637. The Stability of Transition-metal Complexes.

By H. Irving and R. J. P. Williams.

Published and original data on the stability of complexes formed by bivalent ions of the first transition series have been collected and examined critically. The order Mn $<$ Fe $<$ Co $<$ Ni $<$ Cu $>$ Zn has been found to hold for the stability of nearly all such complexes irrespective of the nature of the co-ordinated ligand or of the number of ligand molecules involved. A theoretical justification for this stability order follows from considerations of the reciprocal of the ionic radii and the second ionisation potentials of the metals concerned, and it is shown why other (empirical) orders, or stability orders which include other elements, can have no general validity.

The extent to which variations in characteristic co-ordination number, stereochemical considerations, and entropy factors may affect such a stability order is discussed theoretically and illustrated by examples. Changes in bonding orbitals concomitant with changes in the nature of the ligand are shown to lead to certain complexes of anomalously high stability, notably in the case of ferrous ions.

Although studies of the relative stabilities of solid complex salts and co-ordination compounds are almost inevitably complicated by considerations of lattice energy, yet with certain specialised types, *viz.*, the solid adducts of electron-deficient molecules of the type BF_3 or MR_3 (where M = Group III metal and R = alkyl) with donor molecules of the type AR_2 (where A = O, Se, and Te) or BR_3 (where B = N, P, As, etc.), measurements of dissociation pressures have provided thermodynamic data of great theoretical interest (Brown *et al.*, *J. Amer. Chem. Soc.*, 1944, **66**, 431; 1947, **69**, 1332; 1948, **70**, 2848; Coates, *J.*, 1951, 2003; *Quart. Reviews*, 1950, **4**, 217; cf. Kabesh and Nyholm, *J.*, 1951, 3245).

Although the disturbing features of lattice energy can be avoided by measurements of complex stabilities in homogeneous solution the systems become complicated in other respects, for the formation of any complex ML_n from a metal M and a ligand L must proceed stepwise through such successive stages as

$$M + L \rightleftharpoons ML;\ ML + L \rightleftharpoons ML_2;\ \ldots .\ ML_{n-1} + L \rightleftharpoons ML_n$$

and, since all the species ML_n, N being the maximum co-ordination number are in mutual equilibrium, the full description of such systems demands a knowledge of n equilibrium constants (otherwise termed complexity or formation constants) defined by $K_n = [ML_n]/[ML_{n-1}][L]$. [For the sake of generality the charges on dissolved species and any indication of their relative degrees of hydration are omitted; and while L may be a mono- or a poly-dentate ligand it is assumed that the solution contains no polynuclear complexes and no complexes in which ligands of more than one type (excluding water) are bound to the same metal atom.] Quite apart from the freedom from lattice effects, equilibrium studies in solution chemistry have certain unique advantages in that they permit the evaluation of the stabilities of individual members of groups of closely related and chemically very similar compounds [*e.g.*, the hydrated ions $Ni(NH_3)_n,aq.,^{++}$ $n = 0$—6] which may not be capable of isolation in the pure state at all—inasmuch as they exist only in solution and in dynamic equilibrium with other species.

The concentration of free metal ions in solution in a system where the total metal concentration is C_M and the free ligand concentration is [L] is readily shown (Bjerrum, " Metal Ammine Formation in Aqueous Solution," Copenhagen, 1941) to be

$$[M] = C_M/\Sigma_0^n\ \beta_n[L]^n, \text{ where } \beta_n = K_1K_2 \ldots K_n \text{ and } \beta_0 = 1$$

The effect of complex formation in changing this concentration of free metal ion is of the greatest importance in analytical chemistry where it is exploited in " masking " and " de-masking " reactions (cf. Feigl, " The Chemistry of Specific, Selective, and Sensitive Reactions," New York, Academic Press Inc., 1949); it is fundamental to discussions of the pH of precipitation of metal hydroxides, sulphides, and organic complexes (Irving and

Williams, *Analyst*, 1952, **77**, 813) and to any quantitative treatment of solvent extraction (cf. Irving, *Quart. Reviews*, 1951, **5**, 200); it will modify the kinetics of metal-catalysed decarboxylations and similar reactions (cf. p. 3196), and may be the dominant feature in those biological systems where trace metals play a vital rôle (Williams, *Biol. Reviews*, in the press). Where metals display more than one valency state, complexing by any given ligand favours one state rather than the other, and the resultant changes in redox potential are again of importance in biochemical as well as in analytical and purely theoretical discussions. Since, in general, two or more different metals will form complexes of unequal stability with one and the same ligand, possibilities of analytical separations arise; and should the ligand be an organic reagent of suitable molecular geometry, it may happen that relatively few metals, or at best only one, will form a strong chelate complex with it so that its use as a selective or " singular " reagent—or even as a truly specific reagent—could be realised (Irving and Williams, *loc. cit.*).

In all these fields a knowledge of the magnitude of the stability constants of complexes is a necessary preliminary to quantitative treatment. But since these constants are also a measure of free-energy changes (in view of the relationship $-\Delta G = 2{\cdot}303\boldsymbol{RT}\log_{10}\beta$), there ought to be some correlation with the strength of the metal–ligand bonds to which these constants can be referred—and hence to those fundamental properties of the metal ion and ligand molecule which control the type and the strength of the bonding involved. Somewhat restricted relationships have been traced between complex stability and the basic strength of the ligand employed (cf. Bjerrum, *Chem. Reviews*, 1950, **46**, 381, and refs. therein) but the part played by the metal has received little attention.

Available Data.—Many values have been pubished for the formation (complexity) constants of various metal–ligand systems, especially in recent years, but the experimental methods employed and the precision attained have varied considerably. Some authors have worked at unspecified " room temperature " and with solutions in which the ionic strength must have varied appreciably during the experiments and can only be estimated approximately from their figures. The data of others refer almost exclusively to one fixed temperature, often 25·0°, and to solutions containing a salt " background " of known ionic strength; in the best work (*e.g.*, by Schwarzenbach) corrections are made for any competitive complexing between metal and anions present. The order of magnitude of effects caused by changes in temperature or ionic strength may be inferred from the following formula given by Bjerrum (*op. cit.*) to represent his data for the copper–ammonia system in ammonium nitrate (or chloride) solutions of concentration up to 5N :

$$\log K_n = \log K_n^\circ + 0{\cdot}080[\mathrm{NH_4NO_3}] + 0{\cdot}013(30^\circ - t^\circ)$$

where $\log K_1^\circ = 3{\cdot}99$, $\log K_2^\circ = 3{\cdot}34$, $\log K_3^\circ = 2{\cdot}73$, and $\log K_4^\circ = 1{\cdot}97$. Values of $\mathrm{d}(\log K_n)/\mathrm{d}T$ for various transition-metal complexes with ethylenediamine (present authors; unpublished observations), diethylenetriamine (Jonassen, LeBlanc, Meibohm, and Rogan, *J. Amer. Chem. Soc.*, 1950, **72**, 4968), and triethylenetetramine (Jonassen and Meibohm, *J. Phys. Coll. Chem.*, 1951, **55**, 726) range only from 20 to 50×10^{-3}, and since the decrement per °c in $\log_{10} K_n$ never exceeds 0·5% of its absolute value, variations in temperature may be ignored for the purpose of the present paper.

Somewhat more disturbing are variations between the results of different workers for the same metal–ligand system; these are illustrated by data in Table 1 for complexes of glycine and alanine with a number of transition metals. To some extent such discrepancies originate from differences in the values adopted for the dissociation constants of the ionic species $^+\mathrm{NH_3{\cdot}R{\cdot}CO_2H}$ and $^+\mathrm{NH_3{\cdot}R{\cdot}CO_2^-}$, for these are used in the relevant calculations; but this only implies a similar lack of agreement between measurements by different authors of the strength of the corresponding proton amino-acid complexes and emphasises the difficulty of obtaining reliable results for complex stabilities. Fortunately, the same techniques and experimental conditions have generally been used throughout by each individual author when measuring the stabilities either of a series of related ligands with the same metal or of a series of metals with a chosen ligand. For the discussion which follows we have made free use of such sets of data which are likely to be reasonably consistent internally so far as salt-effects, temperature, and intrinsic accuracy are concerned, and we have avoided drawing conclusions from results obtained under widely different conditions or by methods of low or dubious accuracy. Nevertheless, it must be emphasised that the order of magnitude of effects to which we shall now draw attention in this paper is such that quite considerable experimental uncertainty in the actual values of individual stability constants would not invalidate our conclusions.

Sometimes the low solubility of a metal chelate prevents the use of water as a solvent, and a number of stability constants have been measured in aqueous mixtures with, *e.g.*, alcohol or dioxan. With increasing dioxan content there are significant increases in the measured stability constants of those metal (or proton)–ligand complexes so far studied (Mellor and Maley, *Austral. J. Sci. Res.*, 1949, **2**, 92; Albert, *Proc. Biochem. Soc.*, 1950, **46**, ix; H. Marsh, Thesis, Oxford, 1952), but quantitative correlation with the physical properties of the medium cannot yet be predicted on theoretical grounds, although in recent work (Davies and Monk, *J.*, 1951, 2719) the effect of changes in the dielectric constant of the medium on the dissociation constants of certain metal complexes has received careful study. All measurements which do not refer to pure water as solvent are carefully distinguished in Table 2 and elsewhere.

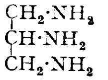
Although individual complexes of a wide variety of elements have been examined quantitatively, the most extensive data refer to two main groups, *viz.*, those of Group II and those of the first transition series. Complexes of Group IIA metals have already been discussed by one of us in a paper (Williams, *J.*, 1952, 3770) originally designed to follow the present paper which will deal predominantly with complexes of elements of atomic number 25—30. Elements of Groups IIB and IIIB will be considered in later papers.

Orders of Stability.—Bjerrum (*op. cit.*) did not remark any special features among the values he had determined for the stabilities of ammonia or ethylenediamine complexes of the bivalent transition metals which could be related to properties of the elements concerned. On the other hand, Mellor and Maley (*Nature*, 1947, **159**, 370) reported that the order of decreasing stability of bivalent metal chelates with salicylaldehyde in 50% dioxan, *viz.*, Pd > Cu > Ni > Pb > Co, Zn > Cd > Mg, was the same as that furnished by their then unpublished values for glycine and 8-hydroxyquinoline (as VIII) save that "occasionally the position of neighbouring elements is reversed." The following year (*idem, ibid.*, 1948, **161**, 436) the stability order Pd > Cu > Ni > Co > Zn > Cd > Fe > Mn > Mg was shown to hold for ethylenediamine complexes and to be consistent with the sequence of comparative stabilities $Cu^{++} > Ni^{++} > Fe^{+++} > Zn^{++} > Mg^{++}$ noted by Pfeiffer, Thielert, and Glaser (*J. pr. Chem.*, 1939, **152**, 145) for pyridine complexes.

Independently, we observed that if the successive stability constants of complexes of bivalent ions of the first transition series were plotted against the atomic number of the element (cf. Figs. 1 and 4) there was a monotonic increase to a maximum at copper whether the ligands were ammonia, ethylenediamine, propylenediamine, or salicylaldehyde. In a preliminary communication (Irving and Williams, *Nature*, 1948, **162**, 746) we pointed out that this order of stabilities could be intelligibly correlated with the electronic structure and fundamental properties of the ions concerned, notably with the second ionisation potential (cf. p. 3203). The limited range of experimental values then available for the stability constants of transition-metal complexes was supplemented by observations on the pH of incipient precipitation (or 50% precipitation) of certain metal complexes, and the pH of 50% extraction of metal dithizonates. The justification for such correlations which are now realised to be of somewhat limited validity has recently been discussed (Irving and Williams, *Analyst*, 1952, **77**, 813).

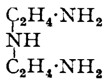
Since 1948 there has been intense activity in the field of quantitative solution chemistry and our generalisation that the "natural" order of the stability of complexes of bivalent transition metals is Mn < Fe < Co < Ni < Cu > Zn irrespective of the nature of the ligand has been strikingly confirmed by results now available for a great variety of ligands such as ethylenediamine ($NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ = en), propylenediamine ($NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}NH_2$ = pn), 1 : 3-diaminopropane ($NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ = dimp), 1 : 2 : 3-triaminopropane (I; ptn), diethylenetriamine (di-2-aminoethylamine) (II; den), triaminotriethylamine (tri-2-aminoethylamine) (III; tren), triethylenetetramine (IV;

trien), 2 : 2′-dipyridyl (V; dipy), 1 : 10-phenanthroline (phenan; VI; R = R′ = H), a great variety of α- and some β-amino-acids (cf. Fig. 2), and " complexones " such as nitrilotriacetic acid (NA_3, where A = $CH_2{\cdot}CO_2H$) * and ethylenediaminetetra-acetic acid (enta acid, $NA_2{\cdot}CH_2{\cdot}CH_2{\cdot}NA_2$), tropolone, and 1 : 3-diketones and β-keto-esters of the type X·CO·CH_2·COY, *o*-hydroxyaromatic aldehydes (as VII), 8-hydroxyquinoline and its derivatives (as VIII), 4-hydroxypteridine (IX), riboflavin (X), folic acid (XI), and many mono- and di-carboxylic acids. Table 2 includes most of the published data and gives values of the individual stability constants log K_1, log K_2 . . . etc., for the attachment of the first, second, etc., molecule of ligand irrespective of whether it is mono- or poly-dentate. The values of log β_2 = (log K_1K_2), log β_3 (= log $K_1K_2K_3$), and log β_N (= log K_1K_2 . . . K_n), and the gross or over-all stability constants for the attachment of two, three, or *N* molecules of ligand (again irrespective of its degree of functionality) are quoted in some cases. The order followed is one of increasing complexity through mono-, di-, tri-, to polydentate ligands, dealing first with molecules co-ordinated through one or more nitrogen atoms (" nitrogen-type " ligands) followed by chelating parts which include both oxygen and nitrogen bonds (" nitrogen–oxygen-type " ligands), and finally mono- or poly-dentate ligands co-ordinated through oxygen atoms only (" oxygen-type " ligands).



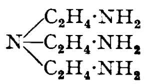
$$\begin{array}{l} CH_2{\cdot}NH_2 \\ | \\ CH{\cdot}NH_2 \\ | \\ CH_2{\cdot}NH_2 \end{array}$$

(I; ptn)



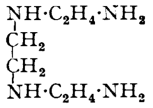
$$\begin{array}{l} C_2H_4{\cdot}NH_2 \\ | \\ NH \\ | \\ C_2H_4{\cdot}NH_2 \end{array}$$

(II; den)



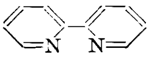
$$N\begin{cases} C_2H_4{\cdot}NH_2 \\ C_2H_4{\cdot}NH_2 \\ C_2H_4{\cdot}NH_2 \end{cases}$$

(III; tren)

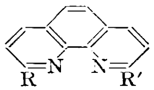


$$\begin{array}{l} NH{\cdot}C_2H_4{\cdot}NH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ NH{\cdot}C_2H_4{\cdot}NH_2 \end{array}$$

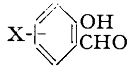
(IV; trien)



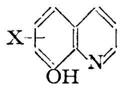
(V; dipy)



(VI; phenan)



(VII)



(VIII)

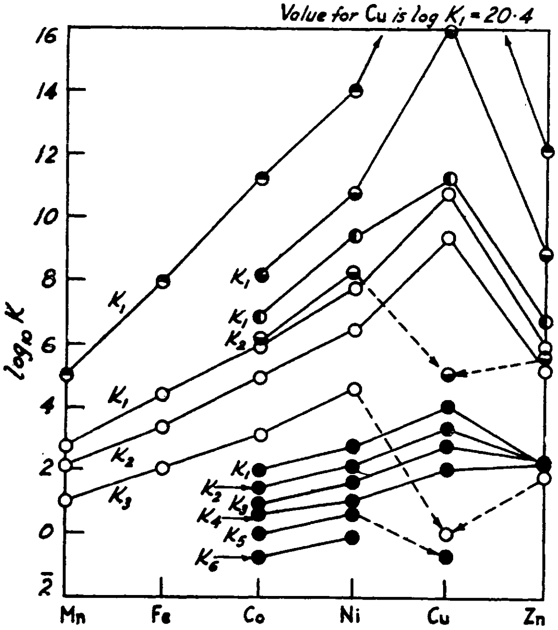


FIG. 1. *The stability of some complexes of the transition metals with nitrogen-type ligands as a function of atomic number.*

● *Ammonia. Data valid for* 30° *and* μ = 0.

○ *Ethylenediamine. Data valid for* 30° *and* N-KCl.

◐ 1 : 2 : 3-*Triaminopropane. Data valid for* 20° *and* μ = 0·1.

◒ *Diethylenetriamine. Data valid for* 20° *and* μ = 0·1.

◓ *Triethylenetetramine. Data valid for* 20° *and* μ = 0·1.

Fig. 1 displays for bivalent metals of the first transition series the variation with atomic number of the stability of complexes with typical monodentate (ammonia), bidentate

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* More recent data for polydentate amino-acids will be presented in a later paper.

(ethylenediamine), tridentate (triaminopropane, I; and diethylenetriamine, II), and tetradentate (triethylenetetramine, IV) ligands. The essential feature of this graph—the monotonic rise in stabilities to copper followed by a lower value for zinc, independent of the kind of ligand and of the number of ligands attached (but see p. 3205)—reappears in Fig. 4 and could be reproduced by plotting almost any of the data given in Table 2.

Values for the strengths of metal complexes of a large number of amino-acids given in Tables 1 and 2 are presented graphically in Fig. 2, where the ligands are arranged in order of their published p*K* values. It is not intended that any special correlation should be noted between the stability of proton- and metal-complexes of any given ligand and it has been pointed out that the measurements are not all of equal precision; some may be in error by as much as 0·5 logarithmic unit. Nevertheless, it is quite obvious that for each one of these dozen ligands the stability of the metal complexes follows the same sequence of metals already noted. This sequence, Mn < Fe < Co < Ni < Cu > Zn, which we shall term the " natural " or Irving–Williams order, remains valid when the basic skeleton of the amino-acid chelating system, *viz.*, $:N{\cdot}C{\cdot}C{\cdot}OH$, forms part of a heterocyclic system as in 8-hydroxyquinoline and its 5-sulphonic acid (as VIII) or 4-hydroxypteridine (IX), and applies equally to " nitrogen-type," " nitrogen–oxygen-type," and " oxygen-type " ligands (cf. Tables 2 and 1).

Additional Evidence for the Irving–Williams Order of Stabilities.—The decarboxylation of the nitroacetate ion, $NO_2{\cdot}CH_2{\cdot}CO_2^-$, is retarded both by protons and by a variety of cations, and Pedersen (*Acta Chem. Scand.*, 1949, **3**, 676) has recently shown that the kinetics can be completely interpreted by postulating that complex formation controls the effective concentration of the decomposing species. The values calculated from kinetic measurements (cf. Table 2) for the stability constants of the metal–nitroacetate ion complex, $(NO_2{\cdot}CH_2{\cdot}CO_2M^{II})^+$, arrange themselves in the order Ba < Ca < Mg < Co < Zn < Ni < Pb < Cd < Be < Cu. On the other hand, the decarboxylation of certain keto-acids (but not the corresponding esters) is positively catalysed by metal ions which are supposed to form complexes involving

TABLE 1. *Stability of metal complexes of glycine and alanine.*

(*a*) Glycine, $NH_2{\cdot}CH_2{\cdot}CO_2H$. [a]

			Manganese			Iron			Cobalt	
Refs.	Temp.	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2
1, 2	20°	3·2	2·3	5·5	4·29	3·66	7·95	5·06	3·85	8·91
3, 4	25	3·66	2·97	6·63	—	—	—	4·95	3·99	8·94
5, 6	25	3·44	—	—	—	—	—	5·23	4·02	9·25
			Nickel			Copper			Zinc	
1, 2	20	6·14	4·98	11·12	8·47	6·91	15·38	5·25	4·05	9·30
3, 4	25	6·12	5·03	11·15	8·51	6·91	15·42	5·33	4·39	9·72
5, 6	25	6·18	4·96	11·14	8·62	6·97	15·59	5·52	4·44	9·96

(*b*) α-Alanine, $NH_2{\cdot}CHMe{\cdot}CO_2H$. [b]

			Manganese			Iron			Cobalt	
Ref.	Temp.	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2
3, 4	25°	3·24	2·81	6·05	—	—	—	4·83	3·95	8·78
5, 6	25	3·02	—	—	—	—	—	4·82	3·66	8·48
			Nickel			Copper			Zinc	
3, 4	25	—	—	—	8·18	6·65	14·83	5·16	4·34	9·50
5, 6	25	5·96	4·70	10·66	8·51	6·86	15·37	5·21	4·33	9·54

[1] Albert, personal communication. [2] *Idem, Biochem. J.*, 1950, **47**, 531. [3] Maley and Mellor, *Nature*, 1950, **165**, 453. [4] Mellor and Maley, *Austral. J. Sci. Res.*, 1949, **2**, 579. [5] Monk, *Trans. Faraday Soc.*, 1951, **47**, 285. [6] *Idem, ibid.*, p. 297. [a] Additional values for log β_2 for copper obtained polarographically are 15·13 ($\mu = 0{\cdot}1$) and 15·28 ($\mu = 1{\cdot}0$) by Keefer, *J. Amer. Chem. Soc.*, 1946, **68**, 2329; 15·1 ($\mu = 0{\cdot}1$) by Laitinen, Onstott, Bailar, and Swann, *ibid.*, 1949, **71**, 1550; and 15·3 ($\mu = 1{\cdot}0$) by Irving, Williams, Ferrett, and Williams, paper in preparation. Flood and Lorås (*Tiddskr. Kjemi* 1945, **5**, 83) report for copper at 20° : log K_1 = 8·50, log K_2 = 6·83, and log β_2 = 15·33, and at an unspecified temperature (*idem, ibid.*, 1944, **4**, 35) : log β_2 = 10·6 (nickel) and 15·19 (copper). [b] Other values for log β_2 are 8·4 for cobalt and 15·1 for copper at 20° (ref. 2). Polarographic measurements at 25° give log β_2 for copper as 15·01 ($\mu = 0{\cdot}1$; Keefer, *loc. cit.*) and 14·82 ($\mu = 1{\cdot}0$; Li and Doody, *J. Amer. Chem. Soc.*, 1950, **72**, 1891).

a carboxyl group and the carbonyl group of the keto-tautomeride. Data for dimethyloxaloacetic acid, $HO_2C\cdot CO\cdot CMe_2\cdot CO_2H$, placed the strength of such metal complexes in the order Mn < Fe < Ni < Cu (Steinberger and Westheimer, *J. Amer. Chem. Soc.*, 1949, **71**, 4158; 1951, **73**, 1951), and Prue (*J.*, 1952, 2331) reports the order Mg < Cd < Mn < Pb < Co < Zn < Ni < Be < Cu from kinetic studies of the decarboxylation of acetonedicarboxylic acid. Similarly, the bromination of β-keto-esters is catalysed by metal ions which appear to facilitate proton transfer from ester to base: on the assumption that a small amount of metal complex is formed between the metal ion and the keto-form of ethyl 2-oxo*cyclo*pentanecarboxylate, Pedersen (*Acta Chem. Scand.*, 1948, **2**, 385) has shown that the strength of the metal–ligand complex increases in the order Mg < Cd < Pb < Zn < Ni < Cu. It will be seen that these stability orders obtained kinetically do not agree completely either with Mellor and Maley's order (p. 3194) or with each other. But without exception the data are consistent with our sequence of stabilities Mn < Fe < Co < Ni < Cu > Zn.

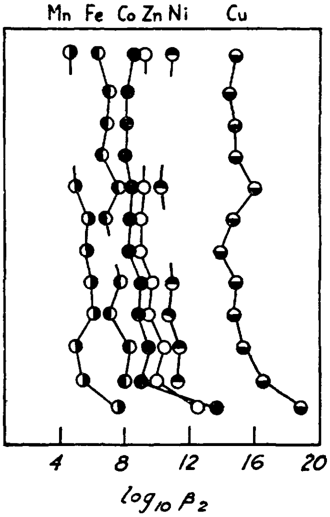


FIG. 2. *Ligands of type* $NH_2\cdot CHR\cdot CO_2H$.

Ligand	p*K*
Asparagine	8·9
Serine	9·15
Methionine	9·21
Phenylalanine	9·24
Tryptophan	9·39
Valine	9·72
Leucine	9·74
Glycine	9·8
D-Alanine	9·87
Norleucine	9·96
Proline	10·60
Histidine	9·18

The points in the Figure, reading from top to bottom, are in the same order as the ligands in the list.

Absorption Spectra of Metal Complexes.—On chelation to a metal there is generally a bathochromic shift in the wave-length of maximum absorption of the ligand, and Yamasaki and Sone (*Nature*, 1950, **166**, 998) comment on the fact that the magnitude of the shift in the case of acetylacetone ($\lambda_{max.}$ in EtOH = 273 mμ) amounts to 9, 21, 23, and 7 mμ on chelation with cobalt, nickel, copper, and zinc, respectively, and so follows the Irving–Williams order of stabilities: this might be expected if the extent of wave-length displacement indicated the degree of polarisation or deformation of the ligand. Similar regularities have been observed in the absorption spectra of metal complexes of 8-hydroxyquinoline-5-sulphonic acid (Marsh, *loc. cit.*), but a comparative study of other ligands (cf. *inter alia*, phthiocol; Geyer and Smith, *J. Amer. Chem. Soc.*, 1941, **63**, 3071) suggests that any over-simplified treatment of absorption spectra may be misleading, especially when chelation modifies the electron levels of the central metal ion (cf. Irving and Williams, *Analyst*, *loc. cit.*).

Validity of Mellor and Maley's Order and Similar Empirical Sequences.—Reference to the extensive data presented in Tables 1 and 2 shows that the empirical stability order noted by Mellor and Maley has only a very limited validity, for it does not remain the same when the ligand is changed. Thus, the order Mn < Fe < Cd < Co < Zn < Ni < Cu, valid for (almost) all amino-acids, fails for 8-hydroxyquinoline, where the position of iron and cadmium must be interchanged. With nitroacetic acid and diethylenetriamine, cadmium and cobalt are out of place; with salicylaldehyde, nitriloacetic acid, 8-hydroxquinoline-5-sulphonic acid, and histidine, cobalt and zinc exchange places; and with riboflavin (X) and folic acid (XI) no less than three pairs of metals must be interchanged to restore a

TABLE 2. *Successive stability constants of transition-metal complexes.*

	Mn	Fe	Co	Ni	Cu	Zn
Ammonia.[1, 3]						
log K_1	—	—	2·11	2·79[2]	4·15	2·37
log K_2	—	—	1·63	2·24	3·50	2·44
log K_3	—	—	1·05	1·73	2·89	2·50
log K_4	—	—	0·76	1·19	2·13	2·15
log K_5	—	—	0·18	0·75	−0·52	—
log K_6	—	—	−0·62	0·03	—	—
Pyridine.[4]						
(N/Z log K + 1·74	(0·1)	0·6	1·1	1·7	3·2	1 9
Triethanolamine.[5]						
log K_1	—	—	1·73	—	4·23	2·00
Ethylenediamine.[6]						
log K_1	2·73	4·28	5·89	7·52	10·55	5·71
log K_2	2·06	3·25	4·83	6·28	9·05	4·66
log K_3	0·88	1·99	3·10	4·26	−1·0[7]	1·72
Propylenediamine.[8]						
log K_1	—	—	—	7·41	10·58	5·89
log K_2	—	—	—	6·30	9·08	4·98
log K_3	—	—	—	4·29	—	1·70
NN′-*Dimethylethylenediamine.*[9]						
log K_1	—	—	—	6·67	9·69	—
log K_2	—	—	—	3·85	6·63	—
1 : 3-*Diaminopropane.*[10]						
log K_1	—	—	—	—	9·77	—
log K_2	—	—	—	—	7·17	—
1 : 3-*Diaminopropane-2-ammonium ion,* $(NH_2{\cdot}CH_2)_2CH{\cdot}NH_3^+$ (*Hptn*$^+$).[11]						
log K_1	—	—	4·1	6·0	8·8	4·25
Histidine.[12]						
log K_1	4·23	—	7·52[13]	—	10·56	7·14
log K_2	3·51	—	6·34	—	7·77	5·74
1 : 2 : 3-*Triaminopropane.*[11]						
log K_1	—	—	6·8	9·3	11·1	6·75
log K_2	—	—	—	—	9·0	—
Diethylenetriamine.[14]						
log K_1	—	—	8·1	10·7	16·0[16]	8·90
log K_2	—	—	6·0	8·25	5·3	5·5
Triethylenetetramine ion, $NH_2{\cdot}C_2H_4{\cdot}NH{\cdot}C_2H_4{\cdot}NH{\cdot}C_2H_4{\cdot}NH_3^+$ (*Htrien*$^+$).[15]						
log K_1	—	—	6·8	8·9	14·0	7·3
Triaminoethylamine.[17]						
log K_1	5·8	8·8	12·8	14·8	18·8	14·65
Triethylenetetramine.[15]						
log K_1	4·9	7·8	11·0	14·0	20·4	12·1
β-Alanine.[18, 19]						
log K_1	—	—	—	4·63	7·13	—
log K_2	—	—	—	3·40	5·47	—
log β_2	—	—	~7[21]	8·03	12·6[20]	~4[21]
Sarcosine.[22]						
log K_1	—	—	—	4·96	7·32	4·12
log K_2	—	—	—	3·68	2·84	2·96
DL-*Valine.*[23]						
log K_1	2·84	—	4·57	—	7·93	5·00
log K_2	2·72	—	3·67	—	6·52	4·10
log β_2	5·56	6·8[21]	8·6[21]	—	15·1[21]	9·10
Leucine.[23]						
log K_1	2·78	—	4·55	7·89	4·92	—
log K_2	2·67	—	3·71	6·45	4·01	—
Norleucine.[21]						
log β_2	~5	8·6	9·4	11·1	15·5	10·4
Phenylalanine.[21]						
log β_2	—	6·3	7·9	—	14·9	—
Asparagine.[21, 24]						
log β_2	~4·5	6·5	8·4	10·6	14·9	8·7
Serine.[21]						
log β_2	—	7·0	8·0	—	14·6	—
Methionine.[21]						
log β_2	—	6·7	7·9	—	14·7	—

TABLE 2. (*Continued.*)

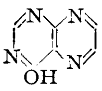
	Mn	Fe	Co	Ni	Cu	Zn
Proline.[21]						
log β_2	~5·5	8·3	9·3	11·3	16·8	10·2
Tryptophan.[21]						
log β_2	~5	7·6	8·5	10·2	15·9	9·3
Taurine.[21]						
log β_2	—	0	~4	—	~8	—
Glycylglycine.[52]						
log K_1	2·15	—	3·49	4·49	6·04	3·80
log K_2	—	—	2·39	3·42	5·62	2·77
Nitroacetic acid.[26]						
log K_1	—	—	0·00	0·06	0·44	0·03
Nitriloacetic acid.[27]						
log K_1	7·44	8·84	10·61	11·26	12·68	10·45
Ethylenediaminetetra-acetic acid.[23]						
log K_1	13·47	14·22	16·10	18·45	18·38	16·15
2 : 2′-*Dipyridyl*.						
log K_1	—	4·20 [29]	—	—	—	—
log K_2	—	<5	—	—	—	—
log K_3	—	$>7·3$	—	—	—	—
log β_3	—	16·53	—	—	17·85 [30]	—
1 : 10-*Phenanthroline*.[34]						
log K_1	—	5·9 [31]	—	—	—	6·43 [33]
log K_2	—	—	—	—	—	5·72
log K_3	—	—	—	—	—	4·84
log β_3	—	21·3 [32]	—	—	—	17·0
Acetylacetone.[35]						
log K_1	—	—	6·30	6·82	—	—
log K_2	—	—	4·88	5·20	—	—
Tropolone.[49]						
log K_1	—	—	7·04	7·61	very large	7·48
log K_2	—	—	5·71	6·03	7·83	6·29
Salicylaldehyde.[36]						
log K_1	3·73	4·22	4·67	5·22	7·40	4·50
log K_2	3·06	3·40	3·63	3·97	5·91	3·60
Salicylaldehydesulphonic acid.[37]						
log K_1	—	—	3·42	3·79	5·35	3·00
log K_2	—	—	~2·2	2·77	3·92	~2·4
8-*Hydroxyquinoline*.[38]						
log K_1	—	9·83	10·85	11·65	15·0	10·91
log K_2	—	9·01	9·70	10·35	14·0	9·90
log K_1 [39]	6·8	8·0	9·1	9·85	12·2	too insol.
8-*Hydroxyquinoline*-5-*sulphonic acid*.[40]						
log K_1	—	—	9·25	—	11·5	8·70
log K_2	—	—	7·45	—	10·7	7·20
4-*Hydroxypteridine* (IX).[41]						
log K_1	2·35	3·40	3·84	4·36	4·82	3·41
log K_2	2·12	2·70	2·81	3·5	4·72	pptn.
Riboflavin (X).[42]						
log K_1	3·44	7·12	3·88	4·11	6·62	5·58
Folic acid (XI).[41]						
log β	6	7·93	8·12	9·00	7·82	7·5
Cyanide ion.[43]						
log K_1	—	2 ?	4·9	4·7	8 ?	6·5
Hydroxide ion.[44]						
log K_1	2·83	—	3·6	3·8	7·8	4·5
Sulphate ion,[45]						
log K_1	2·28	—	2·47	2·40	2·3 [48]	2·40
Thiosulphate ion.[45]						
log K_1	1·95	—	2·05	2·06	—	2·40
Oxalic acid.[46]						
log K_1	3·89	—	4·70	5·30	6·16 [47]	4·89
Malonic acid.[46]						
log K_1	3·29	—	3·72	4·01	5·75 [47]	3·68

TABLE 2. (*Continued.*)

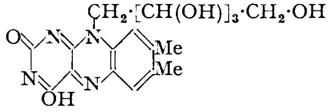
	Mn	Fe	Co	Ni	Cu	Zn
Succinic acid.[47]						
log K_1 ……………	—	—	—	—	3·33	2·48
Glutaric acid.[47]						
log K_1 ……………	—	—	—	—	3·16	2·30

[1] All values valid for 2M-NH_4NO_3 at 30°; Bjerrum, *op. cit.* For copper–*n*-butylamine complexes, see *idem, Acta Chem. Scand.*, 1950, **4**, 997. [2] Calvin (unpublished work quoted by Frank and Evans, *J. Chem. Phys.*, 1945, **13**, 507) reports log β_6 = 9·13 (23°) and 8·81 (30°). [3] For nickel–methylamine complexes Calvin (*loc. cit.*) reports log β_6 = 8·64 (15°) and 9·12 (35°). [4] Bjerrum's values [*Chem. Reviews*, 1950, **46**, 381 (Table 4)] are quoted. Measurements for Cu at 25° in 0·5M-Py,HNO_3 gave log K_1 = 2·41, log K_2 = 1·88, log K_3 = 1·14, and log K_4 = 0·60, whence log β_4 = 6·03 (Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, **2**, 297). Bruehlman and Verhoek (*J. Amer. Chem. Soc.*, 1948, **70**, 1401) give slightly higher values for 0·5M-KNO_3 at 25°, leading to log β_4 = 6·54. For Cu and γ-picoline complexes (*idem, ibid.*) log β_4 = 7·74 at 25°. [5] Valid for 0·5N-salt at 25° (Bjerrum, *Nord. Kem.*, Lund, 1947, p. 227). [6] All values valid for N-KCl at 30°. Data for Mn, Fe, and Co from Bjerrum, *op. cit.*, p. 293, and for Ni, Cu, and Zn from Carlson and McReynolds (*J. Amer. Chem. Soc.*, 1945, **67**, 1334). Additional data for Ni (Bjerrum, *op. cit.*), Cu (Bjerrum and Nielsen, *loc. cit.*), Zn (Bjerrum and Andersen, *Kgl. Danske Videnskab. Selsk.*, 1945, **22**, 3). [7] In N-KNO_3 at 25° (Bjerrum and Nielsen, *loc. cit.*). [8] All values valid for 30° (Carlson and McReynolds, *loc. cit.*); Ni and Zn in 0·5M-KCl, Cu in 0·5M-KNO_3. Laitinen, Onstott, Bailar, and Swann (*J. Amer. Chem. Soc.*, 1949, **71**, 1550) obtained log β_2 = 20·17 by polarography in 0·1M-KNO_3 at 25°. [9] Irving and Griffiths, in preparation. [10] Irving, Williams, Ferrett, and Williams (in prepn.) by polarography found log β_2 = 16·67 at 25°. [11] Valid for 0·1M-KCl at 20° (Prue and Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 995). [12] Data for 25° by Maley and Mellor (*Nature*, 1950, **165**, 453) and Mellor and Maley (*Austral. J. Sci. Res.*, 1949, **2**, 579). [13] Calculation from measurements by other workers gives log β_2 = 11·96 (cf. Mellor and Maley, *loc. cit.*). However, Albert (*Biochem. J.*, 1952, **50**, 690) comments on irregular behaviour observed when titrating histidine with either cobalt or copper; his values of log β_2 at 20° are 9·3 (Fe), 15·9 (Ni), and 12·0 (Zn), with log K_1 < 4 for Mn. [14] Valid for 0·1N-KCl at 20° (Prue and Schwarzenbach, *loc. cit.*, p. 985). In 1·00M-KNO_3 + KCl the value log K_1 = 16·11, log K_2 = 3—6 at 30° and log K_1 = 15·63 at 40° have been reported for Cu, and log K_1 = 10·81 (30°) and 10·54 (40°), log K_2 = 8·14 (30°) and 7·83 (40°) for Ni by Jonassen, LeBlanc, Meibohm, and Rogan (*J. Amer. Chem. Soc.*, 1950, **72**, 4968). [15] Valid for 0·1N-KCl at 20°(Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 974). In M-KNO_3 the values log K_1 = 14·3 (30°) and 14·0 (40°) for Ni, and 20·6 (30°) and 20·1 (40°) for Cu complexes of triethylenetetramine have been reported by Jonassen and Meibohm (*loc. cit.*). For Ni, log K_2 = 5·6 (30°) and 5·4 (40°). [16] The value log β_2 = 20·85 at 25° in 0·1N-KCl has been obtained polarographically. [17] Valid for 0·1N-KCl at 20°; Prue and Schwarzenbach (*loc. cit.*, p. 963; Ackermann and Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 1543). [18] Data for glycine and α-alanine are given in Table 1. [19] Glass-electrode measurements at 20° (Irving, Williams, Ferrett, and Williams, *loc. cit.*). [20] For Cu, Albert reports log β_2 = 12·9 (*Biochem. J.*, 1950, **47**, 531), and we find 12·7 (8) by polarography (Irving *et al.*, *loc. cit.*). [21] Albert (*Biochem. J.*, 1950, **47**, 531). [22] Unpublished observation. [23] Data for 25° by Maley and Mellor (cf. ref. 12). [24] For copper and aspartic acid, Li and Doody (*J. Amer. Chem. Soc.*, 1950, **72**, 1891) report log β_2 = 15·20 by polarography at 25° (μ = 1·0) but Albert [20] comments on certain complications, reporting log β_2 as 8·5 (Fe), 10·7 (Co), 12·7 (Ni), and 10·4 (Zn), with log K_1 = 4·0 for Mn. [25] Data for 25° (Monk, *Trans. Faraday Soc.*, 1951, **47**, 297). [26] Pedersen (*Acta Chem. Scand.*, 1949, **3**, 676). [27] Valid for 0·1N-KCl at 20° (Schwarzenbach and Freitag, *Helv. Chim. Acta*, 1951, **34**, 1492). By polarography log K_1 (Zn) = 10·35 at μ = 0·2 (Koryta and Kössler, *Coll. Trav. chim. Tchecosl.*, 1950, **15**, 241). [28] Valid for 0·1N-KCl at 20° (Schwarzenbach and Freitag, *loc. cit.*). Other values [27] for Fe, Cu, and Zn are 14·4(5), 18·8(6), and 16·5(8), respectively. [29] Data for 35° (Baxendale and George, *Trans. Faraday Soc.*, 1950, **46**, 55, 736); this includes values for other temperatures. Krumholtz (*J. Amer. Chem. Soc.*, 1945, **71**, 3654) reports log K_1 = 4·36. [30] Polarographic measurements in 0·1M-KNO_3 at 25° (Onstott and Laitinen, *ibid.*, 1950, **72**, 4724). [31] Data for 25° by Kolthoff, Leussing, and Lee (*ibid.*, p. 2173). [32] Valid for 25° (Lee, Kolthoff, and Leussing, *ibid.*, 1948, **70**, 2348). [33] Valid for 25° (*idem, ibid.*, 1951, **73**, 390). [34] Other less reliable values for complexes of iron with dipyridyl and phenanthroline are quoted in refs. 29—33. For iron and 2-methylphenanthroline (Irving, Cabell, and Mellor, in preparation) log K_1 = 4·2, log K_2 = 3·7, and log K_3 = 2·9. [35] Measured in 50% dioxan–water mixtures at 25° (Mellor and Maley, *Austral. J. Sci. Res.*, 1949, **2**, 92). [36] Valid for 50% dioxan–water at 25° (*idem, ibid.*; *Nature*, 1948, **161**, 436). [37] Data for 25° by Calvin and Melchior (*J. Amer. Chem. Soc.*, 1948, **70**, 3270). For Cu at 40°, log K_1 = 5·64 and log K_2 = 4·15. The stability constants of a large number of complexes of Cu with substituted *o*-hydroxy-benz- and -naphth-aldehydes are given by Calvin and Wilson (*ibid.*, 1945, **67**, 2003). [38] Valid for 70% dioxan–water at 25° (cf. ref. 35). [39] Values obtained in water, presumably at low $\bar{n}$ values, by Albert (*Proc. Biochem. Soc.*, 1950, **47**, xxvii). [40] Data for 25° by Mellor and Maley (*Austral. J. Sci. Res.*, 1949, **2**, 579). [41] Albert (*Proc. Biochem. Soc.*, 1950, **46**, ix; and private communication). [42] Albert (ref. 39) and personal communication). [43] Bjerrum's values for (N/Z) log K + 1·74 are quoted from ref. 4, Table 4. [44] Calculated from hydrolysis measurements at 100° by Kullgren (*Z. phys. Chem.*, 1913, **85**, 466). [45] Denny and Monk (*Trans. Faraday Soc.*, 1951, **47**, 992, and refs. therein). [46] Monk (*ibid.*, p. 297. [47] Peacock and James (*J.*, 1951, 2233). This paper includes stability constants for copper complexes of many other aliphatic acids. [48] Fronaeus (*Acta Chem. Scand.*, 1950, **4**, 72) gives values for K_1, K_2, and K_3. [49] Fernelius, Bryant, and Douglas (*Nature*, 1952, **170**, 247). Valid for 50% dioxan–water at 30°.

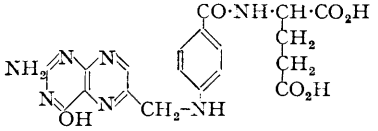
regularly increasing sequence of stability constants. Further examples of changes in the relative stability of iron, zinc, and cadmium complexes are detailed in Table 4.



(IX)



(X)



(XI)

From a consideration of the stability constants of a number of metals with glycine, alanine, glycylglycine, and several carboxylic acids, Monk (*Trans. Faraday Soc.*, 1951, **47**, 297) concluded that "the tendency to form complexes is in the order Cu $>$ Ni $>$ Zn $>$ Pb $\approx$ Co $>$ Mn $>$ Mg $>$ Ca $>$ Sr $>$ Ba, . . . although there are many gaps to fill in to see if this is universally true for all organic acids." This extended sequence has, however, little generality and it fails with, *e.g.*, the phenolic ligand salicylaldehyde, for which the order is $\mathrm{Cu} > \mathrm{Ni} > \underline{\mathrm{Pb} > \mathrm{Co}} > \underline{\mathrm{Zn}} > \underline{\mathrm{Mg} \approx \mathrm{Mn}}$ (points of divergency are underlined), with nitriloacetic acid $(\underline{\mathrm{Cu} > \mathrm{Pb} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Zn}} > \mathrm{Mn} > \underline{\mathrm{Ca} > \mathrm{Mg}} > \mathrm{Sr} > \mathrm{Ba})$, ethylenediaminetetra-acetic acid $(\underline{\mathrm{Ni} > \mathrm{Cu} > \mathrm{Pb} > \mathrm{Zn} \approx \mathrm{Co}} > \mathrm{Mn} > \underline{\mathrm{Ca} > \mathrm{Mg}} \approx \mathrm{Sr} > \mathrm{Ba})$ and nitroacetic acid (p. 3196), while all the evidence against an invariable order Ni $>$ Zn $>$ Co presented above in criticism of Mellor and Maley's thesis is equally applicable here. Though the stability of alkaline-earth complexes has been fully discussed by one of us elsewhere (Williams, *loc. cit.*), it should be emphasised that the "natural" sequence Mg $>$ Ca $>$ Sr $>$ Ba does not hold for many complexones or indeed for all the ligands to which Monk refers (*e.g.*, glycylglycine and malic acid).

Although it is apparent that the empirical stability orders of Mellor and Maley, or of Monk, and of other authors, do not hold for all the ligands cited in Tables 1 and 2 and are often at variance with stability orders established kinetically (cf. p. 3197), yet the Irving–Williams order appears to hold almost without exception. We shall therefore proceed to show how theoretical considerations lead to just this stability sequence, and indeed predict certain points of divergence such as the abnormally high stability of certain ferrous complexes (*e.g.*, those with dipyridyl and phenanthroline, but not with ethylenediamine) and the anomalous low stability of certain copper complexes (*e.g.*, those of ethylenediaminetetra-acetic acid, triaminopropane, and folic acid) which have been observed experimentally.

Factors controlling the Stability of Metal Complexes.—No simple picture of interaction between ligand and metal ion in terms of purely coulombic forces will explain why, *e.g.*, no ammines of Na^+ exist while those of Cu^{++} and Ag^+ are stable in aqueous solution, for the dipole moment of water is larger than that of ammonia. However, ammonia ($\alpha = 2{\cdot}4 \times 10^{-24}$) is more polarisable than water ($\alpha = 1{\cdot}5 \times 10^{-24}$), and by considering ion–dipole and induced dipole interactions, Van Arkel and Boer (*Rec. Trav. chim.*, 1928, **47**, 593) were able to show that the tendency towards ammine formation should increase with decreasing radius and increasing deforming power of the cationic partner. Table 3 shows that the ionic radii of bivalent ions of the first transition series decrease slightly but regularly from manganese to copper and increase again at zinc. The heat of hydration of these ions follows the same sequence (Table 3), so the stability of aquo-complexes of bivalent transition metals follows the same order as that found for other ligands reported above. But if this sequence is extended to include other bivalent ions, the order of decreasing ionic radius will not necessarily coincide with the order of increasing complex stability. For instance, the ions Mg^{++} and Ca^{++} of the alkaline-earth metals have radii respectively smaller and greater than any in the first transition series from manganese to copper, yet their complexes with any given ligand are invariably less stable than those formed by the bivalent transition metal ions. Indeed, Fig. 3 shows that, while the heats of hydration of bivalent ions of the alkaline-earth metals lie on a smooth curve when plotted against the reciprocal of their ionic radii, those of the transition metals deviate in the direction of higher stability and to an extent which closely follows the Irving–Williams order. This disposes of any naive suggestion that complex stability in this series is governed by purely electrostatic forces. A similar effect can be observed among hydroxy-complexes. Davies (*J.*, 1951, 1256) has shown that if complexes between cations and hydroxyl ions were purely electrostatic in character, a simple relation would exist between their dissociation constants, K, and the radius, r, of the unhydrated ion and its valency, z. For the ions Li^+, Na^+, Mg^{++}, Ca^{++}, Ba^{++}, and La^{+++} this takes the form $pK = 0{\cdot}607z^2/r - 1{\cdot}156$. Fig. 3 shows part of this plot for the ions Mg^{++}, Ca^{++}, and Ba^{++}, and it is at once obvious that hydroxy-complexes of the transition metals (and of other bivalent ions such as Pb^{++} and Hg^{++}) are much more stable than can be accounted for by purely electrostatic forces of attraction. A similar conclusion would be drawn from the plot of the stability of metal ammines in aqueous solution, those of the transition metals being very much more stable than could have been expected from the measured values for Mg^{++} and Ca^{++} for which $\log \beta_6 = -3{\cdot}3$ and $-5{\cdot}7$ respectively (Bjerrum, *op. cit.*, p. 191; cf. Table 2). In this case it must not be overlooked that stabilities are measured relatively to those of aqueous complexes. But since these stabilities increase regularly along the series manganese to copper (cf. Table 3) it follows that there is a similar monotonic rise in absolute stability from manganese to copper in the case of the ammine complexes, since the increments in relative stability on replacing water by ammonia molecules (cf. Fig. 1) increase in the same order.

TABLE 3. *Bivalent ions of the first transition series.*

	Mg	Mn	Fe	Co	Ni	Cu	Zn	Cd	Ca
Radius, Å	0·66	0·78	0·76	0·74	0·73	0·72	0·72	0·96	0·99
E_2, kcal.	525·7	534·7	558·6	586	599	648·6	633·5	599·9	417·5
H, kcal.	464·0	444·7	467·9	497	507	507·2	491·5	436·5	381·9

The data are taken from Brewer, Bromley, Gilles, and Lefgren (National Nuclear Energy Series, Division IV–19B, McGraw Hill, 1950, p. 154); E_2 refers to the total ionisation potential at 25° for the process $M\ (gas) \longrightarrow M^{++}\ (gas) + 2e$. The third row gives values for the heat of hydration of gaseous ions at 25° corresponding to the equation $M^{++}\ (gas) + aq. \longrightarrow M\ (aq.)^{++}$. Using the method of Kordes (*Z. phys. Chem.*, 1939, **43**, 213), we calculate a radius of 0·71 Å for Cu^{++}.

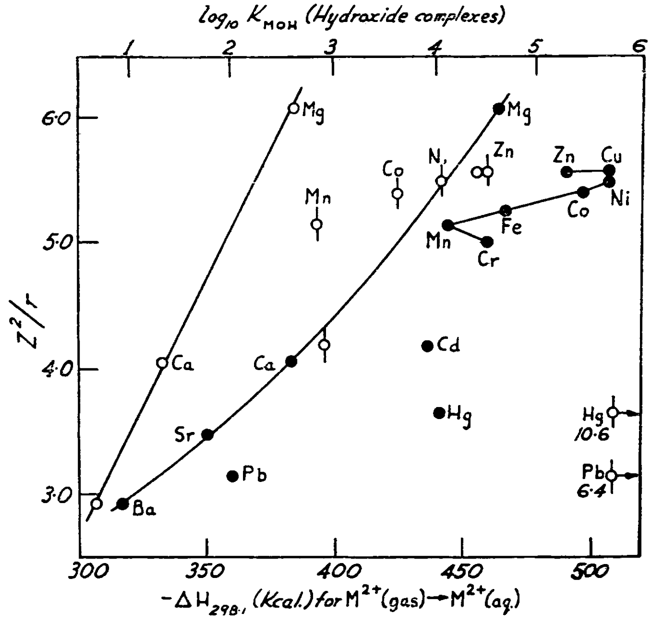


FIG. 3. *Hydroxy- and aquo-complexes of bivalent ions.*

○ Hydroxide complexes.

ϙ Values calc. from Kullgren's data, ref. 60.

● Heats of hydration.

That replacement of water by a more polarisable ligand should lead to an enhanced stability is not surprising. That the *increments* in stability should increase monotonically along the Irving–Williams series (but not necessarily along a series including other bivalent ions even when arranged in order of diminishing radius) can only mean that some additional stabilising factor is in operation which increases in extent as we move along the series : this must be the tendency towards the formation of a covalent bond between metal and ligand. This point is brought out more clearly in Fig. 4, which shows that, while the stability sequence follows the Irving–Williams order for all the ligands represented, the stability increment from metal to metal is greatest for nitrogen-type ligands (*e.g.*, ethylenediamine), less for nitrogen–oxygen-type ligands (*e.g.*, glycine), and still less for oxygen–oxygen-type ligands (*e.g.*, salicylaldehyde and oxalic acid). Indeed, the difference between the " slopes " of the stability graphs leads to the important result that the order of stability ethylenediamine > amino-acids > salicylaldehyde, which holds for the elements cobalt to zinc, is actually reversed for manganese. Although an invariable order of stability may well be possible for different ligands acting with a limited series of metals, yet an invariable order for different metals forming complexes with an arbitrary sequence of ligands is highly improbable. Furthermore, the more electropositive the co-ordinating atom of the ligand, the greater the stability increment from metal to metal; this emphasises the significance of covalent bonding in determining the stability of complexes.

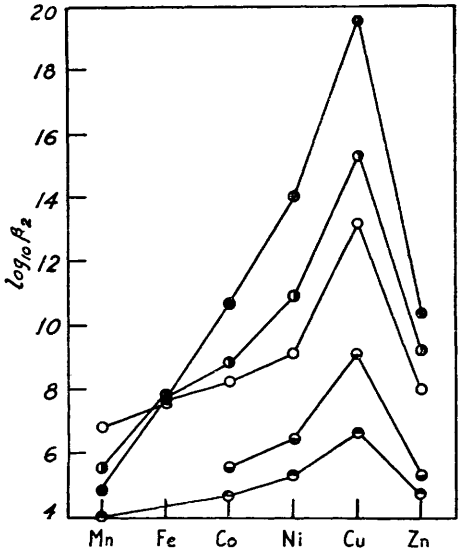


FIG. 4. *Transition-metal complexes with various types of ligand.*

○ Salicylaldehyde.
◑ Glycine.
● Ethylenediamine.
⊖ Salicylaldehydesulphonic acid.
◓ Oxalic acid (values of $\log_{10}\beta_1$).

Now any more elaborate picture of co-ordination must take into account the available electronic levels of the (acceptor) metal ion and the electron availability of the (donor) ligand. Thus, Walsh (*Proc. Roy. Soc.*, 1951, **207**, *A*, 13; cf. *J.*, 1948, 398) relates the strength of the co-ordinate link (among other factors) to the product $\chi_L\chi_M$, where χ_L and χ_M are the effective electronegativities of the metal and ligand respectively. As a measure of the electron-affinity of the acceptor cation, we may adopt the second ionisation potential corresponding to the process $M(gas) \longrightarrow M^{2+}(gas) + 2e$. This refers to the free atom and reflects the ground-state energy levels of the electrons. The strength of the co-ordinate link may thus be related to the loss of potential energy when electrons are donated from the high-energy levels of the ligand to the lower-energy levels of the metal ion. Such a picture is, of course, oversimplified, for on co-ordination both sets of levels are mutually adjusted and the effect of bond polarity must be taken into account (cf. Walsh, *loc. cit.*). Nevertheless, the clear correlation between ionisation potential and complex stability must not be underestimated, and it is of the greatest significance that, as Table 3 shows, the second ionisation potential rises along the transition series to a maximum at copper and falls again at zinc. This correlation with the stability of transition-metal complexes was first pointed out by us in 1948 (*Nature*, **162**, 146) and has since been noted by Schwarzenbach, Ackermann, and Prue (*ibid.*, 1949, **163**, 723), and by Calvin and Melchior (*J. Amer. Chem. Soc.*, 1948, **70**, 3270) in connection with their measurements of complexes of salicylaldehyde-5-sulphonic acid with the four metals copper, nickel, cobalt, and zinc, although in this case reference was made only to the second-stage ionisation process, $M^+ \longrightarrow M^{++} + e$, which clearly has less fundamental significance.

In our picture of co-ordination, the electron donation from ligand to cation must bring about a reduction in its formal charge. This process is in fact that envisaged in Pauling's *postulate of the essential neutrality of atoms* (*J.*, 1948, 1461; Volume commemoratif Victor Henri, Liege, 1947, p. 1), but the use of the second ionisation potential ($M \longrightarrow M^{++}$) as a measure of the driving force of this process supplies a quantitative element which is absent from this theory. Indeed, in its present form, Pauling's theory fails to account even qualitatively for the order of stability of metal complexes. For, from considerations of the standard electrode potentials of the bivalent ions from V^{2+} to Zn^{2+} (which form a measure of the free-energy change in transference of metal from the solid lattice to hydrated ions in solution), and the stability of their respective metal lattices as indicated by his values for their metallic valencies, Pauling concludes (Volume commemoratif, *loc. cit.*) that the hydrated ions of Fe^{++}, Co^{++}, and Ni^{++} "are associated with a special instability" and that there is "a much greater instability for the cupric and zinc ions which causes the electrode potential to be lowered by as much as 1·5 volts." This deduction conflicts with the experimental results (Table 3), which place the stability of the hydrates in the familiar order $Mn < Fe < Co < Ni < Cu > Zn$.

Even the additional assumptions (*idem, loc. cit.*) that maximum bond stability in the complex ML_n is achieved when the number of available strong orbitals, m, is equal to n (when unsynchronised resonance is permitted) while less stable structures result when $m < n$ (since only unsynchronised resonance is then possible), do not permit of the reliable prediction of any orders of relative stability for complexes of different transition metals with the same ligand. This is scarcely surprising, since the basic simplifying assumption that the electronegativities of all the transition metals are about 1·5 units necessarily ignores the important specific features of metal–ligand interaction which we know to be of paramount importance.

Although Pauling's theory does not predict the Irving–Williams order and cannot explain why it holds so extensively, we suggest that it is essentially a consequence of the fact that the two parameters which respectively serve as a guide to the magnitude of the electrostatic and covalent interactions, *viz.*, the reciprocal of the ionic radius, and the second ionisation potential, both increase monotonically throughout the series from manganese to copper. Thus, if water is replaced by a ligand of greater electron-donating power, the gain in stability will increase with the second ionisation potential of the metal concerned. If water is replaced by a ligand with a formal negative charge, the stability increment through purely electrostatic forces will increase as the radius of the cation decreases, *i.e.*, in the same order. Hence, in our limited sequence, provided there is any increase in interaction energy on replacement of water by some other ligand, there is bound to be a monotonic gain in stability in passing along the series from manganese to copper irrespective of the extent to which either or both of these factors may operate. For the same reason the stability order $Cu > Zn$ must always be true, in agreement with experience. But there is no such invariable relation to be expected between the stability of zinc complexes and those of the other transition metals, since zinc has a higher ionisation potential but a lower radius than, *e.g.*, nickel and cobalt. Orbital stabilisation, which generally increases the stability of copper complexes and sometimes those of ferrous iron, will be considered later (p. 3206).

Mellor and Maley (*loc. cit.*) naturally considered the significance of ionic radius and electronegativity in discussing their empirical order of stability which included elements such as Cd, Pd, Pb, Mg, etc., as well as members of the first transition series. Their failure to observe any clear correlation between complex stability and ionic radius or any other parameter such as electronegativity which might be related empirically to this magnitude) springs solely from the inclusion in their series of ions which perturb the dual monotonic sequences of ionic radius and ionisation potential which characterise the metals of the Irving–Williams sequence. If, for example, we were to include cadmium in our series, and note that the ionic radius of cadmium is greater than that of nickel although the ionisation potentials are almost identical (Table 3), it is clear that the relative stabilities of cadmium and nickel complexes must depend upon the nature of the ligand, and no invariable order could be expected. Consider first the hydroxide complexes. For this ligand, OH^-, there is an increase both in formal charge and in electron-donating power, compared with water, so the order will be Ni $>$ Cd. When water is replaced by the iodide ion, however, there is admittedly a slight increase in electron-donating power, but since the iodide ion is so much larger than a water molecule the decrease in electrostatic interaction due to the greater charge separation will be more significant with the smaller nickel ion, and since the gain in covalent interaction energy is much the same (ionisation potentials Ni $\cong$ Cd) the stability order becomes Cd $>$ Ni. An obvious extension of this argument will show why all bivalent ions of large radius and high ionisation potential, *e.g.*, Pb, Hg, Pt, and Sn, should tend to form strong complexes with iodide, bromide, and chloride ion, whereas ions with large radius and low ionisation potentials, *e.g.*, Ba, Sr, and Ca, will not. With ions of moderately small radius and moderately high ionisation potential, changes of ligand produce changes in the relative significance of the two factors (electrostatic and covalent interaction) and no reliable prediction of an order of stability can be attempted save in the favourable case—exemplified by the bivalent ions of the first transition series from Mn to Cu—where the two factors invariably co-operate.

Factors which may cause a Derangement of the Irving–Williams Order.—The formation in solution of the most stable co-ordination compound which can be formed from a given hydrated ion and ligand molecules is attained by the interplay of various factors which can be roughly analysed as follows under three headings. (i) There is the tendency to pack as many ligands as possible around the central ion so as to obtain the maximum total interaction by way of the greatest number of individual interactions. This factor is limited by the " interference volume " of the ligand molecules compared with that of the water molecules which they must displace from around the central ion. (ii) The atomic electrons will tend to remain in their most stable ground state. This factor is often opposed by factor (iii), which is the tendency to make each individual interaction as strong as possible through the use of the strongest possible hybrid bonding orbitals.

Bjerrum (*op. cit.*, p. 58) gives great weight to the view that " in the main, metal ammine formation proceeds statistically " (cf. Burkin, *Quart. Reviews*, 1951, **5**, 1). We would agree that a ligand would replace water statistically from its co-ordination positions round a cation in solution provided that (*a*) the interference volume of the ligand did not differ significantly from that of water, (*b*) the electrostatic repulsion between the new ligands did not differ significantly from that between water molecules, and (*c*) there was no change in orbital configuration at any stage during complex formation. Clearly, cases of strictly statistical addition and replacement of ligands must be rather exceptional. Consider, for example, the co-ordination of amines to nickel, zinc, and copper, respectively. In the case of nickel, addition of ammonia proceeds uniformly up to a co-ordination number $N = 6$, and magnetic data do not suggest any changes in the number of unpaired electrons throughout this process. The same is true for ethylenediamine and 1 : 10-phenanthroline which form tris-complexes, and the effect of complex formation is only to quench the orbital contribution and to reduce the total magnetic moment from $\sim$3 to 2·83 Bohr magnetons (Russell, Cooper, and Vosburg, *J. Amer. Chem. Soc.*, 1943, **65**, 1301). With zinc, however, only four molecules of ammonia can be co-ordinated and, as these are certainly not added statistically (cf. Table 2, and Bjerrum, *op. cit.*), it seems possible that they are replacing six water molecules, and in an irregular way. The zinc ion normally uses $4s4p^3$ tetrahedral orbitals and the high ionisation potential of the metal coupled with the electronegativity of nitrogen must favour, at some stage, the attachment of ammonia molecules through these hybrid bonds rather than the weaker attachment of water molecules: factor (ii) predominates here. Ethylenediamine has a smaller interference volume than ammonia (Irving, Williams, Ferrett, and Williams, *loc. cit.*), and two molecules co-ordinate readily and a third with markedly greater difficulty, while 1 : 10-phenanthroline molecules displace water to give a tris-complex of about the stability expected on statistical grounds from a knowledge of the stability of the 1 : 1 and 1 : 2 complexes (cf. Table 2). With ethylenediamine, and still more so with phenanthroline, factor (i) appears to prevail—unless $4s4p^34d^2$ orbitals are called into play. In the case of copper the use of dsp^2 orbitals would favour four coplanar bonds, though there is the possibility of weaker interaction in the plane perpendicular to these (cf. Kuhn, *J. Chem. Phys.*, 1948, **16**, 727). Possibly $4s4p^24d$ hybridisation is used, the ground state of the Cu^{2+} ion remaining completely unchanged on complex formation. But it is only with great reluctance that a fifth molecule of ammonia or a third molecule of ethylenediamine is co-ordinated (Table 2) so that factor (ii) is here of paramount importance.

In the absence of orbital stabilisation (factor iii) both the number and the kind of hybrid orbitals available for bonding are to a large extent determined independently of the nature of the ligand. This implies that both the maximum co-ordination number and the favoured stereochemistry will normally be independent of the nature of the ligand. Conformability with these restrictions, or exceptional behaviour, will be of equal importance when considering the validity of stability orders; behaviour of either type will be of significance in, *e.g.*, analytical chemistry. Of even greater theoretical and practical importance are those cases discussed in the next section, where factor (iii) dominates the others.

Orbital Stabilisation.—Since our stability order is largely independent of the nature of the ligand concerned, the observed correlation with the second ionisation potential may be taken as indicating that co-ordination has not altered the electronic ground states of the metal ions, or that any modifications are of secondary importance. That this is an over-simplification is shown immediately by the fact that the cupric ion utilises dsp^2 orbitals in all its complexes rather than the sp^3 orbitals expected from consideration of its ground state; the gain in bond energy more than compensates for the energy needed to promote the unpaired $3d$ electrons to a higher level (Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1948, p. 104). It is perhaps fortuitous that this orbital stabilisation occurs with an ion which would in any case form the strongest complexes of all the bivalent transition cations (see above) so that no derangement of stability order is caused. This is no longer the case with certain ferrous complexes where orbital stabilisation gives rise to complexes of abnormally high stability; and since the effect does not operate with its neighbours manganese or cobalt, or even with nickel and copper, a derangement of the " natural " order of stability appears.

Although, *e.g.*, ethylenediamine or triethylenetetramine gives paramagnetic and almost colourless complexes with ferrous iron, certain other nitrogen–nitrogen types of ligand such as 1 : 10-phenanthroline (VI) and 2 : 2′-dipyridyl (V) give complexes of unexpectedly high stability (Table 4) in which electronic rearrangement is revealed by the appearance of a high intensity absorption band in the visual region and the complete loss of paramagnetism which in the case of the aliphatic complexes corresponds to three unpaired $3d$ electrons. As in the case of the isoelectronic hexamminocobaltic complexes, the six atomic electrons of the ferrous ion have formed three shared pairs, leaving two $3d$ orbitals for use in strong octahedral d^2sp^3 hybrid bonds. The implications of such orbital stabilisation in analytical chemistry will be discussed elsewhere in connection with the " ferroin " and " cuproin " reactions (Irving, to be published shortly; cf. Irving and Williams, *loc. cit.*), but its effect in modifying or reversing an arbitrary order of stability can be seen in the data presented in Table 4 for certain complexes of zinc, cadmium, and iron, where the number of ligand molecules co-ordinated per atom of metal is shown in the second column and the arrangement within each of the three groups is that of increasing stability of the ferrous complexes. It will be obvious that no invariable " order of stability " can be laid down for these three metals (cf. p. 3197). Complexes of zinc are generally stronger than those of cadmium, but to no very marked extent; in some cases the difference in stability is negligible or even in the reverse order. For iron, on the other hand, the stability will be seen to increase relative to zinc or cadmium whenever additional resonance energy stabilisation is introduced through a ligand with an aromatic ring system (indicated by asterisks in Table 4) and in such circumstances the three metals may give complexes of closely similar stability while, consistently with the hypothesis that favourable electronic rearrangement is stabilising ferrous, but not zinc or cadmium complexes, the stability order is ultimately reversed to give Fe > Cd and Zn. There is some evidence from the trend in stability constants here and with some nickel complexes that a measure of *d* orbital stabilisation takes place before there is any reason to suspect this from changes in magnetic moment. Since the hydrated ferrous ion is paramagnetic while the trisphenanthroline and dipyridyl complexes are diamagnetic, orbital stabilisation may have occurred concurrently with the chelation of the first, second, or third molecule of ligand (Williams, Thesis, Oxford, 1950; Irving, "Discussion on Co-ordination Chemistry," September 1950, Imperial Chemical Industries Limited, Report No. BRL/146). It is hoped later to present results which will correlate paramagnetic susceptibility measurements with the degree of complex formation, not only for these ligands, but also for others such as 2-methyl-1 : 10-phenanthroline where weaker complexes are known to be formed as a consequence of steric hindrance (Irving, Cabell, and Mellor, *loc. cit.*) and for complex ligands of biological interest such as 4-hydroxypteridine, folic acid, and riboflavin, whose behaviour is somewhat exceptional in other respects.

TABLE 4. *Some complexes of zinc, iron, and cadmium.*

Ligand	No. of molecules	log of	Zn	Fe	Cd	Refs.[1]
Ammonia	2	K_1K_2	4·43	1	4·47	2
4-Hydroxypteridine (IX) *	1	K_1	3·41	3·40	3·41	3
Salicylaldehyde (as VII) * [4]	1	K_1	4·50	4·22	5·47	5
Ethylenediamine	1	K_1	5·71	4·28	5·47	6, 7
o-Phenanthroline (VI) *	1	K_1	6·50	5·90	6·6	8
Riboflavin (X) *	1	K_1	5·58	7·12	4·72	10
8-Hydroxyquinoline (as VIII) * [11]	1	K_1	9	8·0	7·2	10
Ammonia	4	$K_1K_2K_3K_4$	9·48	2	7·12	2
Glycine	2	K_1K_2	9·3	4	8·1	12
Tryptophan	2	K_1K_2	9·3	4	8·1	12
Asparagine	2	K_1K_2	8·7	4	6·8	12
Proline	2	K_1K_2	10·2	4	8·7	12
Ethylenediamine	2	K_1K_2	10·34	7·53	10·02	6, 7
Salicylaldehyde (as VII) * [4]	2	K_1K_2	8·10	7·62	7·76	5
Triethylenetetramine (IV)	1	K_1	12·1	7·8	10·75	13, 14
Folic acid (XI) *	2	K_1K_2	7·5	7·93	6·7	3
Norleucine	2	K_1K_2	10·4	8·61	8·7	12
8-Hydroxyquinoline * [11] (as VIII)	2	K_1K_2	20·81	18·84	—	—
Ethylenediamine	3	$K_1K_2K_3$	12·09	9·53	12·09	6, 7, 9
2 : 2′-Dipyridyl (V) *	3	$K_1K_2K_3$	—	16·5	10·5	15
o-Phenanthroline (VI) *	3	$K_1K_2K_3$	17·0	21·5	15·2	9
Ethylenediaminetetra-acetic acid	1	K_1	16·15	14·22	16·48	16

The asterisk * is used to call attention to ligands containing an aromatic ring system.

[1] References to data for zinc and iron complexes from Table 1 and 2. [2] Bjerrum (*op. cit.*). [3] Albert (*Proc. Biochem. Soc.*, 1950, **46**, ix). [4] Values measured in 50% dioxan : in water the values would be about 0·8 log K unit lower per molecule of ligand. [5] Mellor and Maley (*Nature*, 1948, **161**, 436). [6] Carlson and McReynolds (*J. Amer. Chem. Soc.*, 1945, **67**, 1334). [7] Bjerrum and Andersen (*Kgl. Dansk Videnskab. Selsk.*, 1945, **22**, 3). [8] Estimated from the value log $\beta_2 = 13{\cdot}2$ of ref. 9. [9] Douglas, Laitinen, and Bailar (*J. Amer. Chem. Soc.*, 1950, **72**, 2484). [10] Albert (*Proc. Biochem. Soc.*, 1950, **47**, xxvii). [11] Measured in 70% dioxan: values in water will be 1·5—2·0 log K units lower per molecule of ligand. [12] *Idem* (*Biochem. J.*, 1950, **47**, 531). [13] Schwarzenbach (*Helv. Chim. Acta*, 1950, **33**, 974). [14] The value 13·9 has been obtained polarographically, ref. 9. [15] Baxendale and George (*Trans. Faraday Soc.*, 1950, **46**, 55, 736; Krumholtz, *J. Amer. Chem. Soc.*, 1949, **71**, 3654) [16] Schwarzenbach and Freitag (*Helv. Chim. Acta*, 1951, **34**, 1492).

Steric Considerations.—Steric interference between ligands arises from mutual repulsion and, apart from special features of ligand geometry, will be greater the greater the size of the ligand and the smaller the radius of the cation. Among the transition metals the radii of bivalent ions are much the same (0·78—0·71 Å) and the varying geometry of the ligand is of predominant importance. This will no longer be true when ions of very different size are considered as, *e.g.*, among the alkaline-earth metals (Williams, *J.*, 1952, 3770).

An estimate of the magnitude of steric hindrance can be made by calculating the free-energy change incurred when one ligand is replaced by another of similar type. Thus since log K_1(en) and log $K_1K_2(NH_3)$ are measures (in units of $4{\cdot}57T$ cal./mole) of the free-energy changes of the reactions

$$\mathrm{M^{++}(aq.) + en(aq.) = M(en)(aq.)^{++}} + n\mathrm{H_2O}$$

and

$$\mathrm{M^{++}(aq.) + 2NH_3(aq.) = M(NH_3)_2(aq.)^{++}} + m\mathrm{H_2O}$$

it follows that log $K_1(\mathrm{en})/K_1K_2(\mathrm{NH_3})_2$ is a similar measure of the free-energy change in the displacement reaction

$$\mathrm{M(NH_3)_2(aq.)^{++} + en(aq.) = M(en)(aq.)^{++} + 2NH_3(aq.) + (}n - m\mathrm{)H_2O} \qquad (1)$$

Since the extent of hydration and thence the number of water molecules involved in such reactions cannot be determined unequivocally—although it will certainly vary from one ligand species to another—too much emphasis cannot be placed on the absolute values for the logarithmic differences quoted in Table 5 although it is possible to see how the free energy changes as the type and extent of chelation is altered. However, a comparison of reactions of type (1) for a number of different metals with the same pair of ligands should reveal features specific to these metals provided the degree of hydration (or more precisely the difference, $n - m$) remains the same throughout. It is permissible in this way to compare bivalent ions of the first transition series, for they are all of similar size and kind, and the degree of hydration should not vary greatly. But similar comparisons between ions of greatly different radii would be of doubtful validity.

TABLE 5.

(a) *Changes in free energy when one ligand replaces another.*

Reaction represented by:	Co	Ni	Cu	Zn
log K_1(en) − log $K_1K_2(\mathrm{NH_3})$	2·15	2·49	2·90	0·90
log K_2(en) − log $K_3K_4(\mathrm{NH_3})$	3·02	3·36	4·03	0·01
log $K_1(\mathrm{Hptn^+})$ − log $K_1K_2(\mathrm{NH_3})$	0·4	1·07	1·15	−0·6
log $K_1(\mathrm{Hptn^+})$ − log K_1(en)	−1·8	−1·5	−1·8	−1·5
log K_1(ptn) − log $K_1K_2K_3(\mathrm{NH_3})$	2·0	2·5	0·6	−0·6
log K_1(den) − log K_1(ptn)	1·3	1·4	4·9	2·15
log K_1(den) − log $K_1K_2K_3(\mathrm{NH_3})$	3·3	3·9	5·5	1·6
log K_1(trien) − log $K_1K_2K_3K_4(\mathrm{NH_3})$	5·45	6·05	7·7	2·65
log K_1(tren) − log $K_1K_2K_3K_4(\mathrm{NH_3})$	7·25	6·85	6·1	5·2
log K_1(tren) − log K_1(trien)	1·8	0·8	−1·6	2·55
log K_1(tren) − log K_1K_2(en)	2·08	1·0	−0·83	4·29

(b) *Energy increments per atom of nitrogen co-ordinated when a polydentate ligand replaces ammonia in the co-ordination sphere.*

$\frac{1}{2}$ [log $K_1(\mathrm{en})/K_1K_2(\mathrm{NH_3})$]	1·07	1·25	1·45	0·45
$\frac{1}{3}$ [log $K_1(\mathrm{den})/K_1K_2K_3(\mathrm{NH_3})$]	1·10	1·30	1·83	0·53
$\frac{1}{4}$ [log K_1(trien)/log $K_1K_2K_3K_4(\mathrm{NH_3})$]	1·39	1·51	1·92	0·66
$\frac{1}{4}$ [log K_1(tren)/log $K_1K_2K_3K_4(\mathrm{NH_3})$]	1·81	1·69	1·53	1·30

Values throughout are in units of 4·57T cal./mole.

Values of log [$K_1(\mathrm{en})/K_1K_2(\mathrm{NH_3})$] show that there is always a gain in stability when the monodentate ligand ethylenediamine replaces two molecules of ammonia. Moreover, the stability increments follow the Irving–Williams order Co < Ni < Cu > Zn. Values of log [$K_2(\mathrm{en})/K_3K_4(\mathrm{NH_3})$] show that this is equally true for the replacement of the third and the fourth attached group. The much smaller gain in stability when one molecule of the charged bidentate ligand, $\mathrm{(NH_2{\cdot}CH_2)_2{\cdot}CH{\cdot}NH_3^+}$(Hptn$^+$), replaces two molecules of ammonia, and the actual decrease in stability when Hptn$^+$ replaces " en " is due partly to the repulsion between the metal cation and the charged 'onium group (Schwarzenbach, " Discussion on Co-ordination Chemistry," *loc. cit.*; cf. *Angew. Chem.*, 1950, **50**, 74) and partly to the increased size of the chelate ring (Irving, Williams, Ferrett, and Williams, *loc. cit.*); differences in hydration may well be of importance here. Table 5 shows the notable gain in stability when two chelate groups are attached simultaneously through a tridentate group, the values again attaining their maximum with copper. Values of log $K_1(\mathrm{den})/K_1(\mathrm{ptn})$ show that there is always a gain in stability on replacing triaminopropane (ptn) by an unbranched triamine (den) which can more readily adapt itself to the stereochemistry of the atom to which it is co-ordinated and which is especially well suited to the formation of three coplanar rings when chelating to an ion which uses planar *dsp*^{2} orbitals. Among the metals listed in Table 5 this gain is especially marked in the case of copper, and conversely the use of ptn produces an abnormally weak copper complex in which it probably acts as a bidentate ligand (cf. Mann, *J.*, 1926, 2680).

Table 5 shows that the stability increment per atom of nitrogen co-ordinated when a polydentate ring replaces an equivalent number of ammonia molecules increases in the order bidentate $<$ tridentate $<$ quadridentate, *i.e.*, in the order of increasing number of chelate rings simultaneously attached, and with the exception of tren in the familiar order Co $<$ Ni $<$ Cu $>$ Zn. The exceptional behaviour of triaminoethylamine (tren) is most clearly shown in the values of log K_1(tren)/K_1(trien) which strikingly demonstrate the need for mutal compatibility between the geometry of the ligand and the stereochemistry favoured by the cation if maximum stability is to be attained. That the configuration of tren is particularly well adapted to complexing with metals favouring a tetrahedral disposition of bonds (cf. Mann, *loc. cit.*; Schwarzenbach, *loc. cit.*) is shown by the maximum value occurring with zinc. The stability increments decrease in the order Zn $>$ Co $>$ Ni $\gg$ Cu (the reverse of the usual order), there being a marked preference in the case of copper for the ligand trien which alone can form the desired coplanar chelate rings.

Increase in the size of a chelate ring from five to six or more members invariably decreases the stability (Irving, Williams, Ferrett, and Williams, *loc. cit.*), but there is no effect upon orders of stability (cf. Table 2). Comparison of data for ethylenediamine and propylenediamine shows that *C*-alkylation does not greatly alter chelating power. *N*-Alkylation, however, by increasing the interference volume of a ligand, tends to reduce stability; the effect is particularly noticeable in the increased difficulty of adding a second molecule of a bidentate ligand such as *NN'*-dimethylethylenediamine (cf. Table 2 and Irving *et al.*, *loc. cit.*). Similarly, the introduction of substituents α to one or both of the nitrogen atoms in 1 : 10-phenanthroline or its aza-derivatives (Irving and Williams, *Analyst*, 1952, **77**, 813) must oppose the close packing of ligand molecule around the central ion and so distort bond angles, increase metal–nitrogen distances, and reduce stability. The effect is immediately obvious in certain visual absorption spectra; thus, the addition of ferrous ions to phenanthroline or 2-methyl- or 2 : 9-dimethyl-phenanthroline gives deep red, pale yellow, and colourless solutions respectively, and measurements of stability constants (Table 2) show unequivocally the concomitant decreases in stability.

Steric effects which affect the ease of packing of ligands round a central ion will be specially sensitive to (*a*) structural modifications in the ligand, (*b*) the size of the central ion, and (*c*) the orbitals available, since these will impose, or tend to impose, a particular geometric arrangement of ligands. In exceptional cases such steric factors, assisted perhaps by orbital stabilisation through electronic rearrangements, may prevent the stability of metal ligands from following the normal order even within the first transition-metal series, and the possibility of designing ligands with the deliberate intention of exploiting these effects in analytical chemistry has already been envisaged (Irving and Williams, *loc. cit.*).

Maximum Co-ordination Number.—So far, no clear distinction has been drawn between stability sequences based upon over-all constants β_N (where N is the maximum co-ordination number) and those based upon, *e.g.*, values of K_1 or β_2 ($= K_1K_2$). In the first place N itself is not constant for all the bivalent transition metals. Thus nickel and cobalt form hexammines whereas copper and zinc only form tetrammines, so that, whereas the Irving–Williams order holds for ammonia, for values of K_1, K_2, K_3, and K_4 through the whole series, and for K_5 and K_6 from manganese to nickel, there is a discontinuity at copper owing to the low value of K_5 and the negligible value of log K_5 for zinc. Similarly, the sequence holds for ethylenediamine for K_1 and K_2 but again fails at copper owing to the low value for log K_3. Similar effects may be seen with other polydentate ligands such as diethylenetriamine and probably ethylenediaminetetra-acetic acid. Owing to the great stability of copper complexes compared with those even of its neighbour nickel, values of log β_N are normally greater for this element (even when $N = 4$) than for those of other transition elements, so the stability order is not often deranged and the significance of changes in maximum co-ordination have hitherto been to a large extent overlooked.

In conclusion, we would again point out that the " effective " co-ordination number (which Bjerrum, *op. cit.*, terms the " characteristic co-ordination number, Z ") is dependent upon the ligand used. Thus with zinc it is clearly four in the case of ammonia, but six in the case of phenanthroline; with ethylenediamine the situation is intermediate, since the first two ligands are added more readily than the third. In such cases the relative values of the ratio of successive stability constants, K_n/K_{n+1}, can provide a quantitative measure of steric hindrance, orbital changes, or changes in co-ordination number. Such data will be considered in a later paper.

Entropy Effects.—So far we have tacitly assumed that $-\Delta F$, the free-energy change which measures the stability of metal complexes, is dominated by the heat term, $-\Delta H$, of the corresponding process. But since $-2{\cdot}303\boldsymbol{R}T\log_{10}\beta = \Delta F = \Delta H - T\Delta S$, this assumption is equivalent to the statement that the entropy term $T\Delta S$ can be neglected in comparison with ΔH. This simplifying assumption accords fairly well with the existing data on uncharged ligands, where the influence of the entropy term is insufficient to derange the " natural " order of stability of transition metal complexes. However, with reactions such as the following

$$M^{2+}(aq.) + nL^{-q}(aq.) \rightleftharpoons ML_n^{(2-nq)}(aq.) + mH_2O$$

there will be a net gain in entropy which may become of preponderating significance. But the most important single factor in the entropy change of such a reaction, *viz.*, the entropy of hydration of M^{2+}, increases as the radius of the transition ion decreases, *i.e.*, monotonically along the series manganese to copper (Latimer, *Chem. Reviews*, 1936, **18**, 355), so that the stabilising influence of the entropy change in the reaction will also follow the Irving–Williams order. This will no longer be true if other elements which break the monotonic sequence of ionic radius are included in our transition-metal stability order.

All the ligands discussed thus far have been the conjugate bases of weak acids, *i.e.*, their proton complexes have been more stable than the proton–water complex (hydroxonium ion); a similar stability has characterised their complexes with metals. But ligands such as I^-, Br^-, Cl^-, $H_2PO_4^-$, PO_4^{3-}, SO_4^{2-}, ClO_4^-, BrO_3^-, and IO_3^-, which are conjugate bases of strong acids, interact with protons less strongly than water does, and their interactions with metals are also feeble. Such ligands do not form strong complexes with transition metals because the heat of formation of the metal–ligand bond is comparable with, and often less than, the heat of formation of the metal–water bond. But in virtue of their negative charge there will be a partial or complete neutralisation of the positive charge on the cation on co-ordination, so that the entropy gain (see above) will, to a greater or less extent, offset the loss of interaction energy which occurs when water is replaced by such a ligand. The net free-energy change may be very small, and the resulting stability order might not necessarily follow the Irving–Williams order in the transition series. The closely similar stability constants for sulphate complexes should be noted in this connection (Table 2), and though the malonates clearly follow the natural order of stabilities, measurements for the zinc complex ($\Delta F = -5110$, $\Delta H = +3060$, $\Delta S = +27{\cdot}5$; James, *J.*, 1951, 153) show clearly that it is stabilised by the entropy term ΔS. The same is true of the magnesium–malonate complex (Evans and Monk, *Trans. Faraday Soc.*, 1952, **48**, 934). For chloride ion complexes Bjerrum (*Chem. Reviews*, 1950, **46**, 381) quotes mean affinity constants of 1·0, 0·0, 0·6, and 1·5 for iron, cobalt, copper, and zinc, respectively, which suggest that the stability sequence has here been deranged and invalidated by the opposing influences of heat and entropy terms of comparable magnitude. However, the data may refer to complexes of the form of ion-pairs where—to make a formal distinction from the mode of complex formation discussed hitherto—the ligand molecule does not replace an equivalent number of water molecules in the hydration sheath immediately surrounding the cation. This aspect has been considered by one of us (Williams, *loc. cit.*) with special reference to the complexes of Group IIA metal ions.

In the following papers we shall show how steric effects or increases in the size of a chelate ring can reduce the stability of metal complexes without, however, deranging the stability order among the transition metals which we have shown to be a natural consequence of their ionisation potentials and ionic radii.

INORGANIC CHEMISTRY LABORATORY, OXFORD.

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