*e.g.* HgI^+) reflecting the relative unimportance of term II (Eqn. 3) as compared with the disappearance of species accompanying ion association.

Some trends in the thermodynamic functions for the stepwise formation of complexes can also be explained in terms of the general features discussed above. An increasing exothermicity in going from CdL_3^- to CdL_4^{2-} is accompanied by substantial decreases in the stepwise entropy changes. The effects are larger for iodide as compared with bromide in agreement with the larger structure breaking tendencies of the iodide ion In the step CdL_2 to CdL_3^-, however, positive entropy changes are seen for all three halide ions whilst the enthalpy changes are either approximately zero (for $L^- = I^-$) or else endothermic (for $L^- = Cl^-$ and Br^-).

Breaking of ion–solvent bonds appears to be of greatest importance during this association step.

The behaviour of the cyanide ion as a very soft ligand[86] is clearly seen from the thermodynamic data in Table 2. Complexes with the *B*-character metal ions are appreciably stabilised almost without exception by the large exothermic enthalpy changes. Except for the formation of $Cu(CN)_2^-$ and $Ag(CN)_3^{2-}$ the entropy changes are all negative indicating only weak ligand–solvent interactions in addition to the expected loss of rotational entropy of the diatomic cyanide ion when it bonds to the metal ions. The introduction of rotational and vibrational entropy terms has been proposed for the interactions of metal ions with other polyatomic anions such as azide and thiocyanate[79]. It can be seen that the enthalpy change for the formation of $M(CN)_3^{2-}$ from $M(CN)_2^-$ is much more exothermic for $M^+ = Cu^+$ than is the case for Ag^+. The probable existence of multiple bonding in the $Cu(CN)_3^{2-}$ complex has been discussed by a number of workers[81,87,88]. Evidence from both Raman and infrared intensity measurements points[89] to the additional influence of π-bonding in $Cu(CN)_3^{2-}$ but not in $Ag(CN)_3^{2-}$. Such multiple bonding would account for the observed differences in the enthalpies of formation of these species.

We are now in a position, in the light of the arguments presented above, to make some general comments concerning the thermodynamic implications of *A*-character (hard) and *B*-character (soft) interactions. Complexes formed through the predominantly electrostatic interactions between hard acids and bases are entropy stabilised; the enthalpy changes are usually small and endothermic reflecting the energy required for the removal of coordinated solvent molecules from the co-spheres of the ions. *B*-character interactions, on the other hand, are always characterised by exothermic enthalpy changes. The accompanying entropy terms become increasingly negative with increasing softness of the interacting acid–base species. This behaviour is strikingly illustrated by the thermodynamic data given in Table 3 for the interaction of *B*-character metal ions with a soft phosphorus-coordinating ligand diethyl-β-oxyethyl phosphine (Dop)[90]. The complexes are formed with exceedingly large exothermic enthalpy changes and all the entropy term contributions are unfavourable.

TABLE 3

THERMODYNAMIC FUNCTIONS AT 22 °C ($I = 1.0$M) FOR THE REACTIONS[90]

$M^{n+} + Dop \rightleftharpoons M(Dop)^{n+}$

Reaction	$-\Delta G$ *(kcal mole^{-1})*	ΔH *(kcal mole^{-1})*	ΔS *(cal deg^{-1}.mole^{-1})*
$Ag^+ + Dop$	15.97	−19.3	−11.3
$Ag(Dop)^+ + Dop$	12.18	−16.5	−14.6
$Ag(Dop)_2^+ + Dop$	6.56	− 9.1	− 8.7
$Hg^{2+} + Dop$	50.37	−52.8	− 8.2
$CH_3Hg^+ + Dop$	19.72	−22.6	− 9.8

Thermodynamic functions for the formation of the rather weak monothiocyanate complexes are given in Table 2. The entropy changes are small as would be expected for the formation of a charged complex which will retain some of its solvent-ordering properties. The abnormally endothermic enthalpy and large positive entropy changes for the formation of the zinc monothiocyanate complex may reflect the elimination of extra water molecules from the co-sphere of this small cation. Back-coordination to the thiocyanate ion from the filled shell of the zinc ion may result in a more bent complex requiring, for its formation, the removal of more than one water molecule from the hydration sphere of the cation[82].

The thiocyanate ion exhibits linkage isomerism, bonding to the metal ion either through its sulphur or nitrogen atom. Coordination involving the sulphur atom, the most probable site of the negative charge[91] will result in a more effective neutralization of charge in the formation of the complex and a more positive ΔS. Metal ions of *B*-character such as Cd^{II} and Pb^{II} will be expected to show some bonding through the sulphur atom, and it is seen that their complexes are formed with abnormally large and positive entropy changes as compared with data for the other metal ions in Table 2.

(*iii*) *Metal complexes with nitrogen-coordinating ligands*

A number of polyamine systems have been investigated recently calorimetrically and some features of the results will be outlined in this section. The ligands studied include: diethylenetriamine (dien)[92], 2,2′2″-triaminotriethylamine (tren)[93], triethylenetetramine (trien)[94], tetraethylenepentamine (tetren)[95], *N,N,N,′N′*-tetra-(2-aminoethyl)-ethylenediamine (penten)[96], α, α′-dipyridyl (dip)[97,98,99] and 1:10-phenanthroline (phen)[97]. Some thermodynamic data are included in Table 4, and for the aliphatic polyamines it is seen that there is a tendency for successive enthalpy changes to become more exothermic; the effect is particularly marked with $Zn(dien)_2^{2+}$.

Association of metal ions with uncharged ligands is accompanied by smaller entropy changes than for the corresponding reactions with anionic ligands. Nevertheless, the ΔS values for all the 1:1 complexes in Table 4 are positive, indicating that, as was the case with the charged ligands, term II in Eqn (3) is more important than term I. The decrease in entropy resulting from the diminished freedom of the ligand molecules on complex formation, is more than compensated by the release of water molecules in the co-spheres of the metal ions.

Ligand-field effects produce contributions to the heats of complex formation, but the paucity of reliable enthalpy data has led many workers to consider only changes in ΔG. The use of ΔG presupposes that variations in the entropy changes for reactions of the transition-metal ions with a given ligand are negligible. In the light of subsequently determined thermodynamic data, this assumption is seen to be undesirable[1]. $-\Delta H$ Values are plotted in Fig. 1 for some of the hexa-

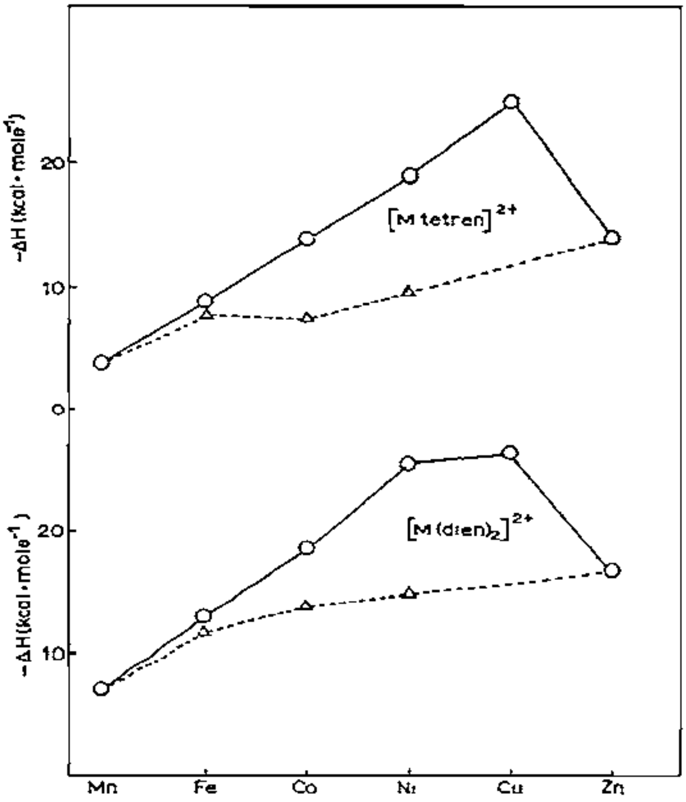


Fig 1 Heats of formation of metal–polyamine complexes plotted as a function of atomic number. The dotted curves have been corrected for crystal field stabilizations.

coordinated polyamine complexes of the bivalent transition metal ions. For all of the aliphatic polyamine ligands, the exothermicity increases from Ni^{II} to Cu^{II} and then decreases to Zn^{II} in agreement with the Irving–Williams order. Corrections for crystal-field stabilizations were made by Ciampolini, Paoletti and Sacconi[100] and it is seen in Fig. 1 that the corrected values lie slightly above the line joining manganese to zinc and that the ligand field theory satisfactorily explains the observed trends in ΔH for these complexes.

The spectra of the $[M(en)_3]^{2+}$ and $[M(NH_3)_6]^{2+}$ species are closely similar to those of $[Fe(dien)_2]^{2+}$, $[Co(dien)_2]^{2+}$ and $[Ni(dien)_2]^{2+}$ indicating that the symmetry of the ligand-field in the latter series of complexes is essentially octahedral[92]. It is seen in Table 4 that the value of $-\Delta H_2$ for $[Cu(dien)_2]^{2+}$ (8.15 kcal. mole^{-1}) is low compared with the value for the first stage of the association, $-\Delta H_1 = 18.00$ kcal.mole^{-1}. Taking the heat of formation of a single copper–nitrogen bond as one-half of that for the formation[104] of $(Cuen)^{2+}$, *viz.* -6.5 kcal.mole^{-1}, it is seen that the binding of three nitrogen atoms in the first molecule of dien is normal. The heat of reaction, -18.00 kcal.mole^{-1} is approximately equal

TABLE 4

METAL COMPLEXES WITH NITROGEN-COORDINATING LIGANDS

Reactants	*I* *(M)*	$-\Delta G$ *(kcal mole^{-1})*	$-\Delta H$ *(kcal.mole^{-1})*	ΔS *(cal deg^{-1} mole^{-1})*
A = diethylenetriamine (dien)[92]				
$Mn^{2+}+2A$	0.1	—	6.95	—
$Fe^{2+}+2A$	0.1	—	12.95	—
$Co^{2+}+A$	0.1	10.90	8.15	9.0
$CoA^{2+}+A$	0.1	8.00	10.25	−7.5
$Ni^{2+}+A$	0.1	14.45	11.85	8.5
$NiA^{2+}+A$	0.1	10.90	13.45	−8.5
$Cu^{2+}+A$	0.1	21.55	18.00	12.0
$CuA^{2+}+A$	0.1	7.10	8.15	−3.5
$Zn^{2+}+A$	0.1	12.00	6.45	18.5
$ZnA^{2+}+A$	0.1	7.50	10.15	−9.0
A = N,N,N′,N′-tetra-(2-aminoethyl)-ethylenediamine (penten)[96,103]				
$Mn^{2+}+A$	0.1	12.58[a]	8.85	12.5
$Fe^{2+}+A$	0.1	15.16[a]	9.65	18.5
$Co^{2+}+A$	0.1	21.16[a]	14.75	21.5
$Co^{2+}+HA^{+}$	0.1	16.98[a]	14.00	10.0
$Ni^{2+}+A$	0.1	26.06[a]	19.65	21.5
$Ni^{2+}+HA^{+}$	0.1	21.33[a]	18.35	10.0
$Cu^{2+}+A$	0.1	30.16[a]	24.50	19.0
$Cu^{2+}+HA^{+}$	0.1	27.48[a]	24.80	9.0
$Zn^{2+}+A$	0.1	21.95[a]	14.50	25.0
$Zn^{2+}+HA^{+}$	0.1	19.12	14.65	15.0

[a] Corrected to 25° from the determined 20° values[103].

to -3×6.5 kcal.mole^{-1}. In the next stage of association, a ΔH_2 value of -8.15 kcal.mole^{-1} corresponds to the binding of more than one nitrogen atom of the second dien molecule to [Cu dien]$^{2+}$. The value is larger than the expected -2×6.5 kcal.mole^{-1} for two Cu–N bonds on account of the smaller crystal-field stabilization energy for [Cu(dien)$_2$]$^{2+}$ as compared with that[92] for [Cudien]$^{2+}$. This conclusion is in agreement with the previous suggestion of Martell and his coworkers that the three nitrogen atoms of [Cudien]$^{2+}$ lie in a plane with water molecules occupying the other three positions[101]. The resulting tetragonal distortion of the octahedral configuration stabilizes the ground state owing to the removal of the t_{2g} and e_g orbital degeneracy by the tetragonal component of the electric field acting on the copper ion. As a consequence of the lower tetragonal distortion of the [Cu(dien)$_2$]$^{2+}$ ion, the crystal-field stabilization energy decreases and $-\Delta H_2$ is abnormally low. It can be seen from Table 4 that the overall entropy change ($\Delta S_1+\Delta S_2$) for [Cu(dien)$_2$]$^{2+}$, 8.5 cal.deg^{-1}.mole^{-1} is considerably larger than the values 1.5 and 0.0 cal.deg^{-1}.mole^{-1}, respectively, for the corresponding cobalt and nickel complexes. The planar [Cudien]$^{2+}$ has a smaller dipole moment than that of the octahedral [Codien]$^{2+}$ and [Nidien]$^{2+}$. As a consequence, fewer water molecules will be orientated by [Cudien]$^{2+}$ and its entropy will be larger[102]. In addition, since the second dien molecule is bound by fewer than three nitrogen atoms, the freedom of movement of the uncoordinated part of the molecule will contribute to the entropy increase[92].

Reference has already been made to the tendency of zinc(II) to form complexes in which the coordination number is less than six. The abnormally low $-\Delta H$ and high ΔS values for the formation of $[\mathrm{Zndien}]^{2+}$ points to the formation of a tetrahedral ion of the type $[\mathrm{Zn(H_2O)dien}]^{2+}$ with the additional endothermic and entropy effects arising from the displacement of more than three coordinated water molecules[92]. Similar arguments have been advanced to explain the abnormally low $-\Delta H$ and high ΔS values for the formation of a tetrahedral $[\mathrm{Zntrien}]^{2+}$ ion[94].

The penten molecule probably acts as a sexadentate ligand[96] since the $-\Delta H$ values for the $\mathrm{Mn^{II}}$, $\mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$ and $\mathrm{Ni^{II}}$ complexes are higher than the corresponding values for the $[\mathrm{Mtetren}]^{2+}$ ions[95]. The considerable strain in the five resulting 5-membered chelate rings is reflected in the apparent ease with which one of the

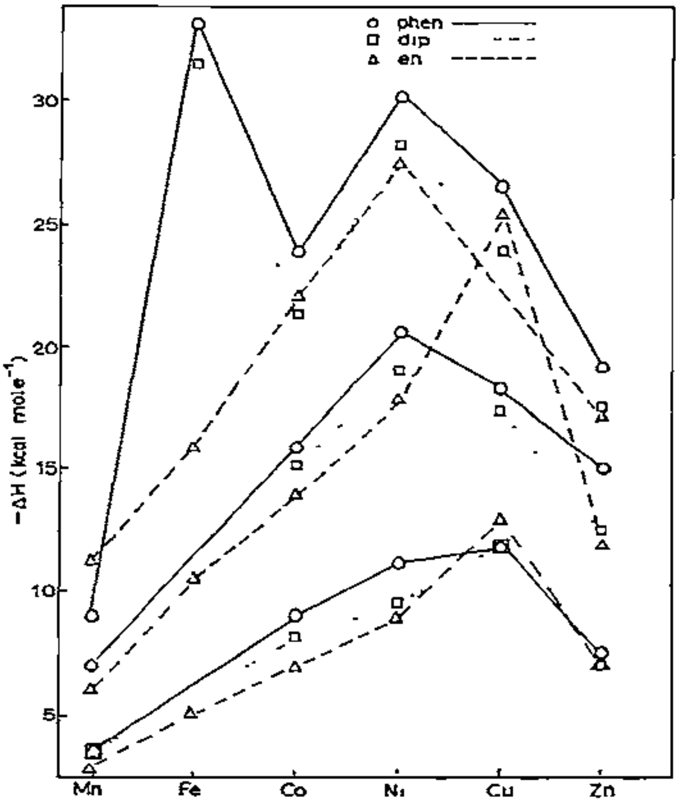


Fig. 2. Heats of formation plotted as a function of atomic number for metal 1:10 phenanthroline, ethylenediamine and dipyridyl complexes. Reproduced, with permission from *Helv. Chim Acta*, 46 (1963) 2819.

amino groups can be split from the metal and protonated to form $[\mathrm{MpentenH}]^{3+}$ species. In Table 4 it can be seen that the ΔH values are approximately the same for the formation of the copper and zinc complexes $[\mathrm{Mpenten}]^{2+}$ and $[\mathrm{MpentenH}]^{3+}$ and it is likely that penten behaves as a quinquedentate ligand in both these species[103]. Further evidence for the coordination of only five N atoms in $[\mathrm{Cupenten}]^{2+}$ is provided by the absence of any shift in the spectrum of $[\mathrm{CupentenH}]^{3+}$ as compared with $[\mathrm{Cupenten}]^{2+}$. The relatively greater value of $-\Delta H$ for the formation of $[\mathrm{Mnpenten}]^{2+}$ (Table 4) may reflect the tendency of the large manganese ion to form complexes in which the coordination number is greater than six. The inclusion of water molecules in the first coordination shell in addition to the six N atoms would account for the rather small entropy of formation, 12 5 cal deg^{-1}.mole^{-1}. X-ray structural evidence for the formation of seven-coordinate manganese in $\mathrm{Mn[Mn(H_2O)HY]_2 \,.\, 8H_2O}$ (in which $\mathrm{Y^{4-}} = \mathrm{EDTA^{4-}}$) supports this hypothesis[105].

Dipyridyl (dip) complexes of divalent metal ions have been extensively studied calorimetrically[98,99,106]. The results obtained by Anderegg[106] at 20° and by Davies and Dunning[98] at 30.3° are in general agreement but the ΔH values of Atkinson and Bauman[99] at 25° are consistently lower than either of the other studies. The differences have been discussed[107] in the light of the validity of the assumption made by Atkinson and Bauman of a linear dependence of ΔH on n.

We will confine our discussion to the thermodynamic functions obtained by Anderegg and by Davies and Dunning, and some enthalpy values are presented in Fig. 2 as a function of atomic number; data for ethylenediamine (en)[104] and 1 : 10-phenanthroline (phen)[106] are included for comparison. It can be seen that the values of the overall heats of formation ΔH_n for mono-, bis- and tris-complexes of ethylenediamine are very similar to those of the corresponding dip and phen complexes for cobalt, nickel and zinc. For the 1 : 1 and 1 : 2 complexes the points for Mn$^{\mathrm{II}}$, Fe$^{\mathrm{II}}$, Co$^{\mathrm{II}}$ and Ni$^{\mathrm{II}}$ lie practically on a straight line. The differences for the tris complexes of the aromatic amines, however, are striking; the Fe$^{\mathrm{II}}$ complexes are formed with much larger exothermic enthalpy changes than for the corresponding $\mathrm{Fe(en)_3}^{2+}$.

The stabilities of the $\mathrm{Fe(phen)_3}^{2+}$ and $\mathrm{Fe(dip)_3}^{2+}$ complexes are such that the systems can be characterised by a single overall stability constant β_3. The concentrations of mono- and bis-complexes are extremely small[99]. Magnetic susceptibility measurements have shown that $\mathrm{Fe(dip)_3}^{2+}$ is diamagnetic[108] whereas the corresponding ethylenediamine complex is paramagnetic as is also the hydrated Fe$^{\mathrm{II}}$ ion. The larger exothermic enthalpy change for the formation of $\mathrm{Fe(dip)_3}^{2+}$ can therefore be accounted for by the change in the ground state of the metal when the complex is formed from $\mathrm{Fe(H_2O)_6}^{2+}$. The entropy changes for the formation of $\mathrm{Fe(dip)_3}^{2+}$ (−27.0 cal.deg^{-1}.mole^{-1})[106] and $\mathrm{Fe(phen)_3}^{2+}$ (−15.4 cal.deg^{-1}. mole^{-1})[106] are also considerably more negative than those for the other metal ions. This probably reflects the strong binding and immobilization of the ligand molecules in these complexes. In general, phen complexes are formed with more positive entropy changes than the corresponding dip species and the trend can be accounted for by the greater rigidity of 1:10-phenanthroline as compared with dipyridine.

The availability of thermodynamic data for the polyamine complexes enables the nature of the chelate effect to be examined in more detail and thermodynamic functions for the reactions

$$M(NH_3)_n^{2+} + L \rightleftarrows ML^{2+} + n(NH_3), \qquad (4)$$

are given in Table 5.

TABLE 5

THE CHELATE EFFECT METAL–POLYAMINE COMPLEXES

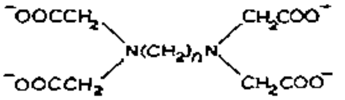
M^{2+}	n	L	$-\Delta G$ (kcal mole^{-1})	ΔH (kcal.mole^{-1})	ΔS (cal deg^{-1})	Ref.
Ni^{2+}	3	dien	5.33	−1.35	13.4	92
Cu^{2+}	3	dien	7.24	−3.0	14.2	92
Ni^{2+}	4	trien	8.09	0	27.1	94
Cu^{2+}	4	trien	10.2	−1.55	29.0	94
Ni^{2+}	5	tetren	12.10	−1.4	35.9	95
Cu^{2+}	5	tetren	14.65	−1.75	43.3	95
Ni^{2+}	6	penten	15.44	+1.35	56.0	96

It can be seen that the complexes are, without exception, stabilized with respect to the corresponding ammonia complexes, not by the enthalpy changes but by the large positive entropy changes accompanying these reactions. The entropy increases with increasing denticity of the chelating ligand. Notwithstanding the arguments[109] based upon the elimination of the cratic effects by expressing the association constants in term of mole fractions rather than moles per litre that much of this effect disappears, it is clear that the large negative free energy changes for reaction (4) can be attributed to the positive entropy changes accompanying the release of increasing numbers of ammonia molecules.

(iv) *Metal complexes with nitrogen- and oxygen-coordinating ligands*

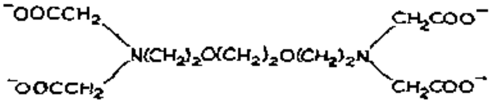
Extensive calorimetric studies have been made of the formation of metal complexes with aminopolycarboxylate ions. Schwarzenbach[110] has pointed out that when ligand molecules contain more than two potential donor atoms, the presence of a nitrogen atom enables the special structural requirements to be met for the formation of relatively strain-free chelate rings. Whereas the polyamine complexes are stabilised by appreciable exothermic heat changes, the aminopolycarboxylate complexes are also stabilised by positive entropy changes accompanying the charge neutralisation and subsequent solvent release from the co-spheres of the interacting ions. Ligands containing nitrogen atoms alone show a high selectivity in their complexing ability and, for the *A*-character cations, no stable complexes are formed. The introduction of carboxylate groups produces ligand molecules which can form stable complexes with both *A*- and *B*-character cations.

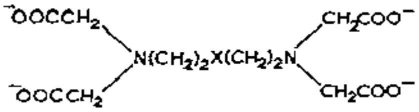
In order to discuss some of the important factors involved in the formation of these complexes, thermodynamic data will be selected from those available for iminodiacetate[111](IDA), methyliminodiacetate[57,112](mIDA) and ethylenediaminetetraacetate homologues:



in which $n = 2$ for EDTA[114,115,116]; $n = 3$ for TMTA[117]; $n = 4$ for TETA[117]; $n = 5$ for PETA[111]; $n = 6$ for HDTA[111,117]; and $n = 8$ for ODTA[111],

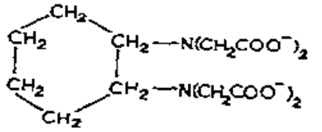
EGTA[65,111]





in which X = – O for BATA[111], X = – S for BSTA[111] and X = – N(CH_2–COO^-)$_2$ for DTPA[38,113],

DCTA[113,114],



and NTA[118,119][$N(CH_2COO^-)_3$].

The mIDA molecule constitutes one half of the EDTA molecule and the availability of enthalpy and entropy data makes it possible to examine the source of the chelate effect in more detail than can be done from a consideration only of the free energy changes. Thermodynamic functions for the reaction

$$M(mIDA)_2^{2-} + EDTA^{4-} \rightleftharpoons MEDTA^{2-} + 2mIDA^{2-} \quad (5)$$

are given in Table 6. With the exception of calcium, the chelate effect is clearly one of entropy reflecting the increase in the number of solute particles in the reaction (5). The endothermic heat changes for some of the reactions are probably due to the strain involved in fitting another chelate ring around the metal ions. The effect is particularly marked in the case of copper which, as discussed previously, has special spatial requirements for short bonds in the xy plane; the chelate effect is

TABLE 6

THE CHELATE EFFECT

$M(mIDA)_2^{2-}$ $\rightarrow MEDTA^{2-}$	$-\Delta G$ (kcal mole^{-1})	ΔH (kcal mole^{-1})	ΔS (cal deg^{-1} mole^{-1})
Mg^{2+}	3.65	1.31	17.1
Ca^{2+}	5.27	−4.62	2.7
Mn^{2+}	5.68	−4.33	3.05
Co^{2+}	3.21	1.28	15.3
Ni^{2+}	3.57	0.10	12.5
Cu^{2+}	1.17	3.96	17.4
Zn^{2+}	3.23	0.98	14.6
Cd^{2+}	5.27	−1.78	11.9

smallest with this metal ion. In contrast to these results, it is seen in Table 6 that the chelate effect for the calcium manganese complexes is principally one of enthalpy. The exothermicity of reaction (5) for calcium, manganese and cadmium can be explained by the relatively strain-free structures of their EDTA complexes as

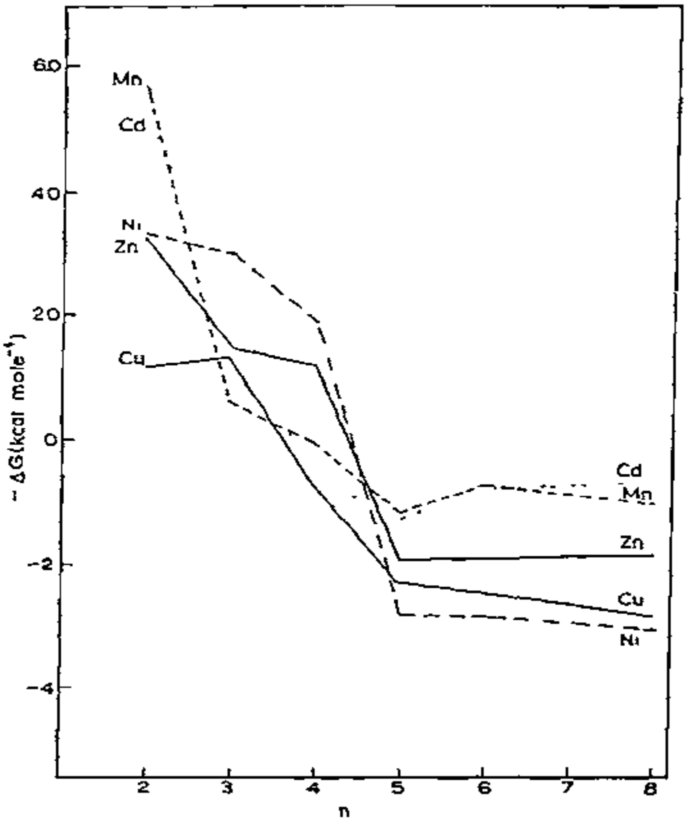


Fig. 3 The chelate effect Free energy changes for EDTA homologues (reaction 6) plotted as a function of chain length

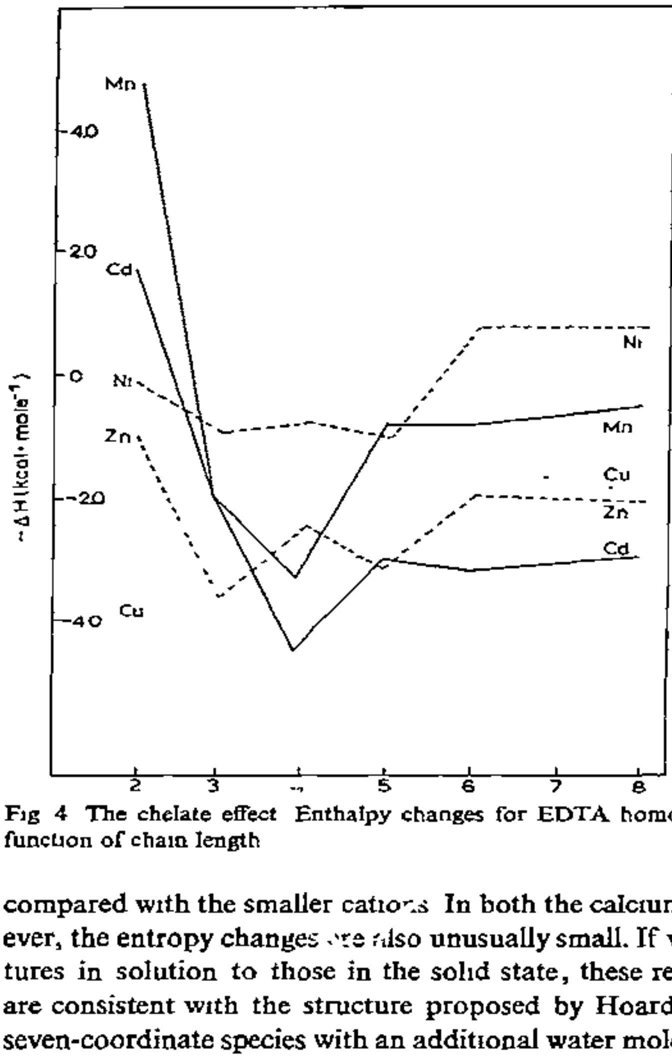


Fig 4 The chelate effect Enthalpy changes for EDTA homologues (reaction 6) plotted as a function of chain length

compared with the smaller cations In both the calcium and manganese cases, however, the entropy changes are also unusually small. If we can assume similar structures in solution to those in the solid state, these results for manganous EDTA are consistent with the structure proposed by Hoard and his associates[105] of a seven-coordinate species with an additional water molecule bound to the metal ion. Although no X-ray structural data are available for the corresponding calcium complex, it is possible that a similar $Ca(OH_2)EDTA^{2-}$ species is formed in solution.

It is of interest to consider the variation of chelate effect with n, the number of methylene residues in the central chain of the EDTA homologues. Thermodynamic functions for the reaction

$$M(mIDA)_2^{2-}+L^{4-} \rightleftharpoons ML^{2-}+2mIDA^{2-} \tag{6}$$

in which $n = 2$ (EDTA); $n = 3$ (TMTA); $n = 4$ (TETA); $n = 5$ (PETA); $n = 6$ (HDTA); and $n = 8$ (ODTA), are presented graphically in Figs. 3, 4 and 5 for a number of metal ions. It can be seen that increases in the number of methylene groups causes the association constant of ML to decrease rapidly.

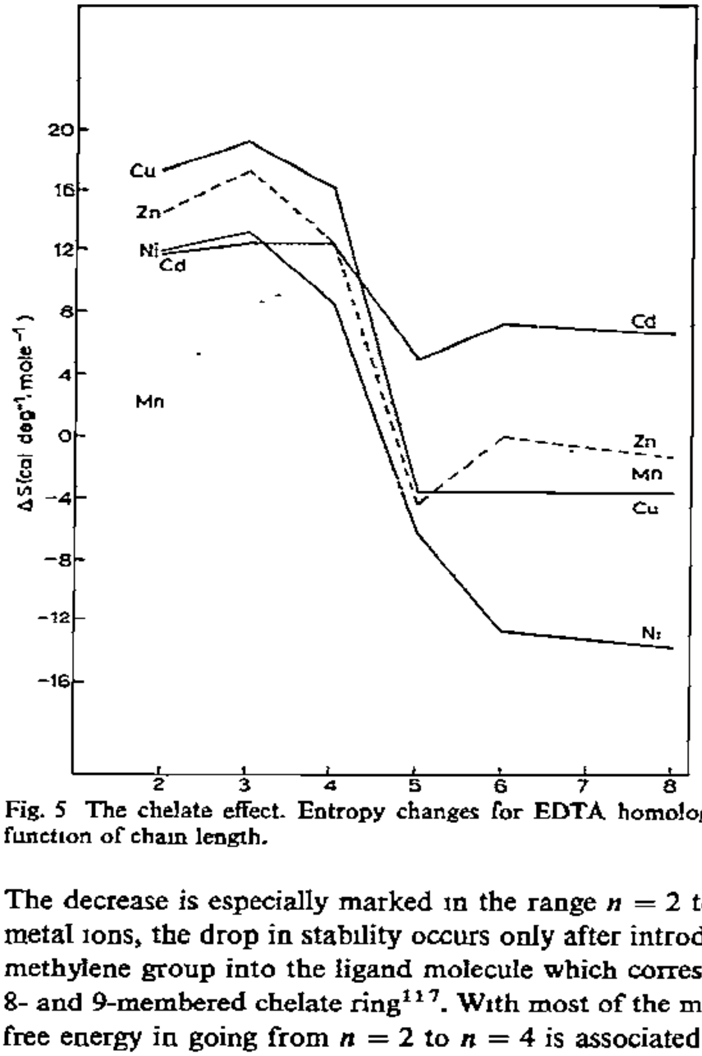
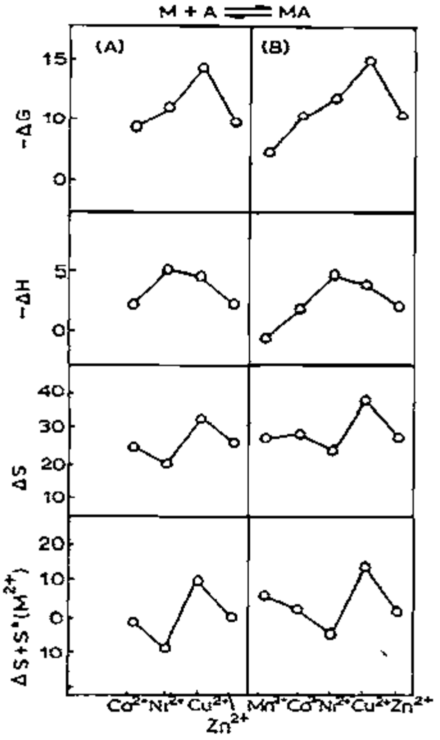


Fig. 5 The chelate effect. Entropy changes for EDTA homologues (reaction 6) plotted as a function of chain length.

The decrease is especially marked in the range $n = 2$ to $n = 5$. For some of the metal ions, the drop in stability occurs only after introducing the fourth and fifth methylene group into the ligand molecule which corresponds, respectively, to an 8- and 9-membered chelate ring[117]. With most of the metal ions, the difference in free energy in going from $n = 2$ to $n = 4$ is associated with an increasing endothermicity caused by the greater ring strain in the higher homologues. The entropy changes are not appreciably different, indicating that the coordination in the complexes is approximately the same. At higher n values the stabilising influence of chelation disappears and ΔG for reaction (6) falls to small positive values as the ligand molecules behave more and more like two independent mIDA molecules.

Thermodynamic functions for the stepwise formation of 1 : 1 and 1 : 2 bivalent transition-metal IDA and mIDA complexes are shown as a function of atomic number in Figs. 6 and 7, respectively. The position of copper is particularly interesting since, although the ΔG values for the formation of Cu L follow the well-established Irving–Williams order, it does not follow that the enthalpy changes, reflecting important crystal-field effects, follow the same order. The 1 : 1



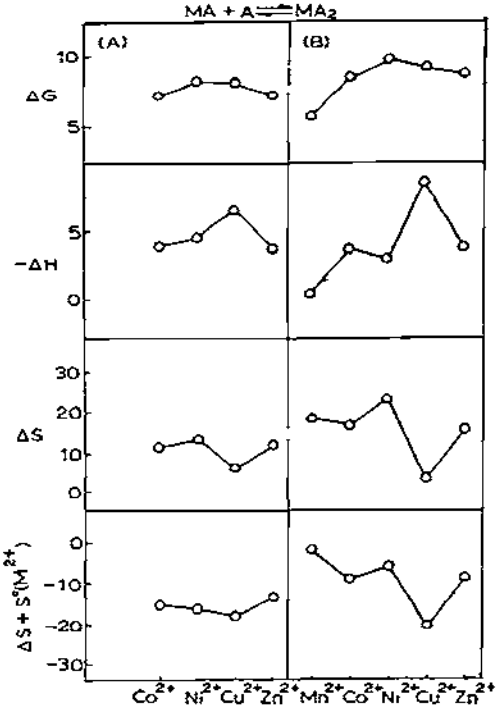


Fig. 6. Thermodynamic functions for the formation of mono-IDA and mono-mIDA complexes plotted against atomic number (A, IDA, B, mIDA)

Fig 7. Thermodynamic functions for the stepwise formation of bis-IDA and bis-mIDA complexes plotted against atomic number (A, IDA, B, mIDA).

copper complexes are formed with unusually endothermic enthalpy changes and the high stability of these complexes is clearly an entropy effect. The explanation for this behaviour, in terms of the influence of Jahn–Teller stabilization upon the thermodynamic properties, has already been considered in the section dealing with oxygen-coordinated complexes. The larger entropy changes are associated with a more effective charge neutralization resulting from the formation of short bonds in the xy plane of the metal ion and also with the greater freedom of the two axial water molecules. It can be seen in Fig. 7 that in the formation of $Cu(IDA)_2^{2-}$ and $Cu(mIDA)_2^{2-}$ from the corresponding monocomplexes, it is now the exothermic enthalpy change accompanying Cu–N bond formation which stabilizes the complexes. The entropy change is small compared with the other transition metal ions indicating that much of the water release had occurred, as suggested, in the formation of the 1 : 1 complexes. The higher stability of the complex $CuNTA^-$ as compared with the NTA complexes of the other transition metal ions is also a result of a higher entropy of formation[118]. ΔS ($CuNTA^-$) = 53 0 cal deg^{-1}. mole^{-1} whereas the values for $NiNTA^-$ and $ZnNTA^-$ are 44.1 and 46.0 cal.deg^{-1}.

mole^{-1}, respectively. The ΔH (CuNTA$^-$) value (-1.84 kcal.mole^{-1}) is larger than the corresponding Ni^{II} value (-2.53 kcal.mole^{-1}). These data are consistent with the special factors discussed above, which must be considered in the case of the copper complexes. In addition, with the tetradentate NTA ligand molecule and the known preference for a distorted octahedral configuration in its complexes, it is possible that the copper(II) ion can coordinate only three of the four donor atoms[119], causing the complex with one free $-CH_2COO_2^-$ to have a relatively large entropy [a less negative term I in Eqn. (3)]. It might be expected, however, that part of the effect may be lost in the tendency of such a group to coordinate water molecules [a less positive term II in Eqn. (3)].

The absence of complicating crystal-field effects makes the alkaline earth complexes of aminopolycarboxylic acid ligands particularly interesting for thermodynamic analysis. It is convenient to divide the ligand molecules into three groups: (i) those with the EDTA skeleton, including DCTA; (ii) those with an additional potential coordinating atom in the central chain (e.g. BATA, BSTA and DTPA); and (iii) those with two potential coordinating centres in the central chain (e.g. EGTA). The trends in the available thermodynamic functions for the alkaline-earth cations are illustrated in Fig 8. It is seen that in group (i), the greater stability of the DCTA complexes as compared with those of EDTA is entirely due to a much more favourable $\Delta S + S°$ (M^{2+}) for the former. This difference in entropy is able to outweigh the unfavourable enthalpy difference. The explanation lies in

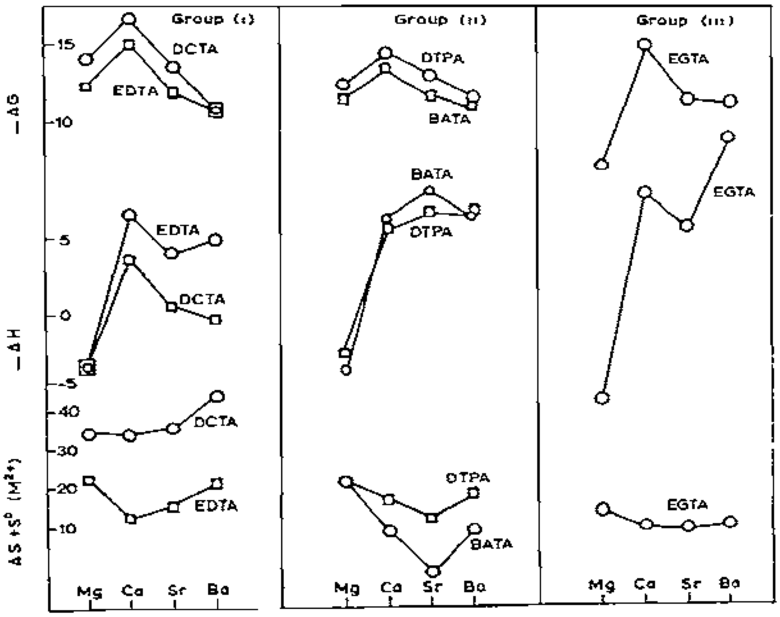


Fig. 8. Plots of the thermodynamic functions for the formation of alkaline earth amino carboxylate complexes. Group (i): EDTA, DCTA, group (ii). DTPA, BATA, group (iii): EGTA.

the fact that in DCTA, the two nitrogen atoms are restricted in their movement by the carbocyclic chain, and so term I in Eqn. (3) will be more positive than for EDTA In addition it has been suggested[114] that the relative rigidity of the carboxyl groups in DCTA as compared with those in EDTA results in a localisation of charge leading to a more effective orientation of water molecules in DCTA. $-\Delta S_h$ (DCTA) will be larger than $-\Delta S_h$ (EDTA) making term II in Eqn (3) more positive for DCTA The increased endothermicity accompanying the formation of DCTA complexes is a consequence of the steric hindrance imposed by the cyclohexyl ring[114]. The value of $\Delta G\,(\mathrm{MgL}^{2-}) - \Delta G\,(\mathrm{CaL}^{2-})$ is about the same for both EDTA and DCTA but the heat and entropy trends are quite different. In going from calcium to magnesium there is an appreciable increase in $\Delta S + S^\circ$ (M^{2+}) for EDTA as compared with that for DCTA, indicating a smaller positive contribution in term II (Eqn 3) for DCTA It is possible that MgDCTA is more hydrated than MgEDTA since there is considerable strain involved in completing the coordination of the rigid DCTA anion to the small magnesium ion. Some support for this suggestion is provided by the rather large drop in $-\Delta H$ in Fig 8 for the formation of MgEDTA

In the case of the group (ii) ligands for which thermodynamic data are presented in Fig. 8, it is seen that the DTPA complexes are, in general, more stable than those of BATA. The larger entropy changes for the formation of MBATA complexes is sufficient to overcome the more endothermic enthalpy changes obtained for the Ca^{2+} and Sr^{2+} complexes Not only will the larger multidentate DTPA molecule have more conformational freedom in its complex owing to a larger number of uncoordinated sites, but the higher charge as compared with BATA will result in a greater release of co-sphere solvent molecules accompanying association. The exception is seen to be in the case of the small Mg^{2+} ion which is probably incapable of coordinating with as many sites on the DTPA molecule as do the larger alkaline earth ions. The retention of charge in the resulting complex will result in a rather smaller entropy of formation for MgDTPA

In the group (iii) ligands, thermodynamic functions for the formation of EGTA complexes are shown in Fig 8. The association constant for the formation of MgEGTA is a factor of 10^8 smaller than that for calcium whereas for the EDTA complexes the difference is rather less than a factor of 10^3. It is seen that the values of $\Delta S + S^\circ$ (M^{2+}) for EGTA complexes are appreciably less than those for the corresponding EDTA complexes This difference may be caused by two factors: (i) the greater loss of configurational entropy of the larger EGTA molecule when it interacts with the metal ion, and (ii) the two carboxylate groups which remain free in the EGTA complexes and which will retain some solvent-ordering properties whilst not being able, through negative charge repulsion, to make full use of their mobility. $\Delta S + S^\circ$ (M^{2+}) Values for EGTA show little difference for the alkaline earth complexes, indicating similar structure for all the complexes in the series The results of NMR studies[14] lend support to this suggestion, and it ap-

TABLE 7

THERMODYNAMIC FUNCTIONS FOR THE ASSOCIATION OF COPPER WITH GLYCINE AND POLYGLYCINES (25°, I = 0.10M)[66,126]

Association reactions[a]	ΔG(*kcal mole*$^{-1}$)	ΔH(*kcal mole*$^{-1}$)	ΔS(*cal deg*$^{-1}$ *mole*$^{-1}$)
$Cu^{2+} + G^- \rightleftarrows CuG^+$	-11.71 ± 0.01	-6.76 ± 0.04^b	$+16.6 \pm 0.3$
$CuG^+ + G^- \rightleftarrows CuG_2$	-9.47 ± 0.02	-6.89 ± 0.1^b	$+8.7 \pm 0.4$
$Cu^{2+} + GG^- \rightleftarrows CuGG^+$	-7.58 ± 0.01	-6.1 ± 0.2	$+4.97 \pm 0.7$
$Cu^{2+} + GGG^- \rightleftarrows CuGGG^+$	-6.87 ± 0.01	-6.3 ± 0.2	$+1.9 \pm 1.0$
$Cu^{2+} + GGGG \rightleftarrows CuGGGG^+$	-7.00 ± 0.02	-6.0 ± 0.6	$+3.3 \pm 2.0$

[a] G^- = glycinate, GG^- = diglycinate, GGG^- = triglycinate, $GGGG^-$ = tetraglycinate anions [b] R M IZATT, J J CHRISTENSEN AND V. KOTHARI, *Inorg. Chem*, 3 (1964) 1565.

pears that both ether-oxygen atoms in the central chain are involved in the bonding to the metal ion. The smaller stability of the magnesium chelate is clearly the result of the more endothermal ΔH reflecting the increased potential energy involved in the interaction between the small Mg^{II} and the EGTA anion.

A number of studies have been made of the heats of formation of complexes of copper with amino acids[120]; the polyglycine complexes have also received considerable attention in view of their biological importance Dissociation of the peptide hydrogen atoms is facilitated in reactions which take place in the physiological range of pH. Although the structures of the complexes have been characterised in the solid state by X-ray diffraction methods[121], there has been considerable discussion as to the nature of the ligand atoms involved in coordination of the copper ion in solution[122,123,124,125]. There is little doubt that, with the elimination of the peptide hydrogen atoms at higher pH, the peptide nitrogen is coordinated to the metal ion. In the cationic complex, CuL^+, at lower pH, however. both peptide nitrogen and oxygen atom coordination have been proposed; the former by Kim and Martell[124,125] and the latter by Datta and Robin[122]. Calorimetric studies of these systems have been made over a range[66,126] of pH and thermodynamic data prior to ionization of the peptide hydrogen atoms are given in Table 7 together with those for the corresponding glycine complex. It can be seen that the substantial decrease in the stability of the polyglycine complexes $CuGG^+$, $CuGGG^+$ and $GuGGGG^+$ as compared with the monoglycinate, CuG^+ essentially an entropy effect. The exothermic enthalpies of formation are remarkably constant throughout, indicating that the polyglycine ligand molecules are bound in bidentate structures similar to that of glycine and not in the multichelated structures which have been proposed[125]. It is likely that the structures in solution resemble those in the solid state with the metal ion bound to the terminal NH_2 and the oxygen of the first peptide group[66,126]. In such structures, the carboxyl groups are unbound and the resulting charge separation will account for the very small ΔS values for all polyglycine complexes in Table 7 as compared with the value for the monoglycine complex.

(*v*) *Complexes of the rare earth metal ions*

With the availability of thermodynamic functions for the formation of rare earth complexes with a considerable number of ligand molecules, it is instructive to examine in more detail trends in the data and their relationships to the well-known "gadolinium break". If interaction of rare-earth ion with the ligand were purely electrostatic in nature, the strength of the M–L bonds would be expected to increase linearly with ionic potential. It has been shown, however, that instead of the expected uniform increase of association constant with decreasing ionic radius along the lanthanide series, a break occurs in the region of gadolinium. Moreover, this behaviour appears to be common for most of the ligands investigated from the simpler iminodiacetates[127], acetates, glycolates[128] and other monocarboxylates[128] to the more stable complexes formed with ligands such as NTA, EDTA, PDTA and DCTA[130]. In an attempt to explain these results, Wheelwright, Spedding and Schwarzenbach[131] suggested that a change occurred in the number of ligand atoms coordinated as the metal ion became smaller. For this interpretation

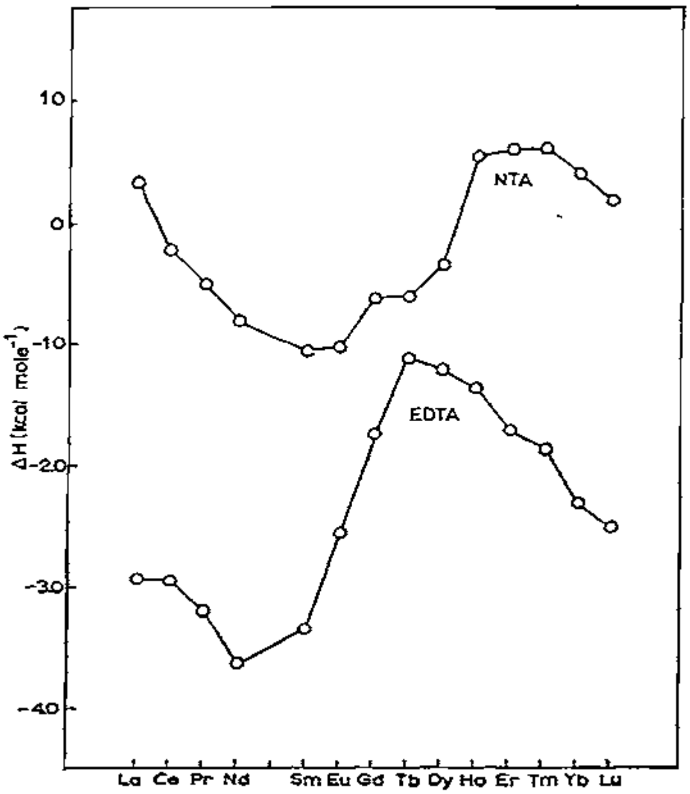


Fig. 9. Enthalpies of formation of some 1:1 rare-earth complexes plotted as a function of atomic number.

to be correct, however, the critical ion size at which the strain introduced into the chelate would be sufficient to change the number of atoms coordinated would have to be the same for a wide variety of coordinated ligand molecules of differing denticity. It would be unexpected if this were the case, and more recently attention has been focussed on possible changes in the hydration structure of the metal ions as the cause of the gadolinium break. Irving and Conesa[130] studied the rare earth complexes of propylenediaminetetraacetic acid (PDTA) which contains one more C-methyl group in the central methylene chain of the EDTA molecule. In spite of the fact that the resulting rare earth complexes are less strained than the corresponding EDTA complexes, the discontinuity in the measured K values still occurred at gadolinium. An excellent linear relationship between log K (MPDTA$^-$) and log K(MEDTA$^-$) constituted convincing evidence that the two ligands coordinate with all the rare earth ions through the same donor atoms, forming complexes very similar in their steric requirements. It was clear that the source of the gadolinium break could not be determined solely on the basis of free energy changes and, with the availability of a number of calorimetric enthalpy data, it is of

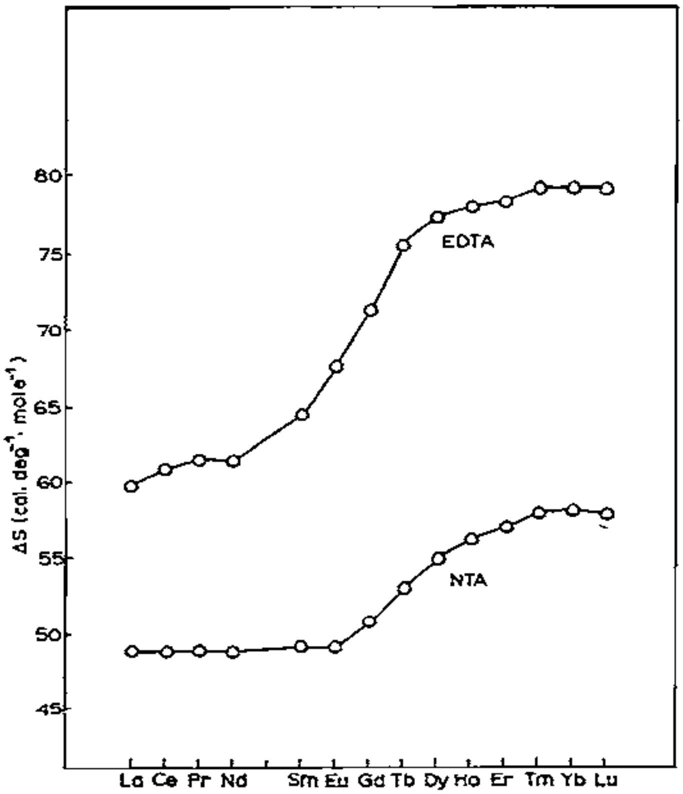


Fig. 10. Entropies of formation of some 1:1 rare-earth complexes plotted as a function of atomic number.

interest to enquire more closely into the reasons for such a discontinuity in the *K* values. In Fig. 9 thermodynamic functions for the formation of 1 : 1 NTA[132,133,134] and EDTA[131,135] complexes are plotted against atomic number. It is seen that the trends in ΔH values are the same for both ligands and similar results have been obtained with diglycolate and dipicolinate complexes[136]. Simple electrostatic theory would predict a linear relationship between ΔH and r^{-1} and it is therefore clear that other factors are involved in these association reactions.

Modification of the simple electrostatic model could be made in order to include the influence of possible ligand-field stabilisation on the 4*f* electrons[137]. These effects would be absent for La^{3+}, Gd^{3+} and Lu^{3+} and the beats of formation of complexes with these metal ions would be expected to vary monotonically. The enthalpy values in Fig. 9 do not conform with this requirement. If it is assumed that a smooth curve through the points for La^{3+}, Gd^{3+} and Lu^{3+} represents solely the effect of the lanthanide contraction on ΔH, then for both ligands, the complexes from Ce^{3+} to Eu^{3+} have added stabilisation whilst those from Tb^{3+}

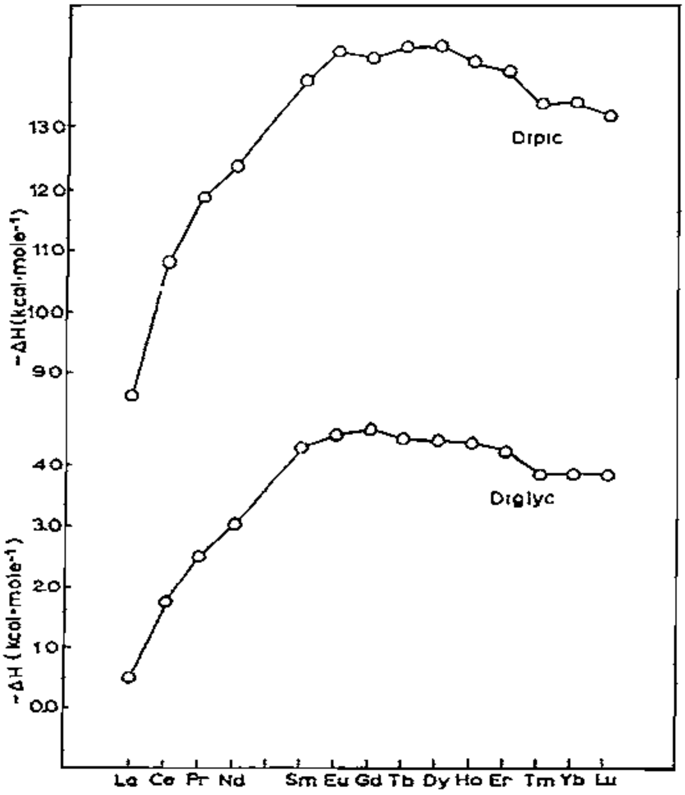


Fig 11 Enthalpies of formation of 1:3 rare-earth dipicolinate and diglycolate complexes plotted as a function of atomic number.

to Yb^{3+} are considerably destabilised. It is not possible to reconcile such a reversal of stabilisation with ligand-field theory.

It can be seen in Fig. 10 that the entropy changes for the formation of the rare earth complexes fall into two distinct groups each of approximately constant ΔS. The changes occur in the region Sm^{3+} to Tb^{3+} for EDTA and Gd^{3+} to Dy^{3+} for NTA and are accompanied by corresponding increases in endothermicity. This general pattern of behaviour for a number of complexes with different ligand molecules provides striking support for the suggested decrease in the effective hydration-number of the rare earth cation around the middle of the series[132]. The release of the additional water molecules would require energy reflected in the increased endothermicity and would lead to a greater entropy of association. Recently, thermodynamic studies have been made of the free lanthanide ions by measuring the heats of solution of the iodate salts[138]. It was found that the entropies of hydration fall into two groups with values of 76 ±1 cal.deg^{-1}.mole^{-1} for La^{3+} to Pr^{3+} and 91 ±1 cal.deg^{-1}.mole^{-1} in the range Dy^{3+} to Lu^{3+}. The difference is approximately the same as the difference between the two entropy plateaux in fig. 10. These results are again consistent with a change in the

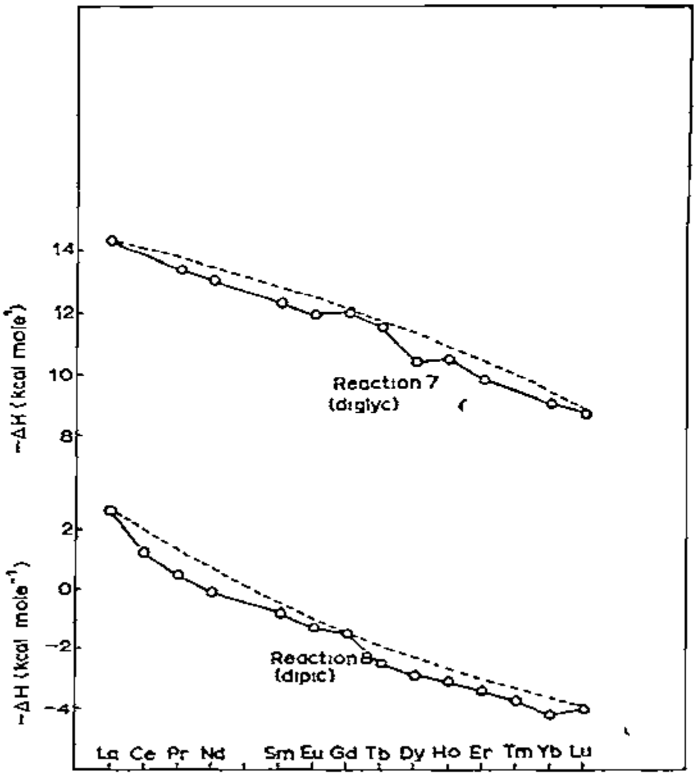


Fig 12 Enthalpy changes for reactions 7 and 8 as a function of atomic number.

size of the hydration sphere around the rare-earth ion being the principal factor reflected in the entropies of association. In the solid state, X-ray diffraction analyses have been made of three dimensional data from single crystals of a number of EDTA complexes by Hoard and his associates[139,140,141]. In lanthanum EDTA, the rare earth bonds three additional water molecules in the nine-coordinate complex ion $[La(OH_2)_3 \ EDTA]^-$. The replacement of La^{3+} by successively smaller rare earth ions will be accompanied by a gradual shrinkage of the complex and, at some stage, an additional water molecule will be ejected in the formation of the complex. If it is assumed that the complex species in solution have the same geometry as those in the crystal, the results provide additional support for the validity of the thermodynamic interpretations outlined above.

Staveley and his co-workers[142,143] have produced convincing evidence for two effects influencing the enthalpies of formation of these rare earth complexes; (i) the change in hydration noted above and (ii) the interaction of the crystal field of the ligands with the $4f$ electrons of the lanthanide ions. Measurements were made of the integral heats of solution of the lanthanide ethylsulphate and bromate salts. The results were used to calculate the heats of formation of the 1:3-diglycolate and 1:3-dipicolinate complexes starting with the rare earth as the solid ethylsulphate or bromate in the reactions

$$Ln(BrO_3)_3 9H_2O(c)+3L^{2-}(aq) \rightarrow LnL_3{}^{3-}(aq)+3BrO_3{}^-(aq)+9H_2O(aq) \qquad (7)$$

and

$$Ln(C_2H_5SO_4)_3 9H_2O(c)+3L^{2-}(aq) \rightarrow LnL_3{}^{3-}(a)+3C_2H_5SO_4{}^-(aq)+ \\ +9H_2O(aq) \qquad (8)$$

A recent crystal structure of $Nd(diglycolate)_3 6H_2O$ has shown the coordination number of the neodymium ion to be nine with all three coordination centres of the diglycolate ion bound to the rare earth ion[144]. By assuming similar structures for the 1:3-dipicolinate and 1:3-diglycolate complexes in solution, Staveley[143] suggested that thermodynamic functions for reactions (7) and (8) would reflect the behaviour of these systems when complications from varying degrees of hydration of both simple and complex ions had been eliminated. In Figs. 11 and 12 are plotted the experimental enthalpies of formation of these complexes both from the simple ions and from the solid ethylsulphate and bromate salts. The data for the latter systems show particularly interesting trends with increasing atomic number, and therefore decreasing ionic size of the lanthanide ion. Compared with the values of ΔH interpolated from a smooth curve through the points for lanthanum, gadolinium and lutecium, it is seen that the remaining complexes are stabilised by slightly more exothermic enthalpies of formation. The differences are in accord with the expected crystal stabilisation effects known to be considerably smaller for $4f$ electron systems as compared with the well-known effects for the $3d$ transition metals

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