Correspondence

Comments on the Internal Conjugate Base Mechanism for Complex Formation of Nickel(II)

AIC50066X

Sir:

The internal conjugate base (ICB) mechanism has been proposed[1] to explain the unusually large rates of complex formation of several polyamines with nickel(II). The complex formation of nickel(II) is generally accepted[2,3] to follow a dissociative ion-pair mechanism[4] in which an outer-sphere complex (ion pair) of metal and entering ligand forms first, followed by rate-controlling release of a first coordination sphere solvent molecule (eq 1).

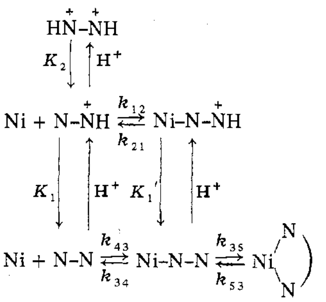
$$\mathrm{Ni(OH_2)_6}^{2+} + \mathrm{L} \underset{\text{fast}}{\overset{K_i}{\rightleftharpoons}} \mathrm{Ni(OH_2)_6 \cdot L}^{2+} \underset{\text{slow}}{\xrightarrow{k_i}} \mathrm{Ni(OH_2)_5L}^{2+} + \mathrm{H_2O} \quad (1)$$

Normally, the rate constant of the second step (k_i) is assumed to be relatively independent of the nature of L, while K_i depends on the charge and dipole moment of L. As a result, for similar ligands (L) reacting with $\mathrm{Ni(OH_2)_6}^{2+}$, one expects to find rather similar observed rate constants (k_iK_i) and indeed this is generally found.[2,3]

On the other hand, for several polyamines, such as ethylenediamine and its derivatives,[2,5,6,7] the observed rate constant has been found to be much larger than expected when compared to ammonia for example. This rate enhancement has been taken as evidence for the ICB mechanism.[1] In the outer-sphere complex one amino group of ethylenediamine is supposed to hydrogen bond to a coordinated water molecule giving it some hydroxide ion properties. This is claimed to facilitate dissociation of a water molecule, i.e., increase k_i, and thus cause the unusually large observed rate constants for these systems.

It is the purpose of this note to determine if the ICB mechanism is really necessary or if the reactivity of the polyamines can be accounted for by normal kinetic effects. This reexamination was prompted by the analysis of simple amino acid systems in which it was found that reaction of the protonated ligand is an important but previously neglected reaction pathway. Reaction of monoprotonated diamines has also been neglected in the analysis of results used to support the ICB mechanism. It will be supposed initially here that there is no ICB effect and that these diamines show normal reaction rates as deduced from monodentate analogues. If this approach fails to explain the kinetic results, then some special mechanism, such as the ICB, would be required.

The $\mathrm{Ni(OH_2)_6}^{2+}$–en system will be reanalyzed in detail here since this system has been the subject of a recent thorough kinetic study.[7] The reaction scheme to be used is eq 2, where



(2)

N–N represents neutral ethylenediamine, and the charge and solvent molecules on nickel(II) have been omitted. The ion-pair formation step is also left out and it is understood that k_{12} and k_{43} are really appropriate k_iK_i products (see eq 1).

The general reaction scheme in eq 2 has been analyzed with the assumption that K_1, K_1', and K_2 are equilibrium constants for rapidly established equilibria and for the usual experimental conditions of $5 \lesssim \mathrm{pH} \lesssim 7$ and pseudo-first-order conditions of [Ni] >> [total ligand] and $[\mathrm{Ni}] \lesssim 0.1$ M. It was found[8] that the observed pseudo-first-order rate constant for approach to equilibrium is given by eq 3.

$$k'_{\mathrm{obsd}} = \{(K_2(k_{12}[\mathrm{H}^+] + k_{43}K_1)k_{35}K_1'[\mathrm{Ni}]/([\mathrm{H}^+]^2 + K_2[\mathrm{H}^+] + K_1K_2)) + k_{53}(k_{21}[\mathrm{H}^+] + k_{34}K_1')\}/ \{k_{21}[\mathrm{H}^+] + K_1'(k_{34} + k_{35}) + k_{53}(K_1' + [\mathrm{H}^+])\} \quad (3)$$

Approximations based on simple model systems will be used to simplify expression 3 and the result applied to the kinetic data for the Ni^{2+}–en system.[9] It will be assumed that $k_{34} \approx 15\ \mathrm{s}^{-1}$ and $k_{43} \approx 900\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, based on results for $\mathrm{Ni(OH_2)_6}^{2+}$ reacting with ethylamine.[10] The ICB approach has been dropped at this point in that a "normal" k_{43} value has been assumed for formation of the first Ni–N bond. In addition, $k_{35} > 10^4\ \mathrm{s}^{-1}$, based on water-exchange rate data;[11] $k_{53} < 1\ \mathrm{s}^{-1}$, from studies of the dissociation of $\mathrm{Ni(OH_2)_4en}^{2+}$ in acid;[2] $k_{12} \approx 400\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, expected for a neutral substituent of a cation complexing with $\mathrm{Ni(OH_2)_6}^{2+}$;[2,8] and $K_1' > K_1$, due to the effect of Ni^{2+} on the acidity of the uncoordinated amino group. It is useful to make the substitution that $k_{21} = k_{12}k_{34}K_1'/k_{43}K_1$ in eq 3 as well. It is then found that $k_{35} >> k_{34}$, $k_{35} >> k_{53}$, and $k_{35}K_1' >> k_{53}[\mathrm{H}^+]$. Furthermore, since $K_1 \approx 10^{-10}$ [7] and $[\mathrm{H}^+] > 10^{-8}$ M, then $k_{12}[\mathrm{H}^+] >> k_{43}K_1$ and $k_{12}[\mathrm{H}^+]/k_{43}K_1 >> 1$. With these conditions eq 3 simplifies to

$$k'_{\mathrm{obsd}} = \{(K_2(k_{12}k_{35}k_{43}K_1)[\mathrm{H}^+][\mathrm{Ni}]/([\mathrm{H}^+]^2 + K_2[\mathrm{H}^+] + K_1K_2)) + k_{53}k_{34}k_{12}[\mathrm{H}^+]\}/\{k_{34}k_{12}[\mathrm{H}^+] + k_{43}k_{35}K_1\} \quad (4)$$

As expected, this observed rate constant for a system coming to equilibrium is the sum of a formation rate constant (k_f') and a dissociation rate constant (k_d). For purposes of comparison to the experimental results of Taylor, Stepien, and Rorabacher[7] it is convenient to separate these terms in eq 4 to obtain, after rearrangement

$$\frac{k_f'}{[\mathrm{Ni}]}\left\{\frac{[\mathrm{H}^+]^2 + K_2[\mathrm{H}^+] + K_1K_2}{K_2}\right\} = \frac{k_{12}k_{35}k_{43}K_1[\mathrm{H}^+]}{k_{34}k_{12}[\mathrm{H}^+] + k_{43}k_{35}K_1} \quad (5)$$

and

$$k_d = \frac{k_{53}k_{34}k_{12}[\mathrm{H}^+]}{k_{34}k_{12}[\mathrm{H}^+] + k_{43}k_{35}K_1} \quad (6)$$

If one defines $k_f = k_f'/[\mathrm{Ni}]$ and takes the reciprocal of both eq 5 and eq 6, then

$$\frac{1}{k_f}\left\{\frac{K_2}{[\mathrm{H}^+]^2 + K_2[\mathrm{H}^+] + K_1K_2}\right\} = \frac{k_{34}}{k_{35}k_{43}K_1} + \frac{1}{k_{12}}\frac{1}{[\mathrm{H}^+]} = (\mathrm{In})_f + (\mathrm{Sl})_f[\mathrm{H}^+]^{-1} \quad (7)$$

Table I. Stopped-Flow Kinetic Data for the Reaction of Nickel(II) with Ethylenediamine (25°, $\mu = 0.1$ M)

	k_f, M^{-1} s^{-1}		$10^2 k_d$, s^{-1}	
pH	Exptl[a]	Calcd[b]	Exptl[a]	Calcd[b]
5.71	5.46	5.22	9.25	9.22
5.77	6.11	6.37	7.90	8.59
5.83	7.30	7.73	7.41	7.97
5.87	8.87	8.77	8.40	7.56
6.00	13.7	13.0	6.79	6.28
6.02	13.9	13.8	6.01	6.09
6.11	15.9	17.7	5.00	5.28
6.19	22.0	22.0	4.42	4.62
6.19	25.1	22.0	5.49	4.62
6.36	31.6	33.8	3.26	3.40
6.45	41.9	41.8	2.92	2.87
6.48	41.9	44.7	2.40	2.70
6.58	50.2	55.6	2.01	2.22
6.60	60.6	58.0	2.16	2.13
6.71	81.9	72.2	1.93	1.70
6.79	113	83.9	1.92	1.43
7.12	266	140	1.29	0.70
7.15	296	146	1.30	0.65

[a] Average of values given in Table II of ref 7. [b] Calculated from eq 7 with parameters in Table II and K_1, K_2, and activity coefficients given in ref 7.

Table II. Summary of Kinetic Parameters[a] for the Nickel(II)–Ethylenediamine Reaction (25°, $\mu = 0.1$ M)

$(\mathrm{In})_f$	1.26×10^3 s	k_{12}	3.13×10^2 M^{-1} s^{-1}
$(\mathrm{Sl})_f$	3.20×10^{-3} M s	k_{53}	0.18 s^{-1}
$(\mathrm{In})_d$	5.50 s	$k_{43}k_{35}/k_{34}$	7.24×10^6 M^{-1} s^{-1}
$(\mathrm{Sl})_d$	1.31×10^{-5} M s		

[a] Obtained by least-squares fit of data in ref 7, with all points having equal weight, to eq 7 and 8.

and

$$\frac{1}{k_d} = \frac{1}{k_{53}} + \frac{1}{k_{53}}\left(\frac{K_1 k_{43} k_{35}}{k_{34} k_{12}}\right)\frac{1}{[\mathrm{H}^+]} = (\mathrm{In})_d + (\mathrm{Sl})_d[\mathrm{H}^+]^{-1} \quad (8)$$

where (In) and (Sl) are the intercept and slope of the appropriate linear plots.

The kinetic data of Taylor et al.[7] for nickel(II) reacting with ethylenediamine have been analyzed according to eq 7 and 8. The complete data set is given in Table II of Taylor et al.,[7] and only average experimental k_f and k_d values are given here in Table I, along with values calculated from a least-squares fit of the data to eq 7 and 8. The least-squares $(\mathrm{In})_f$, $(\mathrm{Sl})_f$, $(\mathrm{In})_d$, and $(\mathrm{Sl})_d$ and constants derived from them are summarized in Table II.

It can be seen in Table I that the results for pH >6.8 are not fitted by eq 7 and 8 in that the reported k_f and k_d are much larger than the calculated values. This failure may be due to the anomalies documented by Taylor et al.[7] for pH >6.8. It should be noted that the original authors[7] also were unable to fit their data completely and, for unexplained reasons, chose to neglect nine sets of runs (see original data) at pH <5.9. In view of the acknowledged[7] experimental complications at pH >6.8 and the fact that only four sets of runs have not been fitted here, it is felt that our fit of the experimental data is quite satisfactory.

The internal consistency of the fitting parameters can be checked because any one of them may be calculated from the other three. For example, $(\mathrm{Sl})_d = (\mathrm{In})_d(\mathrm{Sl})_f/(\mathrm{In})_f = 1.39 \times 10^{-5}$ M s, in good agreement with the least-squares value of 1.31×10^{-5} M s.

The treatment given here can be tested further by comparing derived rate constants to those expected from other studies. The value of k_{53} (0.18 s^{-1}) is in good agreement with the directly measured value of 0.14 s^{-1}.[2] The value of k_{12} (3.1×10^2 M^{-1} s^{-1}) for the reaction of $\mathrm{H_2NCH_2CH_2NH_3^+}$ with $\mathrm{Ni(OH)_6^{2+}}$ seems quite consistent with that of 5×10^2 M^{-1} s^{-1} for $\mathrm{H_2NCH_2CH_2N(CH_3)_3^+}$.[13] Taylor et al.[7] have suggested that a lower rate constant for enH$^+$ might be due to hydrogen bonding, but the differences found here are hardly sufficient to give strong evidence for such an effect.

If the ICB mechanism is not required, then the value of $k_{43}k_{35}/k_{34}$ must be consistent with results from simpler systems. The ICB mechanism implies that k_{43} is unusually large. However, if the reaction of $\mathrm{Ni(OH_2)_6^{2+}}$ with ethylamine[12] is used as a model, one estimates $k_{43} \approx 900$ M^{-1} s^{-1} and $k_{34} \approx 15$ s^{-1} as normal values for these rate constants. Then, with $k_{43}k_{35}/k_{34} = 7.24 \times 10^6$ M^{-1} s^{-1}, one obtains $k_{35} = 1.2 \times 10^5$ s^{-1}. This is quite close to the water-exchange rate constant for $\mathrm{Ni(OH_2)_5NH_3^{2+}}$ of 2.5×10^5 s^{-1},[11] as expected since a dissociative mechanism implies that k_{35} should be the water-exchange rate constant for $\mathrm{Ni(OH_2)_5NH_2CH_2CH_2NH_2^{2+}}$. Both of these rate constants are larger than that for water exchange of $\mathrm{Ni(OH_2)_6^{2+}}$ due to the well-established labilizing effect of a coordinated amino group.[11,14]

The conclusion is that the kinetic data for the $\mathrm{Ni(OH_2)_6^{2+}}$–en system, at least for pH <6.8, can be accounted for on the basis of normal reaction rates and require no special explanation such as the ICB mechanism. It is worthwhile to note that, if an ICB effect is to be established, experimental conditions must be such that $k_{43}K_1 \gtrsim k_{12}[\mathrm{H}^+]$ (see numerator of eq 3). If $K_1 = 10^{-10}$ M, $k_{12} = 300$ M^{-1} s^{-1}, and $k_{43} \approx 10^5$ M^{-1} s^{-1}, then experiments must be done at pH >7 to establish clearly an ICB effect. At these higher pH values care must be exercised to ensure that the reactions of species such as $\mathrm{(H_2O)_5NiOH^+}$ are not being followed.

The conjugate base part of the ICB mechanism implies that a coordinated hydroxide greatly enhances the substitution rate. A logical extension of this idea would seem to be that, for the reaction

$$\mathrm{(H_2O)_5NiOH^+} + \mathrm{N\text{-}\overset{+}{N}H} \xrightarrow{k_{12}\mathrm{OH}} \mathrm{((H_2O)_4(HO)NiN\text{-}\overset{+}{N}H)^{2+}} + \mathrm{H_2O} \quad (9)$$

k_{12}^{OH} is much greater than k_{12}, the analogous rate constant for $\mathrm{Ni(OH_2)_6^{2+}}$. If $\mathrm{(H_2O)_5NiOH}$ is included in a scheme analogous to eq 2, it is a simple matter to obtain a result analogous to eq 5. This can be simplified, since for pH >7, $k_{43}k_{35}K_1 > k_{34}k_{12}[\mathrm{H}^+]$, to give

$$\frac{k_f'}{[\mathrm{Ni}]_{\mathrm{tot}}}\left(\frac{[\mathrm{H}^+]^2 + K_2[\mathrm{H}^+] + K_1K_2}{K_2}\right) = \frac{k_{12}[\mathrm{H}^+]^2}{K_h + [\mathrm{H}^+]} + \frac{k_{12}^{\mathrm{OH}}K_h[\mathrm{H}^+]}{K_h + [\mathrm{H}^+]} \quad (10)$$

where $[\mathrm{Ni}]_{\mathrm{tot}} = [\mathrm{Ni(OH_2)_6^{2+}}] + [\mathrm{(H_2O_5)NiOH^+}]$ and K_h is the hydrolysis constant of $\mathrm{Ni(OH_2)_6^{2+}}$ ($\sim 2 \times 10^{-10}$ M).[15] For pH <9, $[\mathrm{H}^+] \gg K_h$ and the right-hand side of eq 10 reduces to $(k_{12}[\mathrm{H}^+] + k_{12}^{\mathrm{OH}}K_h)$. In earlier work the conjugate base effect has been ascribed to rate constant increases of ~200. If the same factor is applied to k_{12}, one estimates $k_{12}^{\mathrm{OH}} \approx 6 \times 10^4$ M^{-1} s^{-1} for ethylenediamine. Then even at pH 7.2, $k_{12}^{\mathrm{OH}}K_h$ ($\sim 1.2 \times 10^{-5}$) is of similar magnitude to $k_{12}[\mathrm{H}^+]$ ($\sim 1.8 \times 10^{-5}$) and it is clear that $\mathrm{(H_2O)_5NiOH^+}$ might make a significant contribution to the observed rate under these conditions.

In summary, if an ICB effect is to be demonstrated, the experiments must be done at pH >7, and possible reaction of $\mathrm{(H_2O)_5NiOH^+}$ must be eliminated.

Registry No. $\mathrm{Ni(H_2O)_6^{2+}}$, 15365-79-4; ethylenediamine, 107-15-3.

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Twist Angle Definitions

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Sir:

Recently, Dymock and Palenik[1] have commented on the question of the proper definition of the twist angle for coordination polyhedra which can be considered to consist of two "equivalent" polygons. To illustrate their point they have made calculations for and comparison of six definitions of the twist angle applied to seven polyhedra and have recommended that their definition 1 be used in preference to the others. However, they have not considered the possible definitions in any complete and systematic manner, nor have they considered the reasons for calculating twist angles. We wish to present a more systematic set of definitions, which includes the six definitions of Dymock and Palenik as a subset, and to point out that the selection of the appropriate definition depends upon the use to be made of the information.

The twist angle of a pair of equivalent ligand atoms, L_i and L_i', may be defined as the difference between their ϕ coordinates in a suitably defined polar coordinate system. The polar coordinate system may be defined by selecting a direction for the polar axis and a point through which the polar axis is to pass. Consideration of the nature of the polyhedra of the type of interest here suggests six "natural" possible choices for the direction of the polar axis: (1) the vector from the centroid of the "lower" polygon to the centroid of the "upper" polygon, (2) the vector from the metal ion to the centroid of the upper polygon, (3) the vector from the centroid of the lower polygon to the metal ion, (4) the normal to the upper polygon, (5) the normal to the lower polygon, and (6) the normal to the "midplane" of the polyhedron [i.e., the plane defined by the midpoints of the lines between pairs of "equivalent" ligand atoms] and four "natural" possible choices of the point: (1) the metal ion, (2) the centroid of the upper polygon, (3) the centroid of the lower polygon, and (4) the centroid of the polyhedron. In these terms we may identify any particular twist angle as $\phi^i{}_{jk}$, where i ($1-n$) identifies the ligand atoms L_i, j (1–6) identifies the direction of the polar axis, and k (1–4) identifies the point through which the polar axis passes. Among these 24 twist angle definitions, some are, by definition, identical. Thus, $\phi^i{}_{14} \equiv \phi^i{}_{13} \equiv \phi^i{}_{12}$, $\phi^i{}_{22} \equiv \phi^i{}_{21}$, and $\phi^i{}_{33} \equiv \phi^i{}_{31}$. If the polyhedron has any symmetry, further identities may arise. In the ideal case of a polyhedron consisting of two equilateral, parallel polygons whose centroids lie on their mutual normal (e.g., a regular octahedron), with the metal ion lying at the centroid of the polyhedron, all 24 twist angles are identical. The six twist angles considered by Dymock and Palenik are $\phi^i{}_{12}$, $\phi^i{}_{41}$, $\phi^i{}_{51}$, $\phi^i{}_{11}$, $\phi^i{}_{21}$, and $\phi^i{}_{31}$, respectively.

We have calculated the twist angles for the seven polyhedra selected by Dymock and Palenik. Several errors occur in their Table I. We are unable to identify the angles listed as $\phi^6{}_i$ for α-keto-1,1'-trimethyleneferrocene. For $\mathrm{In(pmtc)_3}$, $\phi^3{}_2$ should be 38.6°. Most of our values for $\mathrm{Cu(phen)_3}^{2+}$ differ very slightly from those in the table, in such a manner as to suggest that they probably used coordinates for ligand atom N(2) which are slightly different from those given by Anderson.[2] The values in the table for $\mathrm{Fe(acac)_3}$ have been calculated using ligand atoms O(1), O(3), and O(6) as face 1 and O(2), O(4), and O(5) (misnumbered O(7)) as face 2 although, to be consistent with the treatment of the other three six-coordinate complexes, face 1 should be O(1), O(5), and O(6) and face 2 should be O(2), O(4), and O(3).

In considering which definitions are most useful we can, as pointed out by Dymock and Palenik, dismiss the axis directions 2, 3, 4, and 5 on the basis of their asymmetry, although in special cases these values might be of interest. Perhaps it should be emphasized here that the "twist angle" becomes less significant as the two polygons become less nearly parallel. Similarly, passing the polar axis through the centroid of one of the polygons (points 2 and 3) gives twist angles of lesser uniformity and significance. Thus we are left with four definitions. We may use the line joining the two polygon centroids (axis 1) or the line normal to the midplane of the polyhedron (axis 6) as the direction of the polar axis. For six of the seven cases selected by Dymock and Palenik and for seven out of eight additional $\mathrm{M(acac)_3}$ complexes which we have examined, axis 1 gives less variation of the twist angles than axis 6 (mean of the ranges for 15 cases 2.0° vs. 3.8°). Therefore, except for cases in which there is some other basis for decision, we suggest (in agreement with Dymock and Palenik) that the line joining the centroids of the polygons should be, in general, selected as the direction for the polar axis. Comparing the two choices for the "origin" of the polar coordinate system, we find that the centroid of the polyhedron (as would be expected) gives slightly less variation of the twist angles than the metal ion (mean of ranges for the 15 cases 1.9° vs. 2.1°). However, these are coordination polyhedra, in which the metal ion plays a central role, and we therefore suggest that the metal ion is generally a more appropriate origin. For example, such a coordinate system is the appropriate one for any quantum mechanical calculations involving metal ion orbitals. We therefore recommend that, if only one definition of twist angle is to be used, it be our $\phi^i{}_{11}$ ($\phi^4{}_i$ of Dymock and Palenik). In general, in order to maximize "fact" and minimize "fantasy", one should (a) use twist angles only when they are appropriate, (b) carefully consider which definition is most useful, and (c) define precisely the definition used, e.g., by defining the "axis" and "origin" as illustrated above.

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