Some Recent Studies in the Thermodynamics of Metal Complex Formation

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The purpose of this review is to present a selective account of the contributions of thermodynamics to our understanding of complex formation in transition-metal chemistry. It was remarked by Rossotti[1] in 1959, that 'interpretive speculation has outstripped the precision and quantity of data available, and considerable consolidation is required'. Since 1959, more precise measurements of a wide variety of systems have been reported and their interpretation has been facilitated by the application of crystal field theory. It is hoped that this review will stimulate further research, particularly into those areas which have been relatively neglected.

1 Experimental Methods

The thermodynamic qualities discussed in this review are enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) changes. The latter are calculated from the Gibbs–Helmholtz expression $\Delta G^\circ = -RT\ln K$. Ideally, thermodynamic quantities are calculated under standard conditions and the use of standard states is discussed later (Section 2B). Much early work was concerned only with the measurement of equilibrium constants although later workers also recorded the dependence of log K_n values on temperature in order to calculate approximate ΔH_n values. Experimental procedures have been discussed by Rossotti.[2] In recent years, direct calorimetry has been used to calculate both enthalpy changes and equilibrium constants.[3] A titration procedure is often adopted in conjunction with a least-squares analysis of the data by use of the stepwise constants K_n and ΔH_n as the independent variables. It is possible to assign an incorrect set of K_n, ΔH_n values under certain conditions but this problem can be overcome by the use of a wide range of metal and ligand concentrations.[4]

The calculation of ΔH values from plots of $\partial[(\Delta G/T)/\partial(1/T)]$ over a temperature interval. An exaggerated example of this effect was cited by Langford and Muir[5] who observed a maximum value in a plot of ln K *vs.* $1/T$ at 330 K for the reaction

$$[Co(NH_3)_5H_2O]_{aq}{}^{3+} + Cl_{aq}{}^{-} \rightleftharpoons [Co(NH_3)_5Cl]_{aq}{}^{2+} + H_2O$$

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[1] F. J. C. Rossotti in 'Modern Coordination Chemistry', ed. J. Lewis and R. G. Williams, Interscience, New York, 1960, p. 67.

[2] Ref. 1, p. 5.

[3] J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. A. Partridge, *J. Phys. Chem.*, 1966, **70**, 2003.

[4] S. Cabani and P. Gianni, *J. Chem. Soc.* (*A*), 1968, 547.

[5] C. H. Langford and W. R. Muir, *J. Phys. Chem.*, 1967, **71**, 2602.

This resulted in a change in sign of ΔH for the reaction, and was interpreted in terms of a separation of the outer-sphere and inner-sphere equilibria. Other apparently simple reactions may proceed by similar routes and the interpretation of their accompanying thermodynamic functions may not be straightforward.

2 Interpretation of Data

A. Enthalpy Changes.—The quantities normally calculated for metal complex formation usually refer to the process in solution so that solvation (usually hydration) energy and entropy changes may mask changes in metal–ligand bond energies and ligational entropy changes. As an illustration of the problems which can arise, consider the general reaction (1)

$$\mathrm{M(H_2O)}_{n,\mathrm{aq}}{}^{2+} + p\mathrm{L_{aq}}{}^{n-} \rightleftharpoons [\mathrm{M(H_2O)}_{n-p}\mathrm{L}_p]_{\mathrm{aq}}{}^{(2-pn)+} + p\mathrm{H_2O} \qquad (1)$$

where L is a unidentate ligand. The enthalpy change for the gas-phase reaction is related to that in the aqueous phase in Figure 1, from which equation (2) results (solvent water has been omitted for clarity).

$$\Delta H_{(\mathrm{g})} = \Delta H_{\mathrm{aq}} - \Delta H_h(\mathrm{M}^{2+}) - p\Delta \mathrm{H}_h(\mathrm{L}_{(\mathrm{g})}{}^{n-}) - \Delta \mathrm{H}_h(\mathrm{ML}_p)_{(\mathrm{g})} \qquad (2)$$

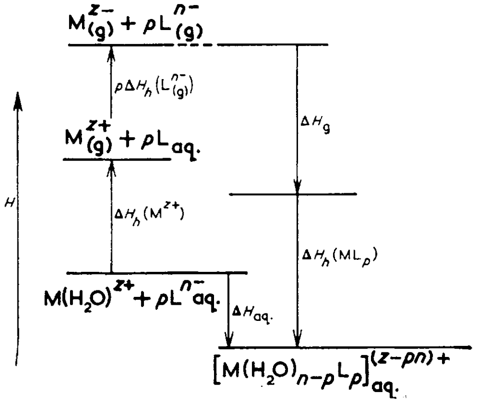

Figure 1 *Enthalpy changes in gaseous and aqueous phases*

Thus, in principle, $\Delta H_{(\mathrm{g})}$ could be calculated from equation (2) and the M–L bond energy would be $\Delta H_{(\mathrm{g})}/p$. In most practical experiments, the calculation of $\Delta H_{(\mathrm{g})}$ is difficult, if not impossible, owing to our lack of knowledge of ancillary data. In equation (2) ΔH_{aq} is known and values of $\Delta H_h(\mathrm{M}^{2+})$ are known for most of the transition metals.[6] $\Delta H_h(\mathrm{L}_{(\mathrm{g})}{}^{n-})$ Values are known for a few ligands but $\Delta H_h(\mathrm{ML}_p)_{(\mathrm{g})}$ is frequently impossible to measure owing to the non-existence of most metal complexes in the gas phase. Similar difficulties exist when one or more of the reactants or products is a solid since, in many cases, sublimation enthalpies can not be evaluated for metal complexes. An example of this problem has been given by Beech and Mortimer[7] who reported

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[6] P. George and D. S. McClune, *Progr. Inorg. Chem.*, 1959, **1**, 428.

[7] G. Beech, C. T. Mortimer, and E. G. Tyler, *J. Chem. Soc.* (*A*), 1967, 925.

enthalpy changes for the decompositions of a series of solid metal complexes. It was not possible to calculate gas-phase enthalpy changes for the decompositions.

In the absence of the necessary ancillary data, it is usually possible to make a series of relative measurements in which either the metal or the ligand differs. In this way, the dependence of, for example, ΔH_{aq} on crystal field stabilisation energy or metal–ligand π-bonding can be inferred. In the first example, ΔH_{aq} should vary periodically with atomic number,[6] and in the second example, ΔH_{aq} should increase for ligands known to be better π-donors or -acceptors.

B. Free Energy and Entropy Changes.—Enthalpy changes reflect changes in intramolecular bonding forces and environmental effects due to the presence of a solvent. The effect of the latter can be made minimal, or at least constant, for a series of measurements by extrapolation to infinitely dilute solution. This extrapolation procedure results in small changes in ΔH for most systems.[8]

In addition to environmental effects, there is also a cratic effect, dependent on the change in the number of particles on complexation. This is popularly referred to as the 'Chelate Effect' and this term describes the apparently enhanced stability of complexes containing chelate rings when compared to the analogous complexes of unidentate ligands. For a reaction of the type (3), where Y is a chelating ligand, Martell and Calvin[9] have stated that a positive entropy change

$$ML_p^{n+} + qY^{m-} \rightleftharpoons [ML_{p-2q}Y_q]^{(n-qm)+} + 2qL \qquad (3)$$

results due to an increase in the number of particles. This positive entropy change would then appear to give a more negative ΔG and, from $\Delta G = -RT\ln K$, a more positive equilibrium constant. The association of positive entropy changes with increased disorder if often incorrect, as shown by McGlashan,[10] and Adamson[11] has demonstrated that the 'chelate effect' is due primarily to an arbitrary asymmetry in standard states for the solute and solvent. The usual choices are unit molar and unit mole fraction, respectively, and to change from the first to the second, the following corrections are required:

$$\Delta H^{o\prime} = \Delta H^{o}$$
$$\Delta G^{o\prime} = \Delta G^{o} + \Delta n\, RT\ln 55{\cdot}5$$
$$\Delta S^{o\prime} = \Delta S^{o} - \Delta n\, R\ln 55{\cdot}5$$

(The primed quantities refer to the unit mole fraction standard state.)

When these corrections have been made, the 'chelate effect' ceases to be of any special importance. The average values of $\Delta S^{o\prime}$ are small and scattered about zero.[11] The non-existence of the 'chelate effect' has also been demonstrated by Agterdenbos,[12] who stated that a direct comparison of equilibrium constants

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[8] J. J. Christensen and R. M. Izatt, in 'Physical Methods in Advanced Inorganic Chemistry', ed. H. A. O. Hill and P. Day, Interscience, New York, 1968, p. 551.

[9] A. E. Martell and M. Calvin, 'Chemistry of the Metal Chelate Compounds', Prentice-Hall, New Jersey, 1952, p. 150.

[10] M. L. McGlashan, *J. Chem. Educ.*, 1966, **43**, 226.

[11] A. W. Adamson, *J. Amer. Chem. Soc.*, 1954, **76**, 1578.

[12] J. Agterdenbos, *J. Chem. Educ.*, 1968, **45**, 230.

was not possible owing to a dimensional asymmetry in these constants. Thus, for the reactions (4) and (5), where γ is a bidentate chelate ligand, the dimensions

$$M_{aq}^{n+} + 3\gamma_{aq}^{m-} \rightleftharpoons [M\gamma_3]_{aq}^{(n-3m)+} + 6H_2O \quad (4)$$

$$M_{aq}^{n+} + 6L_{aq} \rightleftharpoons [ML_6]_{aq}^{(n-6p)+} + 6H_2O \quad (5)$$

of the equilibrium constants K_4 and K_5 are [$mol^3\ l^{-3}$] and [$mol^0\ l^0$]. If the concentration units are changed to [$mol\ ml^{-1}$], the equilibrium constants become $10^{-9}\ K_4$ and K_5 respectively and this change may be sufficient to reverse the relative order.

With the exclusion of cratic terms, certain general observations may be made on entropy and free energy (*i.e.* equilibrium constant) measurements in co-ordination chemistry:

(1) In aqueous solution, there is usually a positive entropy charge when charged ligands co-ordinate. This has been attributed to the release of solvent molecules during co-ordination. The co-ordination of uncharged ligands results in smaller entropy charges.

(2) In the solid state, there is always a positive entropy effect since $T\Delta S$ must exceed ΔH before thermal decomposition can occur.

(3) Equilibrium constants usually decrease with the stepwise addition of each ligand, in the absence of specific stereochemical effects such as a preferred, low co-ordination number or a change of ground state of the actual metal ion.[13]

C. Inner Orbital Splitting.—Many changes in the thermodynamic properties of metal complexes can be interpreted by crystal-field theory. The effects of inner orbital splitting are well-known to most chemists and the reasons for such splittings have been dealt with in numerous texts.[14] Certain points relevant to the subject under review are noteworthy, however, and need to be emphasised.

(1) The majority of the systems studied to date involve the *d*-block transition elements in a ligand field of approximately cubic symmetry. The ground state terms are either *D* or *F*.

(2) The splitting of these originally degenerate levels is at least an order of magnitude less than the overall heat of formation of a co-ordination compound.[15] Therefore, crystal field effects are small and secondary in nature and can only be detected as perturbations added to the otherwise constant or smoothly varying thermodynamic functions.

(3) Ligand-field splittings are larger in second- and third-row transition-metal compounds and exceed the energies of spin-pairing. Therefore, the stabilisation in these compounds should be more readily discernible.

D. π-Bonding and Other Effects.—It is often tempting to propose π-bonding effects to explain the magnitudes of thermodynamic functions when all else

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[13] Ref. 1, p. 38.

[14] See, for example, F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Interscience, New York, 1966, p. 662.

[15] B. N. Figgis, 'Introduction to Ligand Fields', Interscience, New York, 1966, p. 75.

has failed. It is important, however, that this procedure should not be adopted unless there is adequate justification. For example, the enthalpy changes ($-\Delta H$) for the reaction

$Hg_{aq}^{2+} + 2X_{aq}^{-} \rightleftharpoons HgX_{2aq}$; X = Cl, Br, I

are in the order I > Br > Cl from which one might infer that π-bonding strengthens the mercury–halogen bond in the order given. The heats of the gas-phase reaction $Hg_{(g)}^{2+} + 2X_{(g)}^{-} \rightleftharpoons HgX_{2(g)}$ (X = Cl, Br, or I) are in the order I < Br < Cl and it has been shown[16] that this reversal is due to the variation in halide ion hydration enthalpies which is in the order Cl > Br > I.

Other effects, such as the basicity of donor atoms and steric requirements will be discussed in subsequent sections of this review. It is most convenient to discuss the behaviour of separate groups of compounds according to the type of ligand on the central metal ion.

3 Complexes of 3d-Transition Series

A. Complexes of Heterocyclic Bases.—Complexes of pyridine and its derivatives have received a great amount of study and this is due in part to their ease of preparation and their relatively uncomplicated reactions. Spectroscopic[17] and magnetic[18] data have established that the complexes are of three main types:

(*i*) Discrete, octahedral ML_4X_2 (L = pyridine, or substituted pyridine, X = halogen or pseudohalogen). The X groups are axial.

(*ii*) Discrete, tetrahedral ML_2X_2.

(*iii*) Polymeric, octahedral ML_2X_2 with bridging X groups.

Groups (*i*) and (*ii*) co-exist in solution and Nelson and his co-workers[19] have studied the configuration equilibria (6) present both in solution and in the solid state:

$$ML_4X_{2(oct)} \rightleftharpoons ML_2X_{2(tet)} + 2L \qquad (6)$$

L was pyridine or its alkyl-substituted analogues. It was found that the heat of reaction (6) could not be correlated with the basicity of L but was dependent on the position of the alkyl side-chain in L. Thus, for the systems M = Ni, X = I, L = pyridine or β-picoline in chloroform solution it was found that the enthalpy changes were +23·8 and +21·7 kcal/mol^{-1} respectively. Since the 3-methyl substituent directs charge on to the 2, 4, and 6 positions of the pyridine ring, it was inferred that metal to ligand π-bonding must exist in these complexes and was being inhibited by the presence of the 3-substituent. Also, the relative value of the equilibrium constant for reaction (6), with L = 3-methylpyridine, compared to L = pyridine, was found to depend markedly on X and it was possible

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[16] Ref. 8, p. 593.

[17] J. R. Allan, D. H. Brown, R. M. Nuttall, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1895.

[18] J. de O. Cabral, H. C. A. King, S. M. Nelson, T. M. Shepherd, and E. Körös, *J. Chem. Soc.* (*A*), 1966, 1349.

[19] (*a*) S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, 1965, 3284; H. C. A. King, E. Körös and S. M. Nelson, *J. Chem. Soc.*, 1963, 5449; 1964, 4832.

to arrange X in order of π-bond (L to M) promotion:

$NCS \ll Cl < Br < I$

Nelson and his co-workers also calculated the entropy changes for these reactions and they were found to be more negative in all cases than expected simply from the loss in translational entropy. There was not complete loss of rotational entropy and the results implied a degree of double bonding. The entropy change was also dependent on the nature of X. For example, with M = Co, L = 4-methylpyridine, X = Cl or NCS, ΔS°_{293} was calculated to be 48·8 and 34·2 cal deg^{-1} mol^{-1} respectively.

Irving and da Silva[20] have calculated the equilibrium constants for the reactions

$$Ag^+ + 2HL^+ \rightleftharpoons AgL_2^+ + 2H^+ \; ; \; L = \text{pyridine or substituted pyridine.}$$

By choosing as a reference value the equilibrium constant for L = pyridine, a stabilisation factor, $S_f = \log K_L - \log K_{py}$, should reflect changes in π-bond formation relative to σ-bonding. Irving and da Silva found S_f to be a linear function of the Hammett σ-factor. Since increasing values of σ indicate greater electron-withdrawing character of the substituent,[21] the increase in stability can not be due to σ-bonding and may be due to π-bonding. The results of Irving and da Silva indicate the 4-methylpyridine forms stronger π-bonds than the 3-methyl analogue which is contrary to Nelson's results[19] which indicate that 4-methylpyridine forms the stronger π-bonds to nickel.

Mortimer and his co-workers[22] have used differential enthalpimetric analysis to study the thermal decompositions of complexes of the type ML_nX_2 (M = first transition-series metal, L = quinoline, pyridine, or a methylpyridine, X = Cl, Br, or I). For reaction (6) similar conclusions to those of Nelson[19] were reached regarding the relative extents of σ- and π-bonding. In addition, the compounds ML_2X_2 were found to decompose, in stages, to MX_2. With suitable thermochemical cycles,[23] it was possible to calculate the variation in the gas-phase enthalpy changes of these decompositions as a function of atomic number. It was evident that the enthalpy changes reflected changes in crystal-field stabilisation energies (CFSE) and for Ni py_2Cl_2, 10 Dq was estimated to be -8200 cm^{-1} which compares well with the spectroscopic value[24] of -8500 cm^{-1}.

Libus and Uruska[25] have calculated equilibrium constants for reaction (6) in a pyridine–chlorobenzene mixture. A similar periodic dependence of these constants on atomic number was detected.

As stated previously, crystal field effects are secondary in nature and this has

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[20] H. Irving and J. J. R. F. da Silva, *Proc. Chem. Soc.*, 1962, 250.

[21] H. H. Jaffe and G. O. Doak, *J. Amer. Chem. Soc.*, 1955, **77**, 4441.

[22] (*a*) G. Beech, S. J. Ashcroft, and C. T. Mortimer, *J. Chem. Soc.* (*A*), 1967, 929; (*b*) G. Beech, C. T. Mortimer, and E. G. Tyler, *J. Chem. Soc.* (*A*), 1967, 1111; G. Beech, C. T. Mortimer, and E. G. Tyler, *J. Chem. Soc.* (*A*), 1969, 512.

[23] G. Beech, Ph.D. Thesis, University of Keele, 1967, p. 84.

[24] A. B. P. Lever, S. M. Nelson, and T. M. Shepherd, *Inorg. Chem.*, 1965, **4**, 810.

[25] W. Libus and I. Uruska, *Inorg. Chem.*, 1966, **5**, 256.

been proven by Katzin[26] who studied reaction (6) spectroscopically. Katzin found that the change in CFSE was *ca.* $-2{\cdot}1$ kcal mol^{-1} compared with a change in electron repulsion energy of $+7{\cdot}7$ kcal mol^{-1}. Also, it was calculated that the average bond strength in the tetrahedral species was greater than that in the octahedral species by 17 kcal mol^{-1}. This gives a total bond strengthening of some 68 kcal mol^{-1} which is very much greater than any CFSE change yet detected.

B. Metal Ammines and Related Compounds.—*Simple ammines.* These provide the most thoroughly investigated class of compounds.[27] Of the early investigators, Yatsimirskii[28] was the most active and it is impossible to summarise, in a part of this review, more than a small fraction of his contributions. Direct calorimetry was used in many instances by Yatsimirskii and his co-workers and stoicheiometric reactions such as (7) were among the first to be studied[29] where Y or X = Cl, Br, I, NO_2, NO_3. Stepwise reactions were also studied,

$$2[Co(NH_3)_5Y]X_2 + 3Na_2S = Co_2S_3 + 10NH_3 + 4NaX + 4NaY \qquad (7)$$

one example being the stepwise formation of copper(II) and nickel(II) ammines.[30] For these systems, it was found that the average enthalpy change, per mole of ligand, was greater for the copper complex and that the entropy changes decreased with each successive addition. This observation is compatible with decreased solvent ordering with increased shielding and charge neutralisation brought about by addition of ligand.

More recently, the stepwise enthalpy changes accompanying the decomposition of solid metal ammines have been measured by Mortimer and Beech[31] and Sherriff and Galwey.[32] Complexes containing the cation $[Ni(NH_3)_6]^{2+}$ decompose to the anhydrous metal halide in two or more stages,[33] the first product being the diammine complex. The enthalpy changes for the reactions (8) and (9) are shown in Table 1.

Table 1 *Heats of reaction* (8) *and* (9) *for the compounds* $Ni(NH_3)_nX_2$

X	ΔH_8(kcal mol^{-1})	ΔH_9(kcal mol^{-1})
ClO_4^-	$16{\cdot}9 \pm 1{\cdot}5$[59]	
Cl^-	$53{\cdot}9 \pm 0{\cdot}5$[58]	$24{\cdot}8 \pm 0{\cdot}5$[58]
Br^-	$55{\cdot}4 \pm 0{\cdot}3$[58]	$37{\cdot}6 \pm 0{\cdot}9$[58]

$$Ni(NH_3)_6X_{2(cryst)} = Ni(NH_3)_2X_{2(cryst)} + 4NH_{3(g)} \qquad (8)$$

$$Ni(NH_3)_2X_{2(cryst)} = NiX_{2(cryst)} + 2NH_{3(g)} \qquad (9)$$

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[26] L. I. Katzin, *J. Chem. Phys.*, 1961, **35**, 467.

[27] W. W. Wendlant and J. P. Smith, 'The Thermal Properties of Transition Metal Complexes', Elsevier, New York, 1967, p. 2.

[28] K. B. Yatsimirskii and V. P. Vasilev, 'Instability Constants of Complex Complex Compounds', Pergamon, Oxford, 1960.

[29] K. B. Yatsimirskii and L. L. Panova, *Zhur. obshchei Khim.*, 1948, **18**, 2051.

[30] K. B. Yatsimirskii and P. M. Miljukov, *Zhur. fiz. Khim.*, 1952, **31**, 842.

[31] C. T. Mortimer and G. Beech, unpublished observations.

[32] R. A. F. Sherriff and A. K. Galwey, *J. Chem. Soc.* (*A*), 1967, 1705.

[33] T. D. George and W. W. Wendlandt, *J. Inorg. Nuclear Chem.*, 1963, **25**, 395.

The anion appears to have a profound effect on the relative magnitudes of ΔH_8. It is probable that for X = Cl and Br a covalently bonded diammine is formed whereas the perchlorate ion remains un-co-ordinated.

C. Complexes of Substituted Amines.—Saturated organic amines, unlike the unsaturated analogues, do not have suitable π-orbitals to accept back-co-ordinated charge from a metal ion and it would be expected that there would be a direct correlation between the p*K* of the ligands and the thermodynamic stability of their metal complexes. Such a linear relationship has been observed by Bruehlman and Verhoek[34] for the complexes of a series of primary, secondary, and tertiary amines.

In order to assess the extent, if any, of π-bond formation between a metal ion and unsaturated ligands, a comparison with the complexes of the corresponding saturated ligands was proposed by Held and Goldberg.[35] Any gross difference, after allowing for σ-bonding (basicity) differences could be correctly attributed to π-bonding. The ligands chosen were 2-pipecolylamine and 2-(2-aminoethyl)piperidine and their unsaturated analogues. Differing base strengths were accounted for by calculating the ratio $\Delta G_i{}^\circ/[(\Delta G_{\mathrm{H}}{}^\circ)_1 + (\Delta G_{\mathrm{H}}{}^\circ)_2]$ where $\Delta G_{\mathrm{H}}{}^\circ$ refers to the free energy of hydration of each nitrogen atom and $\Delta G_i{}^\circ$ is the free energy of the complexation reaction for the addition of the *i*th ligand. Some representative values of $\Delta G_i/[(\Delta G_{\mathrm{H}}{}^\circ)_1 + (\Delta G_{\mathrm{H}}{}^\circ)_2]$ are shown in Table 2. Although the steric requirements are not identical for the saturated and unsaturated ligands, the ratios are suggestive of a degree of stabilisation which may be due to π-bonding.

Table 2 *Values of the ratio* $\Delta Gi/[(\Delta G_{\mathrm{H}}{}^\circ)_1 + (\Delta G_{\mathrm{H}}{}^\circ)_2]$ *for the formation of* $\mathrm{ML_2}^{2+}$

L	*i*	M = Cu	M = Ni
2-Pipecolylamine	1	0·62	0·40
	2	0·51	0·32
2-Picolylamine	1	0·81	0·61
	2	0·67	0·52
2-(2-Aminoethyl)piperidine	1	0·47	0·29
	2	0·32	0·24
2-(2-Aminoethyl)pyridine)	1	0·56	0·38
	2		0·24

Similar comparisons should be possible between the complexes of pyridine and aniline and their substituted derivatives. Ablov and his co-workers[36] have used heats of solution data to calculate the enthalpy changes for reaction (10),

$$\mathrm{CoA_2X_{2(cryst)}} = \mathrm{CoX_{2(cryst)}} + 2\mathrm{A_{(g)}} \qquad (10)$$

where A is aniline or a substituted aniline. Enthalpy changes for reaction (10) were also reported by Beech *et al.*[37] who used differential scanning calorimetry

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[34] R. J. Bruehlman and F. H. Verhoek, *J. Amer. Chem. Soc.*, 1948, **70,** 1401.

[35] R. P. Held and D. E. Goldburg, *Inorg. Chem.*, 1963, **2,** 585.

[36] A. V. Ablov, Ts. B. Konunova-Frid, and V. A. Palkin, *Russ. J. Inorg. Chem.*, 1960, **5,** 747.

[37] G. Beech, G. Marr, and B. W. Rockett, *J. Chem. Soc.* (*A*), 1969, 629.

Table 3 *Heats of decomposition of metal-aniline complexes* MA_2X_2[a]

Ligand A	Ligand X	ΔH(kcal mol^{-1}) Beech *et al.*[37]	ΔH(kcal mol^{-1}) Ablov *et al.*[36]
An	Cl	35·5 ± 0·5	43·2
o-ClAn	Cl	30·8 ± 0·6	
m-ClAn	Cl	37·7 ± 0·7	45·4
p-ClAn	Cl	39·1 ± 0·7	45·7
An	Br	39·2 ± 0·5	44·7
o-ClAn	Br	38·0 ± 0·8	
m-ClAn	Br	40·5 ± 0·5	46·6
p-ClAn	Br	38·0 ± 0·5	46·6

[a] An = Aniline; *o*-ClAn = *o*-chloroaniline; *m*-ClAn = *m*-chloroaniline; *p*-ClAn = *p*-chloroaniline.

and a summary of the results is presented in Table 3. The disparity between the two sets of data is due in part to the different temperatures used in the two studies, although approximate heat capacity corrections do not appear to be of sufficient magnitude. Ablov concluded that the data indicated appreciable covalency in the Co – N bond since there was little variation in ΔH. Beech *et al.*[37] performed a more detailed analysis and attempted to correlate ΔH with the spectroscopically determined $10Dq$ and B parameters of the complexes. This was not entirely satisfactory and further work remains to be done.

The heats of decomposition of the aniline complexes are higher than those of the analogous pyridine complexes although the pK_a values[38] indicate that pyridine is the stronger base. The differences are small, however, and may well be eliminated in the gas phase.

D. Chelate Complexes of the *d*-Block Transition Elements.—Many chelate complexes are of analytical importance and this, in part, has been responsible for many studies of their thermodynamic properties. A wide variety of chelating ligands have been studied including bidentate ligands, such as acetylacetone, and the more complex polydentate ligands, such as the polyaminocarboxylates.

The acetylacetonates can exist as stable solids and are, therefore, amenable to combustion studies. Also, at elevated temperatures, they possess appreciable vapour pressures which permit measurement of sublimation enthalpies. Wood and Jones[39] have measured the heats of combustion of the compounds M $\text{acac}_{3(\text{cryst})}$ (M = 3*d*-transition element; acac = 2,4-pentanedione). With a knowledge of the sublimation enthalpies and ancillary data, these workers were able to calculate the enthalpy changes for the following processes:

$$M(C_5H_7O_2)_{3\,(g)} \rightarrow M_{(g)} + 3\,C_5H_7O_{2\,(g)}$$

$$M(C_5H_7O_2)_{3\,(g)} \rightarrow M_{(g)}^{3+} + 3\,C_5H_7O_{2\,(g)}$$

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[38] A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 1964, 3591.

[39] J. L. Wood and M. M. Jones, *Inorg. Chem.*, 1964, **3**, 1553.

The homolytic and heterolytic bond energies, ΔH_{hom} and ΔH_{het} respectively, are related to each other by equation (11).

$$6\Delta H_{\text{hom}} = 6\Delta H_{\text{het}} - I_3 + 3E_{\text{L}} \qquad (11)$$

where I_3 is the energy required to produce the triply ionised metal ion and E_{L} is the ligand electron affinity. The homolytic bond energies did not appear to reflect changes in CFSE as markedly as the heterolytic bond energies, the variation of which is shown in Figure 2. The irregular variation in the homolytic bond energies suggests that there may be appreciable (and variable) amounts of covalency in the gaseous molecules. The deviations of the heterolytic bond energies from the interpolated base line gave approximate values of $10Dq$,[39] which were, mostly, similar to the spectroscopic values.[40]

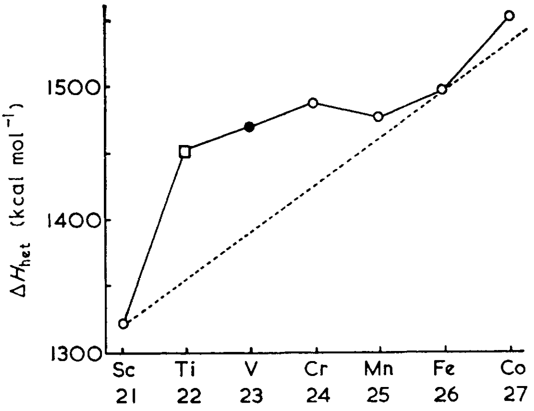

Figure 2 *Heterolytic bond energies of some acetylacetonates*
(Reproduced by permission from *Inorg. Chem.*, 1964, **3**, 1553.)

The apparent nature of the chelate effect has been discussed previously and it was shown that the redefined values $\Delta G^{o\prime}$ and $\Delta S^{o\prime}$, referring to unit mole function, were preferred to the unit-molarity scales. These quantities are better starting points from which to consider specific effects such as relief of ring strain and stable conformations. Since $\Delta G^{o\prime}$ is dependent on ΔH^{o} inductive effects present in the chelate but absent in the non-chelate ligand may affect $\Delta G^{o\prime}$. Thus, Spike and Parry[41] found the heat of formation of $[\text{Cu en}_2]_{\text{aq}}^{2+}$ (en = ethylenediamine) from $\text{Cu}_{\text{aq}}^{2+}$ and ethylenediamine to be greater than that of $[\text{Cu(NH}_3)_4]^{2+}$ by 4·8 kcal mol^{-1}. $\Delta G^{o\prime}$ for the reaction $\text{Cu(NH}_3)_4{}^{2+}{}_{(\text{aq})} + 2\,\text{en}_{(\text{aq})} \rightleftharpoons [\text{Cu en}_2]_{(\text{aq})}{}^{2+} + 4\text{NH}_{3(\text{aq})}$ is 5·7 kcal mol^{-1} and is, therefore, almost entirely accounted for by the difference in enthalpy changes. A similar conclusion was reached by Yatsimirskii[42] in studies of the complexes $[\text{M en}_3]\text{X}_2$ and $[\text{M(NH}_3)_6\text{X}_2$

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[40] T. S. Piper and R. L. Carlin, *Inorg. Chem.*, 1963, **2**, 260.
[41] C. G. Spike and R. W. Parry, *J. Amer. Chem. Soc.*, 1953, 3770.
[42] K. B. Yatsimirskii and A. A. Astasheva, *Zhur. obschei. Khim.*, 1950, **20**, 2139.

(M = Cd or Ni; X = Cl or Br). In each case, the heat of binding of 3 en was found to be greater than that of six ammonia molecules.

A specific structural effect which is well-established in the thermochemistry of chelate complexes is the enhanced stability of five-membered compared to six-membered chelate rings. An interesting example of this effect has been given by Nancollas and his co-workers[43] who calculated thermodynamic functions for the formation of oxalate and malonate complexes of transition metal ions. The quantity $-\Delta G$ was found to be consistently lower for the malonates, in which a six-membered ring is present. There was little difference in the entropy changes so that the dependence of ΔG on ring size appears to have its origin purely in enthalpy effects. The enthalpy effect may, in this case, be due to increased σ-bonding ability of the oxalate ion since oxalic acid is the stronger of the two acids, as judged from pK_a values.[43]

The complexes of many nitrogen-containing chelate ligands, such as 1,1′-dipyridyl and 1,10-phenanthroline, have received great attention. The stepwise reaction of 2,2′-dipyridyl (dipy) with iron(II) was studied by Baxendale and George.[44] The sequence of reactions was as follows (equilibrium constants are at 35°C):

$$\mathrm{Fe^{2+} + dipy \rightleftharpoons Fe\,dipy^{2+}}\ ;\ K_1 = 1{\cdot}6 \times 10^4\ \mathrm{mol^{-1}\,l^{-1}}$$
$$\mathrm{Fe\,dipy^{2+} + dipy \rightleftharpoons Fe\,dipy_2{}^{2+}}\ ;\ K_2 < 10^5\ \mathrm{mol^{-1}\,l^{-1}}$$
$$\mathrm{Fe\,dipy_2{}^{2+} + dipy \rightleftharpoons Fe\,dipy_6{}^{2+}}\ ;\ K_3 > 2 \times 10^7\ \mathrm{mol^{-1}\,l^{-1}}$$

The order of stepwise equilibrium constants is normally $K_1 > K_2 > K_3$ and the reversal in order for the iron(II)–dipyridyl system is thought to be related to a change in spin-state of iron(II)[45] which results in an increasing stabilisation of the more substituted species. Baxendale and George[44] also studied the analogous reaction of iron(III) with 2,2′-dipyridyl which had an overall equilibrium constant of $1{\cdot}6 \times 10^{12}\ \mathrm{mol^{-3}\,l^{-3}}$. The smaller value, compared with that obtained for the iron(II) complex, is not unexpected since no stabilisation due to change in spin-state is anticipated.

The more usual sequence of stability constants is encountered in the copper(II)–2,2′-dipyridyl system.[46] In this reaction, in aqueous solution, the intermediate, $\mathrm{Cu\,dipy_2(H_2O)_2{}^{2+}}$, is in the *cis*-, rather than the expected *trans*-form.[47] However, this unusual aspect of the stereochemistry of copper(II) is not unique. For example, the conversion of aquotetra-amminecopper(II) to aquopenta-amminecopper(II) is accompanied by a decrease in the apparent crystal field splitting.[48] This also may be a consequence of some rather unusual stereochemical requirements.

The equilibria, in aqueous solution, between a divalent transition metal ion and 1,10-phenanthroline have been extensively investigated. Dale and Banks[49]

[43] V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, 1961, 4367.

[44] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, 1950, **46**, 55.

[45] Ref. 1, p. 38.

[46] S. Cabani, G. Moretti, and E. Scrocco, *J. Chem. Soc.*, 1962, 88.

[47] L. O. Morgan, J. Murphy, and P. F. Cox, *J. Amer. Chem. Soc.*, 1959, **81**, 5043.

[48] J. Bjerrum, C. J. Ballhausen, and C. K. Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1275.

[49] J. M. Dale and C. V. Banks, *Inorg. Chem.*, 1963, **2**, 591.

have summarised much of the data concerning the equilibrium constants of reactions (12), (13), and (14) where M is Ag, Mn, Cu, Zn, or Cd, *o*-phen is

$$\mathrm{M_{(aq)}}^{n+} + o\text{-phen} \rightleftharpoons \mathrm{M}(o\text{-phen})_{\mathrm{(aq)}}^{n+} \qquad (12)$$

$$\mathrm{M}(o\text{-phen})_{\mathrm{(aq)}}^{n+} + o\text{-phen} \rightleftharpoons \mathrm{M}(o\text{-phen})_{2\mathrm{(aq)}}^{n+} \qquad (13)$$

$$\mathrm{M}(o\text{-phen})_{2\mathrm{(aq)}}^{n+} + o\text{-phen} \rightleftharpoons \mathrm{M}(o\text{-phen})_{3\mathrm{(aq)}}^{n+} \qquad (14)$$

1,10-phenanthroline and $n = 1$ (Ag) or 2 (Mn, Cu, Zn, or Cd). In most cases the order of the equilibrium constants was found to be $K_1 > K_2 > K_3$ except for M = Ag, for which K_3 was not recorded and K_2 was greater than K_1. This reversal in K_1 and K_2 implies that the substitution sequence is different for $\mathrm{Ag^+}$ than for the other metal ions. The tendency to linear co-ordination, frequently observed in silver complexes,[50] may require 1,10-phenanthroline to be a unidentate ligand and the co-ordination of two of these ligands could result in a linear N–Ag–N structure of enhanced stability, due to an extended π-bonding effect. Alternatively, 2-co-ordination could be preserved by bridging or polymerisation as observed for the ethylenediamine complexes of silver, in the solid state.[51] The precise nature of the species in solution is, as yet, unknown and this example typifies one of the major difficulties in solution thermochemistry, the inadequacy of our knowledge of solvated species. Complexes of a number of substituted phenanthrolines have been studied, including those of 5-$\mathrm{NO_2}$-,[52] 5-methyl-, and 5,6-dimethyl-1,10-phenanthroline.[53] A normal sequence of stability constants for the iron(II) complexes of 5,6-dimethyl-1,10-phenanthroline has been reported[53] which may be compared with the anomalous sequence reported for the iron(II) complexes of the unsubstituted ligand. It is difficult to explain these results as being due to lengthening of bonds by steric repulsion. In more extensive studies Lahiri and Aditya[52] found that the enthalpy changes for protonation of the methyl-substituted 1,10-phenanthrolines were greater than those of the parent compound. If σ-bonding alone were involved in the co-ordination of these ligands, it would be expected that the enthalpy changes for these reactions would also be greater in the case of the substituted ligands. The results of Lahiri and Aditya, for the iron(II) complexes, however, suggest that the more negative ΔG is due to a more positive ΔS. The 5-methyl and 5,6-dimethyl substituents direct charge into the 1,10-positions and this will prevent back π-donation to the ligand, thus nullifying any increase in σ-bonding. The increased entropy effect is doubtless due to increased solvent ordering by the substituted ligands.

E. Ethylenediaminetetra-acetic Acid and Related Ligands.—The complexes of ethylenediaminetetra-acetic acid (edta) are worthy of mention, if only for their analytical importance. Equilibrium constants have been reported[54] for reaction

$$\mathrm{M_{aq}}^{n+} + \mathrm{edta_{aq}}^{(4-n)+} \rightleftharpoons [\mathrm{M\ edta}]_{\mathrm{aq}}^{2-} + 6\mathrm{H_2O} \qquad (15)$$

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[50] Ref. 14, p. 1043.

[51] G. Newman and D. B. Powell, *J. Chem. Soc.*, 1962, 3447.

[52] S. C. Lahiri and S. Aditya, *Z. phys. Chem. (Frankfurt)*, 1964, **43**, 282.

[53] S. C. Lahiri and S. Aditya, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2487.

[54] G. Schwarzenbach, 'Complexometric Titrations', Methuen, London, 1957, p. 8.

(15), and for the divalent ions, Mn^{2+}—Zn^{2+}, log K shows appreciable dependence on Z, reflecting changes in CFSE. This may indicate that the heats of complexation (which depend on CFSE) are primarily responsible for the variation in log K. The enthalpy changes for reaction (15) have been determined by Jordan and Alleman[55] and, although a complete series is not available, ΔH° parallels ΔG° where a comparison is possible. The corrected values of ΔG° ($\Delta G^{\circ\prime}$) and ΔS° ($\Delta S^{\circ\prime}$) do not support a 'chelate effect'.

Recently, Hseu and Wu have reported[56] the thermodynamic properties of some complexes of *trans*-1,2-diaminocyclohexane-*NNN'N'*-tetra-acetic acid (dcta). The log K values of these complexes were found to be approximately two units (*ca.* 10%) higher than those of the analogous edta complexes. In this case, the ΔH° values are not significantly higher than those of the edta complexes. Thus a genuine entropy effect appears to exist and this may be due to the extra rigidity of the cyclohexane ring in dcta.

F. Adducts of Heterocyclic Bases with Metal Chelates.—Bis-2,4-pentanedionates can accept an additional ligand into the fifth co-ordination position. There is, as yet, no evidence to support definite five-co-ordination and, in solution, the sixth position may be occupied by a solvent molecule. Solid adducts can be isolated from solution but in many cases, an equilibrium of the type (16) is set up.

$$M(C_5H_7O_2)_2 + L \rightleftharpoons M(C_5H_7O_2)_2L \qquad (16)$$

May and Jones[57] have reported equilibrium constants and heats of reaction in benzene solution for (16) with M = Cu and L = pyridine, or substituted pyridine. There was little systematic variation in the free energy changes (calculated from log K) but the absolute magnitudes were quite small. The enthalpy changes are, however, quite large and appear to correlate reasonably well with the expected electron releasing power of the substituent. A non-linear dependence of ΔH on the Hammett sigma constant was found. This may be compared with the linear dependence found for the equilibrium constants relating to the formation of simple pyridine complexes.[20] It may be that the strong electron-withdrawing groups, such as $-CN$, weaken the metal–ligand σ-bond but enhance back donation by π-bonding. This could be facilitated in the 2,4-pentanedionates owing to the delocalised bonding which is thought to exist in these complexes and would result in a constancy of ΔH values. The related systems of heterocyclic bases and vanadylacetylacetonate have been studied and equilibrium constants for the reaction analogous to (16) have been measured in nitrobenzene solution.[58] The variation in ΔH for these complexation reactions parallels that observed for the addition of pyridine to boron trihalides. Therefore, π-bonding effects must be insignificant in these complexes and variations in ΔH reflect a combination of steric and inductive effects.

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[55] J. Jordan and T. G. Alleman, *Analyt. Chem.*, 1957, **29**, 9.
[56] Tong-Ming Hseu and Shao-Chung Wu, *J. Chinese Chem. Soc.* (*Formosa*), 1967, **14**, 56.
[57] W. R. May and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1963, **25**, 507.
[58] R. L. Carlin and F. A. Walker, *J. Amer. Chem. Soc.*, 1965, **87**, 2128.

Certain salicylaldiminates are able to co-ordinate two moles of ligand and West[59] has discussed the significance of the equilibrium constants for reactions (17) and (18) where L = *N*-arylsalicylaldimine. The equilibrium constants and

$$CoL_2 + py \overset{K_1}{\rightleftharpoons} CoL_2py \tag{17}$$

$$CoL_2py + py \overset{K_2}{\rightleftharpoons} CoL_2py_2 \tag{18}$$

entropy changes quoted by West for reactions (17) and (18) (in benzene at 15°C) are shown in Table 4. The large, negative ΔS_2^0 with *o*-tolyl as the aryl group was taken to indicate restriction of rotation of the incoming ligand. This, in conjunction with the relatively small value of K_2, indicates that the addition of the second molecule of pyridine is difficult, as expected on steric grounds. The relatively large value of K_1 for the *ortho*-substituted compound has not yet been explained.

Table 4 *Thermodynamic quantities for reactions* 17 *and* 18

Aryl substituent	K_1	K_2	$-\Delta S_1^0$	$-\Delta S_2^0$
H	1·8	2·8	29	21
p-CH_3	0·87	2·1	24	13
m-CH_3	1·3	3·9	25	14
o-CH_3	2·4	0·68	16	47

G. Pentaco-ordinate Systems.—The co-ordination behaviour of a series of chelating ligands has been studied by Ciampolini *et al.*[60] This was one of the earliest thermochemical studies to give unambiguous evidence for penta-co-ordination. The heats of reaction (19) for the following ligands were reported: (1) ethylenediamine (en); (2) diethylenetriamine (dien); (3) 2,2′,2″-triaminoethylamine (tren); (4) triethylenetetramine (trien); (5) *NNN′N′*-tetrakis (2-aminoethyl)ethylenediamine (penten).

$$M(H_2O)_6^{2+} + nL \rightleftharpoons M(H_2O)_{6-x}L_n^{2+} + xH_2O \tag{19}$$

The ligands are bidentate (en), quadridentate (trien, tren), tridentate (dien), and sexidentate (penten). Successive $\Delta H°$ values, for reaction (19), were found to increase slightly with L = en for all the metal ions except Cu^{2+} and Zn^{2+}. The complexes of these two metals with $Hpenten^+$ were formed with enthalpy changes very similar to those observed using the unprotonated ligand. Since penten is potentially sexidentate, it was inferred that a five-co-ordinate species was formed.

A similar, diagnostic application has been reported by Vacca and Paoletti[61] who investigated the thermodynamic and spectroscopic changes on co-ordination of the 'umbrella' ligand tri-(3-aminopropyl)amine (tpt) to various metal

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[59] B. O. West, in 'New Pathways in Inorganic Chemistry', ed. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, Cambridge, 1968, p. 308.

[60] M. Ciampolini, P. Paoletti, and L. Sacconi, 'Advances in the Chemistry of the Coordination Compounds', ed. S. Kirschner, McMillan, New York, 1961, p. 303.

[61] A. Vacca and P. Paoletti, *J. Chem. Soc.* (*A*), 1968, 2378.

ions. Electronic spectra indicated that [Cu tpt]$^{2+}$ and [Cu tpt(OH)]$^{+}$ were five-co-ordinate whereas [Cu Htpt]$^{3+}$ appeared to have an octahedral configuration in aqueous solution. The heat of reaction (20) was −14·7 kcal mol^{-1} while that of reaction (21) was −12·06 kcal mol^{-1}. These results confirmed that in

$$\mathrm{Cu_{aq}}^{2+} + \mathrm{tpt_{aq}} = \mathrm{Cu\ tpt_{aq}}^{2+} \qquad (20)$$

$$\mathrm{Cu_{aq}}^{2+} + \mathrm{Htpt_{aq}}^{+} = \mathrm{Cu\ Htpt_{aq}}^{3+} \qquad (21)$$

(20) one more donor atom was used than in (21) and, therefore, supported the five-co-ordinate assignment of [Cu tpt]$_{aq}^{2+}$. Also the heat of formation of [Cu tpt OH]$_{aq}^{+}$ from [Cu tpt]$_{aq}^{2+}$ was very close to that found for the complex [Cu tren (OH)]$_{aq}^{+}$ which is known to be five-co-ordinate.[62] Thermodynamic properties have also been reported for the five-co-ordinate complexes [Pt diars$_2$X]$^{2+m}$ [diars = *o*-phenylenebisdimethylarsine; X = Cl$^-$, Br$^-$, I$^-$, N$_3^-$, SCN$^-$, or CS(NH$_2$)$_2$] by Dolcetti *et al.*[63] The heterocyclic base adducts of acetylacetonatocopper(II) may be five-co-ordinate in solution but spectroscopic evidence for their assignment appears to be inadequate.[64] The related phosphine oxide complexes are monomeric in benzene and, presumably, five-co-ordinate.[65]

4 Complexes of the *f*-Block Transition Elements

There are, as yet, insufficient data to allow a meaningful discussion of the thermodynamics of the actinide complexes. Such data would be of great interest since moderately strong crystal-field effects are expected[66] in contrast to the weak effects observed for complexes of the lanthanide elements. The latter effects are thought to be small compared with interelectron repulsions and spin–orbit coupling and are, therefore, of little influence in deciding the stereochemistry[67] or electronic properties of a lanthanide complex. It might be thought possible, however, that a crystal-field effect would be detectable in the variation of thermodynamic properties in the same manner as it was detected for the *d*-block elements (Section 2C). It must be recognised, however, that a considerably more complex situation prevails both theoretically and practically. Firstly, the extent and the nature of the splitting of the ground-state terms clearly depend on the symmetry of the surrounding ligand field but the author is unaware of any work which has done other than to assume that each member of a group of similar complexes has a similar stereochemistry. Secondly, even if each member possessed cubic symmetry, the resultant matrix elements are functions of two parameters of the form:[68]

$$< (3, m_l)\ V_{\mathrm{oct}}\ (3, m_l) > \ = \alpha Dq + \beta\, Fr$$

Fr is a parameter of similar magnitude to *Dq* so that it is impossible to make

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[62] P. Paoletti and C. Ciampolini, *Ricerca Sci.*, 1963, **33** (II - A), 399.

[63] G. Dolcetti, A. Peloso, and L. Sindellari, *Gazzetta*, 1966, **96**, 1648.

[64] P. E. Rakita, S. J. Kooperl, and J. P. Fackler jun., *J. Inorg. Nuclear Chem.*, 1968, **30**, 2139.

[65] C. H. Ke and N. C. Li, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2255.

[66] Ref. 15, p. 327.

[67] A. J. Downs, ref. 59, p. 29.

[68] Ref. 15, p. 328.

general predictions concerning the variations in thermodynamic properties in the manner indicated (Section 2C) for the *d*-block elements. This is only possible when single electron wavefunctions are used, which is tantamount to assuming the existence of strong crystal fields. Experimental evidence does not support this assumption and the model is, therefore, inapplicable. The existence of a 'double-humped' curve of any thermodynamic property for a series of lanthanide complexes cannot therefore be taken to be diagnostic of simple crystal-field effects, and only for exceptionally strong crystal fields would a simple dependence be expected.

It is true, however, that many thermodynamic properties are not simple functions of the radius of the central lanthanide ion. Grenthe[69] has used titration calorimetry to study the interactions of glycolate and picolinate with the lanthanide ions. The heats of reaction, and free energy changes, when plotted as a function of atomic number resulted in complex curves with no regular variation. It was pointed out by Grenthe[69] and later by Choppin[70] that at least a part of the observed variation is due to a change in co-ordination number of the hydrated lanthanide ions. This change occurs about half-way through the lanthanide series[71] and is referred to as the 'gadolinium break'. A similar lack of regularity was observed for the α- and β-mercaptopropionate complexes by Choppin and Martinez-Perez.[72] These workers established that the ligands were unidentate because of the similarity of the heats of complexation to those observed for the propionate complexes[73] and the dissimilarity from those observed for the analogous lactate complexes.[74]

It is necessary to eliminate the thermodynamic effects which are due to variable degrees of hydration before specific electronic and structural effects can be studied. This could ideally be done by converting all species to the gas phase but this is usually impossible owing to the lack of essential heats of sublimation data. This has been partially avoided by Staveley and his co-workers[75] in a recent paper in which the heats of solution of the isomorphous solid ethyl sulphates and bromates were reported. These, when combined with heats of complexation yield enthalpy changes for the complexation reactions of the solid bromate or ethylsulphate:

$$\mathrm{Ln(BrO_3)_3,9H_2O_{(cryst)}} \rightarrow \mathrm{Ln_{(aq)}}^{3+} + \mathrm{3BrO_{3(aq)}}^{-} + \mathrm{9H_2O_{(aq)}}\ ;\ \Delta H_{22}$$

$$\mathrm{Ln_{(aq)}}^{3+} + a\mathrm{Y_{(aq)}}^{n-} \rightarrow \mathrm{LnY_{a(aq)}}^{(an-3)-}\ ;\ \Delta H_{23}$$

$$\mathrm{Ln(BrO_3)_3,9H_2O_{(cryst)}} + a\mathrm{Y_{(aq)}}^{n-} \rightarrow \mathrm{LnY_{a(aq)}}^{(an-3)-} + \mathrm{3BrO^-_{3(aq)}} + \mathrm{9H_2O_{(aq)}}\ ;\ \Delta H_{24}$$

$$\Delta H_{24} = \Delta H_{22} + \Delta H_{23}$$

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[69] J. Grenthe, *Acta Chem. Scand.*, 1963, **17**, 2487.

[70] G. R. Choppin and W. F. Strazik, *Inorg. Chem.*, 1965, **4**, 1250.

[71] L. A. K. Staveley, D. R. Markham, and M. R. Jones, *Nature*, 1966, **211**, 1172.

[72] G. R. Choppin and L. A. Martinez-Perez, *Inorg. Chem.*, 1968, **7**, 2657.

[73] G. R. Choppin and H. G. Friedman jun., *Inorg. Chem.*, 1965, **5**, 1254.

[74] G. R. Choppin and H. G. Friedman jun., *Inorg. Chem.*, 1966, **5**, 1599.

[75] L. A. K. Staveley, D. R. Markham, and M. R. Jones, *J. Inorg. Nuclear Chem.*, 1968, **30**, 231.

It is still possible that the complexes in solution are partially hydrated. This can occur when the maximum co-ordination number is not achieved and, in such cases, a complex dependence of enthalpies and free-energy changes persists. For the 1 : 3 diglycollate and 1 : 3 dipicolinate complexes, in which a co-ordination number of nine is achieved,[76] a simple dependence of ΔH_{24} on atomic number is detected, and this indicates that saturation of the co-ordination sphere has been achieved. The simple dependence of ΔH_{24} on atomic number may be taken to indicate that some effect, other than that due to a change in ionic radius, is operative and this may have its origin in crystal-field effects. If this is so, it is likely that crystal-field effects do not exceed more than a few hundred calories but may, nevertheless, be finite. A similar effect was observed[77] for the heats of complexation of trivalent lanthanides (Ln^{3+}) by diethylenetriaminepenta-acetic acid (dtpa). This ligand is potentially octadentate compared to edta, which is sexidentate, so that the edta complexes may possess variable degrees of hydration. The enthalpy changes calculated[77] for reactions of the crystalline lanthanide ethyl sulphates with dtpa and edta are shown in Figure 3. The regularity for the complexes of dtpa contrasts markedly with the irregularity for those of edta and indicates that the latter are partially hydrated. In order that solvent effects could be completely eliminated, Ashcroft and Mortimer[78] have studied the

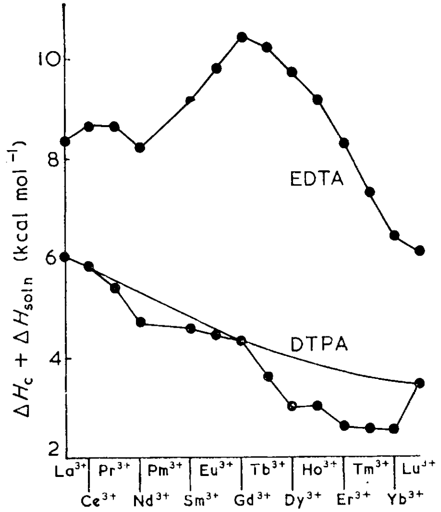

Figure 3 *The enthalpies of reaction of the crystalline lanthanide ethyl sulphates with amino-carboxylic acids*

[Reproduced by permission, from *J. Chem. Soc.* (*A*), 1968, 1384.]

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[76] N.-G. Vannerberg and J. Albertsson, *Acta Chem. Scand.*, 1965, **19**, 1760.
[77] A. S. Carson, P. G. Laye, and P. N. Smith, *J. Chem. Soc.* (*A*), 1968, 1384.
[78] S. J. Ashcroft and C. T. Mortimer, *J. Less-Common Metals*, 1968, **14**, 403.

thermal decomposition (25) in a differential scanning calorimeter.

$$LnCl_3(H_2O)_{n(cryst)} \rightarrow LnCl_3(H_2O)_{m(cryst)} + (n - m)\, H_2O_{(g)} \qquad (25)$$

The decompositions were carried out in an inert atmosphere to prevent the formation of oxychlorides but the decomposition steps were not clearly resolved except when n was unity. An unexpected result was obtained since the heats of reaction (25) were found to be approximately constant along the series from lanthanum to gadolinium but to decrease from holmium to lutetium. This was attributed to decreasing crystal-field stabilisation for the later members of the series but crystal-field dependence would be expected to be periodic as described previously. The authors emphasised, however, that there is a lack of information regarding the structures of the crystalline hydrates. The enthalpy changes must be structure-dependent and, possibly, to an extent which masks small crystal-field effects.

5 Complexes of Amino-acids and other Complexes of Biological Interest

The thermodynamic changes which occur in biological systems are difficult to measure and even more difficult to interpret owing to the complexity of naturally-occurring compounds. Studies of simpler systems may yield unambiguous results from which the behaviour of more complex molecules may be inferred. Thus, it is known that many enzymes are inactive in the absence of traces of certain metal ions. These ions may bind substrates to active centres by means of complexation reactions analogous to the chelation reactions discussed in section 3D since both the active centres of the enzyme and the substrate are usually multidentate. In the simplest cases, a metal ion may be attached to a terminal amino-acid group of an enzyme or to an intra-catenary amino-acid. Thus, useful information may be obtained from thermodynamic data relating to metal ions and simple amino-acids even though the systems of biological interest are of greater complexity.

Christensen and his co-workers[79] have studied the stepwise interactions of α-amino-acids with copper(II) ions in aqueous solution. Surprisingly, very little variation in the values of the stepwise enthalpy changes or equilibrium constants was detected when different amino-acids (glycine, α-aminoisobutyric, sarcosine, or threonine) were used. For a particular amino-acid, the equilibrium constant for the formation of the mono-ligand complex was greater than that for the formation of the bis-ligand complex by at least an order of magnitude.

It would be expected that the formation of a chelated amino-acid complex would depend on the size of the chelate ring by analogy with the results recorded in section 3D for other chelate complexes. Boyd *et al.*[80] have reported ΔH° and ΔG° for the glycinate and β-alaninate complexes of cobalt, nickel, and copper. These amino-acids form five- and six-membered chelate rings respectively. The thermodynamic properties, at 25°C, are listed in Table 5 for the formation

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[79] R. M. Izatt, J. J. Christensen, and V. Kothari, *Inorg. Chem.*, 1964, **3**, 1565.

[80] S. Boyd, J. R. Brannan, H. S. Dunsmore, and G. H. Nancollas, *J. Chem. and Eng. Data*, 1967, **12**, 601.

Table 5 *Thermodynamic quantities for the formation of* $MA_{(aq)}^{+}$ *and* $MG_{(aq)}^{+}$ (A = β-alanine; G = glycine)

	$-\Delta H$(kcal mol^{-1})	$-\Delta G$(kcal mol^{-1})	ΔS(cal K^{-1} mol^{-1})
CoA^{+}	3·32	5·74	8·1
NiA^{+}	3·81	6·84	10·2
CoG^{+}	2·48	6·29	12·8
NiG^{+}	4·14	8·43	14·4
CuG^{+}	6·76	11·71	16·6

of $MA_{(aq)}^{+}$ (M = Co, Ni, and Cu; A = glycine and β-alanine) from $M_{(aq)}^{2+}$ and $A_{(aq)}^{-}$. The increased stability is primarily an entropy effect and this was attributed to a greater loss of librational entropy of the alaninate ion.

CFSE Effects may determine the strength of binding of an amino-acid to a transition-metal ion and this may, in turn, reflect the ability of a metal to activate an enzyme. Table 5 shows that there may be a CFSE dependence of ΔH and this was confirmed by Raju and Mathur[81] who detected an obvious CFSE effect for the complexes of serine and threonine. Stack and Skinner[82] have reported direct calorimetric measurements relating to the ML_2 complexes (L = glycine, α-alanine, β-alanine, serine, and histidine) and found that the heats of formation depended on the metal (M):

$$Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

which is in accord with the predictions of crystal-field theory. A similar dependence was reported by the same authors[82] for the free-energy changes. It is possible that CFSE effects may help to predict enzyme specificity or activity, and thermochemical data relating to simple systems may assist biochemical workers to establish the nature of the active centres.

The thermodynamics of complex formation between histidine and transition-metal ions are of interest since this molecule often occurs in intra-catenary positions on the polypeptide chain. Histidine is a potentially terdentate ligand, co-ordination being possible from the imidazole nitrogen atom and the amino-acid carboxylic and amino-groups. Thus, histidine may act as a unidentate, bidentate, or terdentate ligand. Perrin and Sharma[83] determined stability constants for complexes of the divalent ions of cobalt, copper, lead, manganese, and zinc. Raju and Mathur[84] studied similar systems and calculated enthalpy changes from the temperature variation of ΔG. These workers concluded that histidine behaved as a terdentate ligand and that the secondary imidazole nitrogen was not used in co-ordination. The evidence for this was that the enthalpy changes on complexation of two histidine molecules were very similar to those accompanying the formation of the analogous triethylenetetramine complexes.[60]

[81] E. V. Raju and H. B. Mathur, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2181.

[82] W. F. Stack and H. A. Skinner, *Trans. Faraday Soc.*, 1967, **63**, 1136.

[83] D. D. Perrin and V. S. Sharma, *J. Chem. Soc.* (*A*), 1967, 724.

[84] E. V. Raju and H. B. Mathur, *J. Inorg. Nuclear Chem.*, 1969, **31**, 425.

This may be a reasonable assumption if the metal–carboxylate bonding is weak as would seem to be the case.[85] The entropy changes for the reaction

$$\mathrm{M_{(aq)}}^{2+} + 2\mathrm{his}_{(eq)} \rightleftharpoons \mathrm{M(his)_{2(aq)}}^{2+} \quad (\mathrm{his} = \mathrm{histidine})$$

were all in the range 22—28 cal K^{-1} mol^{-1} except for M = Cu when the entropy change was found to be 14·5 cal K^{-1} mol^{-1}. This was attributed[84] to greater solvent ordering due to lengthening of the axial bonds with exposure of the central metal ion. Perrin and Sharma[83] found that the logarithm of the equilibrium constant for the formation of the monohistidine complex (9·79) was similar to that of the monohistamine complex (9·56). This indicated that the bonding in the copper complex occurred through the amino-group and an imidazole nitrogen. If bonding had occurred to the carboxylate group, the equilibrium constant would be similar to that observed for the analogous glycine complex. The equilibrium constant for this reaction is lower, however, by two orders of magnitude.

The solid complexes of amino-acids, although of little biological interest, are of interest since they are sufficiently stable to be studied by combustion calorimetry. Thus, Skinner and Jones[86] have determined the heats of formation of solid tris(glycinato)chromium(III) and tris(alaninato)chromium(III). The solid compounds had heats of sublimation in excess of 100 kcal mol^{-1} which indicates the presence of polynuclear species.

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[85] V. S. Sharma and H. B. Mathur, *J. Indian Chem. Soc.*, 1965, 3, 475.
[86] C. E. Skinner and M. M. Jones, *Inorg. Nuclear Chem. Letters*, 1967, 3, 185.