A Definitive Physical Model for Chelation: Ideal and Non-ideal Chelation, Short and Long Chelates, and Bridging

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For short chelating ligands of length l comparable with the contact distance a to the co-ordinating ion, ideal chelation is defined to occur when the ratio of the chelating constant K_{chel} to the cumulative formation constant β_2 of the equivalent bis(unidentate ligand) complex is closely approximated by $K_{chel}/\beta_2 = (\frac{4}{3}\pi L a^3)^{-1}\exp(-\Delta u/kT)$ where Δu, the difference in interaction energies associated with K_{chel} and β_2, is equal to zero. For long chelates, ideality is correspondingly defined by $K_{chel}/\beta_2 = (\frac{4}{3}\pi L l^3)^{-1}\exp(-\Delta u/kT)$ with Δu again zero. Specific molecular interactions can then be invoked to account for deviations. Contentions regarding the choice of concentration scale, as well as criteria for inferring chelation and the chelate effect, are resolved. The related associative process of bridging is shown to approximate to co-ordination, by one ion, of two equivalent unidentate ligands.

In this paper two simple models of chelation are examined, that of Prue for small ligands, and of Schwarzenbach for long ligands. Use of data for competing co-ordinative equilibria virtually eliminates any role for the solvent except as a featureless continuum. In the models, when the ligands and metal ion are of similar size they are treated as comprising spheres which on juxtaposition form complexes; when the ligands are long they act as chains, which bond to point ions. The use of these established models is novel, first in their employment to resolve the obscurities in views of chelation outlined in the next paragraph, secondly in providing a system which in ideal cases relates equilibrium constants to approximate but quite realistic sizes of the solutes, and thirdly by introducing bridging as a comparable form of bonding.

While polydentate molecules, perhaps best exemplified by[1] ethylenediaminetetra-acetate (edta), show the greatest extent of the chelate effect analysed below, for simplicity only bidentate ligands such as diamines[2] will be considered, the conclusions being in principle general. Recurrent discussion[3-8] of chelation and the chelate effect has suffered not so much from error, although examples could be cited, as from inconclusiveness and unsubstantiated assertion. It is not the case that chelation, in the sense of molecular interaction producing a ring, is not understood, since it is even possible to calculate[9] quite finely the relative stabilities of different conformations. What is required is a formal framework or model, necessarily idealised in the first instance, which describes the process while concomitantly giving a direct and unambiguous numerical measure of the effect. Particular influences in bonding, such as steric and solvent effects, can hence be clearly elaborated from the ideal model; Martell's useful discussion[10] lacks such a departure point. In particular, there is a pressing need for an exposition in which claims for a ' correct ' or ' most suitable ' unit of composition to be used in quantifying the process are avoided, since a scientifically satisfactory treatment will ensue only if it is independent of the units used in measurement.

Schwarzenbach in his classic paper[11] assigned the ring-closing entity an activity, which can also be represented by a more clearly envisaged volume. Prue,[12] extending the sphere-in-continuum model for associating ions[13] which is still useful,[14] proposed a different model for chelation. He emphasized[12] the approximate nature of continuum models: if, for example, one or both of the species are gas-phase rotators, losing this mode on immersion, the association constant K is decreased by a factor of 10^3 or 10^6.[12] Although even approximate partition functions are not available for polyatomic solutes in solution,[12] the possibility of assessing the relative stabilities of various geometries[9] indicates progress to that end. To bypass unverifiable assertions, in this paper the continuum treatment is employed, and it is established for the first time that the contrasting models of Prue and Schwarzenbach refer to short and long chelates respectively, depending on whether the ligand is less than or greater than *ca.* 8 Å in length.

RESULTS AND DISCUSSION

Short Chelation: the Prue Model.[12]—If two molecules associate, with an interaction energy w, their centres being separated by an association-defining range of distances a (' contact ') to d (just greater than a), then an adequate expression for their association constant K is (1), *i.e.* the volume of the spherical shell, envisaged as being circumscribed about either molecule and given by $4\pi a^2(d - a)$, multiplied by the Boltzmann expression $\exp(-w/kT)$ and by the Avogadro constant L. The defining range $d - a$ is written as δa (see Figure 1).

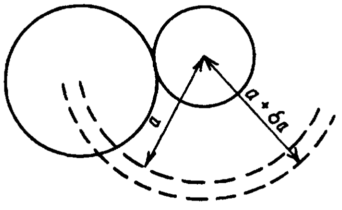

FIGURE 1 Definition of an ion pair

$$K = [4\pi a^2(\delta a)L]\exp(-w/kT) \qquad (1)$$

Other versions are to be found as follows:[12] (*i*) if $w(r)$ is given by Coulomb's law, integration through the shell $4\pi r^2 dr$ from $r = d$ to $r = a$ gives the Bjerrum expression[15] for ionic association; (*ii*) taking $w(a)$ from Coulomb's law, and putting δa equal to $\frac{1}{3}a$, gives Fuoss'[16] simplified K for ion association, $\frac{4}{3}\pi a^3 L\exp[-w(a)/kT]$;

(*iii*) $K = V\exp(-w/kT)$ with coulombic w is Eigen's[17] version for ion association, where V represents the (molar) shell volume.

While expressing reservations about (*iii*), Prue[12] nevertheless found no error in conclusions derived from it regarding ion association. The empty space between randomly packed spheres can be represented[18] by a shell about each sphere, of thickness closely equal to one third of the radius,[19] and the numerical assumption in (*ii*) can then also be accepted[12] as a satisfactory approximation, for the probable range of action of the averaged $w(a)$.

For chelation,[12] for example of ethylenediamine (en), if u is the interaction energy of the central ion with one equivalent unidentate ligand, methylamine ($\mathrm{NMeH_2}$) in this case, then the two points of attachment of en give $K_{\text{chel}} = V\exp(-2u/kT)$, compared with $K_1 = V\exp(-u/kT)$ for the unidentate attachment of $\mathrm{NMeH_2}$. (Only ideally is u exactly the same in the two processes quoted.[12])

In Prue's model[12] it is implied that both ends of the chelating ligand automatically enter the volume element V about the ion. We assume that this will be the case if the ligand is short, two to three times a in length, for example en. This is the requirement for short chelation. More quantitatively, and referring to the following model, short chelation can be said to occur if, for the second chelating end of the ligand, the first end having been attached, $\exp(-u/kT) > Lv_s/V$, where v_s is the total volume available for motion of the second end when free and V is the (molar) shell volume about the central ion, occupancy of which denotes bonding.

In comparing[12] the chelation of A by D–D with complex formation of A with two unidentate ligands D′, as in expressions (2)—(4), we obtain $K_1K_2 = \beta_2 =$

$$\mathrm{A + D'} \xrightleftharpoons{K_1} \mathrm{AD'} \tag{2}$$

$$\mathrm{AD' + D'} \xrightleftharpoons{K_2} \mathrm{AD'_2} \tag{3}$$

$$\mathrm{A + D{-}D} \xrightleftharpoons{K_{\text{chel}}} \overline{\mathrm{A{-}D{-}D}} \tag{4}$$

$V^2\exp(-2u/kT)$. Following Fuoss in (*ii*) above,[12] $V = \frac{4}{3}\pi La^3$. Taking $a = 2.75$ Å as being applicable to en, Prue obtained[12] the expression (5). The observed

$$K_{\text{chel}}/\beta_2 = V^{-1} = 19 \text{ mol dm}^{-3} \tag{5}$$

value[3] of K_{chel}/β_2 is *ca.* 10 mol dm^{-3}, or for the bis(ethylenediamine) chelates,[3] taking the value averaged per en co-ordinated, 100 mol dm^{-3}; these values [(a)—(d) in Table 1] bracket Prue's value. Because of this quite satisfactory agreement en is hence designated as ideal short chelate. Data from the collation in ref. 3, corrected for some transcription errors, are given in Table 1. The conclusion that en is an ideal short chelate is reinforced by the $\Delta H^\ominus$ values shown.

TABLE 1

Formation constants K for ion + n ligand(s) $\rightleftharpoons$ complex, $c^\ominus = 1$ mol dm^{-3}

Complex	log $\{K/(\mathrm{dm^3\ mol^{-1}})^n\}$	n	$-\Delta H^\ominus$ / kJ mol^{-1}	$-\Delta S^\ominus$ / J K^{-1} mol^{-1}
(a) $[\mathrm{Cd(NMeH_2)_2}]^{2+}$	4.81	2	29.4	6
(b) $[\mathrm{Cd(en)}]^{2+}$	5.84	1	29.4	−13
(c) $[\mathrm{Cd(NMeH_2)_4}]^{2+}$	6.55	4	57.3	67
(d) $[\mathrm{Cd(en)_2}]^{2+}$	10.62	2	56.5	−14
(e) $[\mathrm{Cd}(py)_2]^{2+}$	2.2	2		
(f) $[\mathrm{Cd}(bipy)]^{2+}$	4.4	1		
(g) $[\mathrm{Cd}(py)_4]^{2+}$	2.5	4		
(h) $[\mathrm{Cd}(bipy)_2]^{2+}$	7.3	2		

Values selected in ref. 3 from ref. 2, then corrected. Pyridine (*py*) and *bipy* complexes of $\mathrm{Cu^{2+}}$ and $\mathrm{Ni^{2+}}$ show trends similar to the above.[3]

TABLE 2

Comparison of $\mathrm{N_2H_4}$ and $\mathrm{NH_3}$ as ligands

Reaction [2]	log $(K_1/\mathrm{dm^3\ mol^{-1}})$
(i) $\mathrm{Cd^{2+} + NH_3 \longrightarrow [Cd(NH_3)]^{2+}}$	2.53
(j) $\mathrm{Cd^{2+} + N_2H_4 \longrightarrow [Cd(N_2H_4)]^{2+}}$	2.25

Data[2] for $\mathrm{Zn^{2+}}$, $\mathrm{Cu^{2+}}$, $\mathrm{Ni^{2+}}$, and $\mathrm{Co^{2+}}$ show the same relation; slightly differing media and temperatures were used for the two ligands.

Another chelating ligand bipyridyl (bipy) is expected to also have an a value of *ca.* 2.75 Å, but here, averaged over the quoted[3] cations [(e)—(h) and footnote, Table 1], $K_{\text{chel}}/\beta_2 = 10^{3.28}$ mol dm^{-3}, *i.e.* greatly exceeding V^{-1} calculated from a. This enhancement of chelation is correspondingly deemed non-ideality. For $\mathrm{N_2H_4}$, (j), an apparently non-chelating ligand,[20] K values for a given ion are[2] very close to K_1 values for complexing with $\mathrm{NH_3}$ [(i), Table 2], and it is thus non-ideal in the opposite sense, presumably due to steric and orbital incommensuracy associated with its extreme shortness. For non-ideality clearly ascribable to differences in the interaction energies, we obtain (6) where $2u_{\text{u}}$ are the

$$(K_{\text{chel}}/\beta_2)(\text{non-ideal}) = (\tfrac{4}{3}\pi La^3)^{-1}\exp[(2u_{\text{u}} - 2u_{\text{chel}})/kT] \tag{6}$$

summed interaction energies for the co-ordination of the two unidentate ligands, and $2u_{\text{chel}}$ the corresponding quantity for the two ends of the chelating ligand.

Long Chelation: the Schwarzenbach Model.[11]—When the length l of the bidentate ligand D–D greatly exceeds the contact distance a a different model is clearly called for. Thus if one end is bonded to A and the other is free the unattached end can occupy any position in a swept volume $v_s = \frac{4}{3}\pi l^3$ centred approximately on A. In parallel with equilibria (2) and (3) above for unidentate ligands, one may thus write (7) and (8). K_1' can

$$\mathrm{A + D{-}D} \xrightleftharpoons{K_1'} \mathrm{A{-}D{-}D} \tag{7}$$

$$\mathrm{A{-}D{-}D} \xrightleftharpoons{K_2'} \overline{\mathrm{A{-}D{-}D}} \tag{8}$$

be approximated by K_1, and a corresponding approximation might be made for K_2', which is dimensionless, if a local concentration $c_{-\mathrm{D}}$ is assigned to the free end of the ligand. This is an exact analogue of Flory's principle of equal reactivity in the kinetics of polymerisation, where it is assumed that the concentration of the reacting ends governs the rate independently of the length of the attached chains. Thus an equilibrium constant K_2'' expressed in terms of the local concentration $c_{-\mathrm{D}}$ is given by K_2'/c_{-D}. It is K_2'' that can then be approximated by K_2. Since $K_1'K_2' = K_{chel}$, relations (9) follow. This is

$$\beta_2/K_{chel} = 1/c_{-D} = Lv_s = \tfrac{4}{3}\pi Ll^3 \qquad (9)$$

analogous to expression (5) in serving as a criterion for long-chelate ideality.

Following en as an ideal short chelate, tetramethylenediamine (butane-1,4-diamine, tmd) will serve as a touchstone here. For [2] tmd with Cd^{2+} [(k) in Table 3] log (K_{chel}/dm^3 mol^{-1}) = 3.6, and log (β_2/dm^6 mol^{-2}) = 4.8 for $NMeH_2$, giving l, from (9), as 20.1 Å. Together with further estimates in Table 3, this is close enough to reality for tmd to be deemed an ideal long chelate.

TABLE 3

Application of expression (9) to tmd chelates

Ion	log (K_{chel}/dm^3 mol^{-1})	log (β_2/dm^6 mol^{-2})	l/Å
(k) Cd^{2+}	3.6	4.81	20.1
(p) Hg^{2+}	17.96	17.9	8.0
(q) Ag^+	5.9	6.7	14.5
		Mean:	14.2 ± 4.1

Space filling atomic model 10

When non-ideality is ascribable to differences in the interaction energies, we obtain expression (10), u_u and u_{chel} retaining their meanings in (6).

$$(K_{chel}/\beta_2)(\text{non-ideal}) = (\tfrac{4}{3}\pi Ll^3)^{-1}\exp[(2u_u - 2u_{chel})/\boldsymbol{k}T] \qquad (10)$$

Hitherto the chosen concentration unit has been mol dm^{-3} which can be considered our choice of 'standard concentration $c^{\ominus}$', so avoiding any invocation of 'standard states'. The numerical values for the equilibrium constants, quoted above for Cd^{2+}, show the bis(methylamine) complex to be apparently more 'stable' than the chelate. Use of mol m^{-3} as concentration unit, *i.e.* as new standard concentration $c^{\ominus}$, gives log(K_{chel}/m^3 mol^{-1}) = 0.6 and log(β_2/m^6 mol^{-2}) = −1.2, the reverse of the former numerical sequence and now, apparently, showing the chelate complex to be more stable. To avoid this problem, the ideal long-chelate model can be used to provide an objective criterion for such 'stabilisation'. With the chelate length $l_{expt.}$ known from *independent* sources (diffraction data on solids if the packing corresponds to the greatest extension, or, possibly better, from spacial atomic models such as Catalin's) then chelation is unambiguously established if K_{chel}/β_2 is found to be $\geqslant(\tfrac{4}{3}\pi Ll^3_{expt.})^{-1}$. Both sides of this inequality have the dimensions of concentration and *it is immaterial what unit is chosen.* The equality sign indicates ideality, and if the reverse inequality, <, is observed, this clearly means sub-ideal or nil chelation. Nil chelation is confirmed, as with N_2H_4 (Table 2), when K for a ligand having two ligating atoms nevertheless is found to approximate to K_1 for the equivalent unambiguously unidentate ligand.

In the absence of this new criterion, there has always been the freedom to introduce a numerical 'chelate effect', *i.e.* to make $K_{chel}/\beta_2 c^{\ominus} > 1$, by choosing $c^{\ominus}$ to be smaller than $(\tfrac{4}{3}\pi Ll^3)^{-1}$. This observation encompasses much earlier discussion, *e.g.* of Munro,[3] and removes any need for speculation about a most suitable, or realistic,[8] composition scale.

The long-chelate model is in essence that of Schwarzenbach [11] for which he termed $(Lv_s)^{-1}$ an 'activity'. No systems were cited [11] which fulfilled ideal criteria, *i.e.* which closely supported the formulation. Schwarzenbach included statistical factors (from rate comparisons, but equivalent to probabilities) which, being inapplicable in a continuum model, have been omitted here.

The Occurrence of Bridging.—With long chelates the second end of the ligand can either form a chelate ring or bridge to a second co-ordinating ion A. This second equilibrium (11) must thus be included. Since K_{bridge} =

$$\text{A} + \text{D–D} + \text{A} \overset{k_{bridge}}{\rightleftharpoons} \text{A–D–D–A} \qquad (11)$$

$c_{ADDA}/c_{DD}c_A^2$ and $K_{chel} = c_{chel}/c_{DD}c_A$, we obtain (12).

$$K_{bridge}/K_{chel} = c_{ADDA}/c_{chel}c_A \qquad (12)$$

From Figure 2, the relative probability that the unbound end of the ligand will complex with a free A,

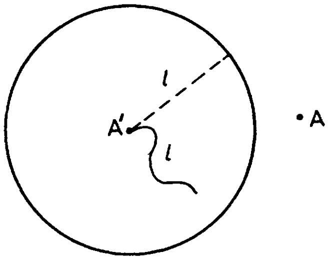

FIGURE 2 Model of A′–D–D– and A in bridging. A has access to the swept sphere of radius l

rather than chelate, is given by the ratio: (number of free A per unit volume about the unbound end)/(number of half-bound A′ per unit volume about the unbound end). The first part of the ratio is equal to Lc_A and the second to $(\tfrac{4}{3}\pi l^3)^{-1}$, giving (13). This relative

$$Lc_A/(\tfrac{4}{3}\pi l^3)^{-1} = c_A\tfrac{4}{3}\pi Ll^3 \qquad (13)$$

probability will be expressed in an observable ratio of concentrations, (14), which is equal to (13). Expressions

$$c_{ADDA}/c_{chel} \qquad (14)$$

(12)—(14) then give (15) for (of course) ideal systems.

$$K_{bridge}/K_{chel} = \tfrac{4}{3}\pi Ll^3 \qquad (15)$$

Further comparison of expressions (9) and (15) establishes the relation (16). Recalling that the con-

$$K_{bridge} = \beta_2 \qquad (16)$$

ditions for such a relation to hold are first that $K_1 = K_2$ (as in Prue's model) and secondly (implicitly) that the chains are long enough to minimise interionic repulsion between the bridged A ions [otherwise expressions (15) and (16) will require $\leqslant$ signs], bridging in a chelating system will occur to an extent equivalent to the formation of bis complexes in the situation where only unidentate ligands are present, and this equality of K_{bridge} and β_2 can be envisaged as originating from simply the number of ion–ligand *bonds* per unit volume in the system, resulting from three-species interaction, regardless of whether these are A–D′ bonds with unidentate D′ in D′–A–D′, or bonds with the long bidentate ligand in A–D–D–A. The continuum model thus clearly establishes that, together with chelation, the extent of bridging is an important parameter of the systems contemplated.

Further Tests: Bridging and Chelation.—The only bridging data found [2] are those of Ag^+ with en. Although en might appear at first sight to be rather short for this test, the univalent cation here is particularly suitable in involving minimal intercation repulsion. For [2] $[Ag(NMeH_2)_2]^+$ $\log(\beta_2/dm^6\ mol^{-2}) = 6.68$—$7.06$, while $\log(K_{\text{bridge}}/dm^6\ mol^{-2}) = 6.46$, representing substantial support for the theoretical expression (16).

Ethylenediamine can be seen not to chelate with Ag^+ since, for co-ordination of one en, $\log(K/dm^3\ mol^{-1}) = 4.7$; use of the log β_2 value just quoted, and expression (5) gives the unacceptable value of $a = 34.1$ Å. Silver ion is said [20] to favour axial (*trans*) co-ordination, which is presumably not achieved by the short en. Since en is shown not to chelate here it is available for bridging, which validates the use of expression (16) for it.*

Co-ordination by [2] Hg^{2+} shows a similar constraint. $\log(\beta_2/dm^6\ mol^{-2})$ for $NMeH_2$ is $8.6 + 9.3$, while, for one en, $\log(K/dm^3\ mol^{-1}) = 14.3$ [for two en, $\log(K/dm^6\ mol^{-2}) = 14.3 + 2.05$, quite close to log β_2 for $NMeH_2$]. The largest equilibrium constant of all (taking $c^{\ominus} = 1$ mol dm^{-3}) is that for bonding to tmd, which we deem chelation: $\log(K_{\text{chel}}/dm^3\ mol^{-1}) = 17.96$ [(p), Table **3**]. The clear implication is that tmd is long enough to achieve axial bonding, *i.e.* is a *trans*-spanning chelate, and Table **3** indicates l to be *ca.* 8 Å. Furthermore, the same notion is applicable to Ag^+, and [2] $\log(K_{\text{chel}}/dm^3\ mol^{-1}) = 5.9$, with [2] log β_2, gives l as 14.5 Å for tmd [(q), Table **3**], again an eminently acceptable value. (The size of l and even its variation are satisfactory for so simple a model, especially when assessed in terms of heuristic value rather than quantitative exactness. At least part of the spread arises from changes of media between measurements.) With only the additional requirement of axiality of bonding, the sequence of stability constants for $NMeH_2$, en, and tmd has been simply rationalised for both Ag^+ and Hg^{2+} by reference to the continuum model.

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* *Note added in proof:* Bjerrum [21] points out that K_1 for $[Ag(en)]^+$ is greater than that for $[Ag(NMeH_2)]^+$, implying some chelation. It would thus be more correct to view $[Ag(en)]^+$ as a severely sub-ideal chelate rather than as non-chelating. Axial bonding by Ag^+ and Hg^{2+}, and further relevant details, have been discussed with clarity.[22]

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