Metal-exchange Reactions between Cobalt(II) Complexes of Polyaminocarboxylic Acid Ligands and Copper(II) Ions

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Reactions between copper(II) and polyaminocarboxylato-complexes of cobalt(II) have been studied by a stopped-flow spectrophotometric technique at an ionic strength $I = 0.10$ mol dm^{-3} and 25 °C. Competitive associative and dissociative steps are observed with different dependences on the entering metal and on acidity. The rates of the reactions shift from first to zero order in [Cu^{2+}] in the case of ethylenediaminetetra-acetate and ethylenebis(oxyethylenenitrilo)-*N,N,N',N'*-tetra-acetate, while only first-order behaviour is observed for ethylenedi-imino-*N,N'*-diacetate and *N*-(2-hydroxyethyl)-ethylenedinitrilo-*N,N',N'*-triacetate. For all the reactions evidence is given for a stepwise unwrapping mechanism followed by attack of Cu^{2+} to give a binuclear intermediate. Experimental reactivities are compared with those computed according to the substitution lability of the exchanged metal ions and the stability of the proposed intermediate.

The exchange of a multidentate ligand L between two labile metal ions [equation (1)] is of interest for interpreting the

$$ML + M' \longrightarrow M'L + M \qquad (1)$$

way in which the single co-ordinating sites of such a ligand interact with a metal centre.[1] Valuable information may also be obtained on factors which affect the rate at which reaction (1) occurs, such as the stability of co-ordination of portions of the ligand L to the entering or leaving metal ions,[2-4] the rigidity of ligand L,[5,6] and the substitution labilities of the metal ions.[7,8] Almost all the available data published so far relate to the reactions of aminopolycarboxylato-complexes,[9] in particular the combination of various metal ions with ethylenediaminetetra-acetate (edta), according to reaction (1).[8,10] The relative reactivity of each metal was interpreted and predicted in terms of the relative stability constants of the metal–ligand complexes formed during the individual stages of the reaction.[11,12] These substitution reactions proceed through an intermediate binuclear complex in which the entering and leaving metal ions are bound to portions of the ligand L; dissociation of this intermediate is the rate-determining step of the overall exchange process and its stability relative to the reactant ML directly affects the rate of reaction (1).

The availability of kinetic data on a series of related reactions involving either a series of ligands,[3] $Zn^{II}L + Cu^{II} \longrightarrow Cu^{II}L + Zn^{II}$, or a series of cations,[1] $M^{II}(nta) + Cu^{II} \longrightarrow Cu^{II}(nta) - M^{II}$ (nta = nitrilotriacetate), enabled the characterization of substituent effects, such as steric ones, and the role of the lability of water molecules co-ordinated to the metal ions. The present paper reports results for the exchange reactions (2) for a series of structurally related

$$Co^{II}L + Cu^{II} \longrightarrow Cu^{II}L + Co^{II} \qquad (2)$$

ligands, namely edda^{2-} (ethylenedi-imino-*N,N'*-diacetate), hedta^{3-} [*N*-(2-hydroxyethyl)ethylenedinitrilo-*N,N',N'*-triacetate, edta^{4-} (ethylenedinitrilo-*N,N,N',N'*-tetra-acetate), and egta^{4-} [ethylenebis(oxyethylenenitrilo)-*N,N,N'N'*-tetra-acetate] (charges henceforth omitted for clarity). Comparison of the results obtained yields interesting information on the reaction mechanisms, on the role of the co-ordinating ability of the exchanged ligands in the intermediate complexes, and on the effect of the stability of the intermediate complexes.

Experimental

Reagents.—Reagent grade ligands were obtained from E. Merck or Fluka, and used as such. Cobalt(II) perchlorate was prepared from the corresponding carbonate and perchloric acid and recrystallized from water. Its solutions were analyzed by means of standard complexometric titrations. Solutions of cobalt(II) complexes were prepared prior to use by adding (see below) an excess of the metal perchlorate to a standard solution of each ligand, and adjusting the pH to *ca.* 5. These solutions were found to be stable for weeks. No oxidation of the metal centre appeared to occur and solutions kept under nitrogen or in the presence of air showed no differences in their spectroscopic or kinetic behaviour.

Procedure.—Reaction rates were followed by means of a stopped-flow spectrophotometric technique, at $\lambda = 800$ nm for the reaction of edda and egta, and at 330 nm for hedta and edta, by monitoring in each case the formation of the $Cu^{II}L$ complex. At these wavelengths the greatest change in absorption between reagents and products was found. Kinetic runs were performed by mixing a $Co^{II}L$ solution (final concentration 5.0×10^{-4} mol dm^{-3}) with different copper(II) solutions (2.5×10^{-3}—20×10^{-3} mol dm^{-3}). All rate measurements were performed at 25.0 ± 0.1 °C and in the presence of an excess of displaced metal ion (2.0×10^{-4}—5.0×10^{-4} mol dm^{-3}) in order to minimize dissociation of $Co^{II}L$; this excess was shown to have no effect on the rate. The reactions were followed for at least 2—3 half-lives and the pseudo-first-order rate constants were reproducible to ±2—3%. At the lower copper concentrations, the first stage of the reaction was monitored in order that pseudo-first-order conditions could be assumed. Both reactant solutions contained sodium perchlorate (total ionic strength $I = 0.10$ mol dm^{-3}) and acetate buffer. The buffer concentration was low with respect to [Cu^{II}] ($c_{buffer} = [MeCO_2H] + [MeCO_2^-] = 2.0 \times 10^{-3}$ mol dm^{-3}) in order to avoid catalysis by acetate.

Results and Discussion

All the reactions investigated have been found to follow pseudo-first-order kinetics, according to the rate expression (3).

$$d[CuL]/dt = -d[CoL]/dt = k_{obs.}[CoL] \qquad (3)$$

Plots of ln $[A_{eq}/(A_{eq} - A_t)]$ *vs.* time (where A_{eq} and A_t represent the absorbances at equilibrium and at time *t*, respec-

Table 1. Stability constants (log K) used [a]

Ligand	Co^{2+}	Cu^{2+}	Ligand	Co^{2+}	Cu^{2+}
edda	11.2	16.2	$MeCO_2^-$	1.5	1.9
hedta	14.4	17.5	$GlyO^-$	4.6	7.6
edta	16.3	18.8	ida	7.0	10.5
egta	12.3	17.7	aeida [b]	11.8	

log K for $Co^{II}L + Cu^{2+} \rightleftharpoons Cu^{II}L + Co^{2+}$: L = edda, 5.0; hedta, 3.1; edta, 2.5; egta, 5.4

[a] Data taken from ref. 13 at conditions as close to the investigated conditions as possible (I = 0.10 mol dm^{-3}, $NaClO_4$, 25.0 °C). [b] N-(2-Aminoethyl)iminodiacetate.

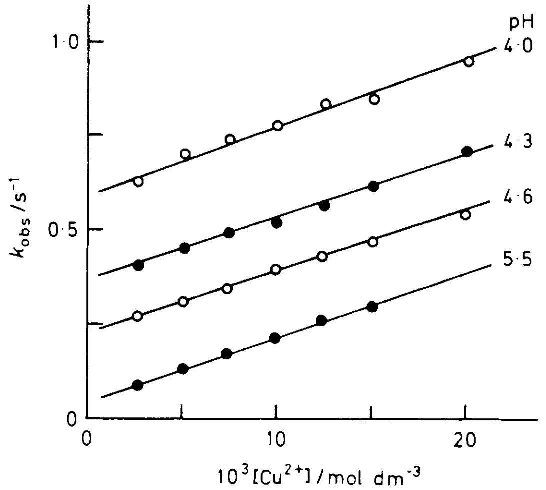


Figure 1. Variation of $k_{obs.}$ as a function of $[Cu^{2+}]$ for the reaction of Co^{II}(edda) with Cu^{2+} at different acidities

tively) were linear at least for 2—3 half-lives, and from their slopes $k_{obs.}$ values were obtained by weighted linear regression analysis. Under the conditions employed the back reaction could be neglected owing to the negative free-energy change for reaction (2). Table 1 lists the equilibrium constants for the reactions together with the stability constants used throughout this work; these constants are taken from previous data obtained under conditions as close to the present conditions as possible.[13]

Different reaction mechanisms have been found to operate as shown by the dependence of $k_{obs.}$ on either the concentration of the entering metal ion or on acidity.

edda Ligand.—The variation of $k_{obs.}$ as a function of copper(II) concentration present in excess, at constant acidity, conforms to equation (4), as shown in Figure 1. Since reverse

$$k_{obs.} = k_a[Cu^{2+}] + k_d \qquad (4)$$

reaction steps can be ruled out, combined associative (k_a) and dissociative (k_d) steps are present; k_a proved to be independent of acidity, while k_d showed a dependence of the form (5). Figure 2 reports the variation of k_d as a function

$$k_d = k_d' + k_d''[H^+] \qquad (5)$$

of acidity. From such plots k_d' and k_d'' have been evaluated, and Table 2 lists the observed rate constants and derived kinetic parameters. Therefore for edda the rate law (6) applies.

$$\text{Rate} = (k_a[Cu^{2+}] + k_d' + k_d''[H^+])[Co^{II}(edda)] \qquad (6)$$

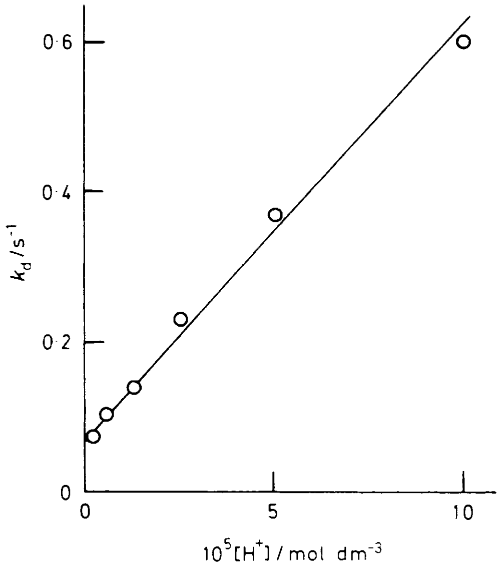


Figure 2. Direct acid dependence of k_d for the reaction of Co^{II}(edda) with Cu^{2+}

hedta Ligand.—For this ligand too (see Table 2) the variation of $k_{obs.}$ as a function of $[Cu^{2+}]$ was linear at each acidity with significant intercepts (k_d) and slopes (k_a), as for edda, but, in turn, k_d was found to have a direct dependence on acidity of the form $k_d = k_d''[H^+]$ and k_a was found to be a combination of two terms, $k_a' + k_a''[H^+]^{-1}$. Therefore the rate law (7) applies (Table 2 lists the derived parameters).

$$\text{Rate} = \{(k_a' + k_a''[H^+]^{-1})[Cu^{2+}] + k_d''[H^+]\}[Co^{II}(hedta)] \qquad (7)$$

edta and egta Ligands.—In the case of edta and egta the dependence of $k_{obs.}$ as a function of the concentration of the entering metal ion varies from first down to zero order, as illustrated for Cu^{2+} and edta in Figure 3. The experimental data for both ligands conform to the linear function (8) (see Figure

$$[Cu^{2+}]/k_{obs.} = A + B\,[Cu^{2+}] \qquad (8)$$

3); A and B values were found to be constant, within experimental uncertainty, in the acidity range investigated. Table 3 lists the experimental kinetic data and the derived kinetic parameters. Recalculated values of $k_{obs.}$ using the rate constants computed from the observed $k_{obs.}$, are included in Tables 2 and 3 for all the reactions studied.

Reaction Mechanisms.—In the case of the three-term rate law (6) for edda the reaction sequence (9)—(13) accounts for the dependences observed. Reactions (9) + (12) and

$$Co^{II}(edda) \xrightarrow{k^{CoL}} Co^{2+} + edda \qquad (9)$$

$$Co^{II}(edda) + H^+ \overset{K_H}{\rightleftharpoons} Co^{II}(Hedda) \qquad (10)$$

$$Co^{II}(Hedda) \xrightarrow{k_H^{CoL}} Co^{2+} + Hedda \qquad (11)$$

$$edda\ (Hedda) + Cu^{2+} \xrightarrow{fast} Cu^{II}(edda)\ (+H^+) \qquad (12)$$

$$Co^{II}(edda) + Cu^{2+} \xrightarrow{k_{Cu}^{CoL}} Cu^{II}(edda) + Co^{2+} \qquad (13)$$

Table 2. Observed rate constants, $k_{obs.}$, and k_a and k_d for the exchange of edda and hedta from Co^{II} to Cu^{II}, at different copper concentrations and acidities; $[Co^{II}L] = 5.0 \times 10^{-4}$ mol dm^{-3}, 25.0 °C, $I = 0.10$ mol dm^{-3}. Values in parentheses are the computed observed rate constants obtained from the derived parameters (see Table 4) [a]

$10^3[Cu^{2+}]$ / mol dm^{-3}	pH 4.0	4.3	4.6	4.9	5.2	5.5
edda ($10k_{obs.}$/s^{-1})						
2.50	6.31 (6.73)	4.06 (3.93)	2.71 (2.53)	1.8 (1.83)	1.24 (1.48)	0.86 (1.30)
5.00	7.11 (7.15)	4.54 (4.36)	3.13 (2.96)	2.17 (2.25)	1.74 (1.90)	1.36 (1.73)
7.50	7.41 (7.58)	4.83 (4.78)	3.47 (3.38)	2.63 (2.68)	2.13 (2.33)	1.77 (2.25)
10.0	7.80 (8.00)	5.20 (5.21)	4.08 (3.81)	3.11 (3.10)	2.43 (2.75)	2.16 (2.58)
12.5	8.50 (8.43)	5.67 (5.63)	4.34 (4.23)	3.33 (3.53)	2.76 (3.18)	2.58 (3.00)
15.0	8.45 (8.85)	6.04 (6.06)	4.70 (4.66)	3.84 (3.95)	3.20 (3.60)	2.95 (3.43)
20.0	9.46 (9.70)	7.09 (6.91)	5.41 (5.51)	4.24 (4.80)	3.96 (4.45)	
hedta ($10^2k_{obs.}$/s^{-1})						
2.50	2.0 (2.0)	1.5 (1.4)	1.2 (1.2)	1.3 (1.1)	1.1 (1.3)	2.0 (1.8)
5.00	3.0 (2.8)	2.3 (2.2)	2.1 (2.0)	2.3 (2.1)	2.7 (2.6)	3.8 (3.7)
7.50	4.0 (3.5)	3.2 (3.0)	3.0 (2.8)	3.3 (3.1)	4.0 (3.9)	5.6 (5.5)
10.0	4.6 (4.3)	3.8 (3.7)	3.8 (3.7)	4.2 (4.1)	5.7 (5.1)	7.6 (7.3)
12.5	5.4 (5.0)	4.6 (4.5)	4.6 (4.5)	5.4 (5.1)	6.2 (6.4)	8.9 (9.1)
15.0	6.3 (5.7)	5.6 (5.3)	5.5 (5.4)	6.6 (6.0)	7.6 (7.6)	11.3 (10.9)
20.0	7.7 (7.2)	6.9 (6.9)	6.7 (7.0)	7.7 (8.0)	10.2 (10.1)	
k_a/dm^3 mol^{-1} s^{-1} [b]	18.0 (3.25)	16.5 (3.25)	15.5 (3.40)	16.0 (4.00)	15.5 (5.20)	15.5 (7.40)
k_d/s^{-1} [b]	0.60 (0.013)	0.37 (0.0065)	0.23 (0.003)	0.14 (0.002)	0.10 ($\leqslant$0.002)	0.06 ($\leqslant$0.002)

[a] Each $k_{obs.}$ value was found reproducible to ±2—3%. [b] Values for edda, and (in parentheses) for hedta.

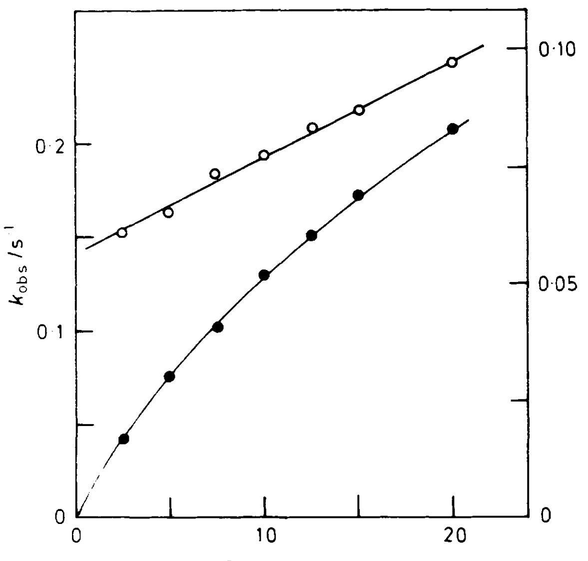


Figure 3. Variation of $k_{obs.}$ (●) and of $[Cu^{2+}]/k_{obs.}$ (○) as a function of $[Cu^{2+}]$ for the reaction of Co^{II}(edta) with Cu^{2+} at pH 4.0

(10)—(12) are responsible for the dissociative paths [see equation (5)] independent of $[Cu^{2+}]$: dissociation of the precursor complex Co^{II}(edda) proceeds with formation of a free edda ligand species which then rapidly complexes with free Cu^{2+}. In both cases the rate-determining step is the dissociation of the cobalt species. Preliminary protonation [equation (10)] facilitates the dissociation; in fact the acid-catalyzed step (10)—(12) predominates over (9) + (12) as can be seen in Figure 2 (compare the small intercept and the contribution from the slope term). Direct interaction of Cu^{2+} with the complex, as in equation (13), gives rise to the associative contribution [first term in equation (6)]. For this step a partial detachment of edda allows co-ordination to copper with formation of a binuclear complex [equation (14)]

$$\mathrm{Co(edda)} + \mathrm{Cu}^{2+} \xrightleftharpoons{K_{eq}} \mathrm{Co(edda)Cu} \qquad (14)$$

which then decomposes leading to the reaction products [equation (15)]. From reactions (14) and (15) one can obtain expression (16) which corresponds to the observed first-order

$$\mathrm{Co(edda)Cu} \xrightarrow{k} \mathrm{Cu(edda)} + \mathrm{Co}^{2+} \qquad (15)$$

$$\frac{d[\mathrm{Cu(edda)}]}{dt} = \frac{kK_{eq}[\mathrm{Co(edda)}][\mathrm{Cu}^{2+}]}{1 + K_{eq}[\mathrm{Cu}^{2+}]} \qquad (16)$$

dependence on $[Cu^{2+}]$ for the associative term, under the condition $K_{eq}[Cu^{2+}] \ll 1$, *i.e.* $K_{eq} < 50$ dm^3 mol^{-1}, which is quite reasonable considering the possible structure of the intermediate. Therefore the expressions (17) are applicable.

$$k_a = k_{Cu}{}^{CoL} = kK_{eq},\ k_d' = k^{CoL},\ k_d'' = k_H{}^{CoL}K_H \qquad (17)$$

Table 4 lists the derived kinetic parameters.

In the case of hedta, a single dissociative acid-catalyzed path is present corresponding to (10)—(12). The absence of a path corresponding to (9)+(12) suggests that the dissociative paths are suppressed by the increasing stability of the reactant complex when going from edda to hedta. With hedta a protonation step as in (10) becomes a prerequisite for promoting the reaction. Besides, an additional associative step with inverse acid dependence operates here, thus showing that the reactive species is $Cu(OH)^+$ [equation (18)].[2,3]

$$\mathrm{Cu(OH)}^+ + \mathrm{Co^{II}(hedta)} \xrightarrow{k_a'} \mathrm{Cu^{II}(hedta)} + \mathrm{Co}^{2+} + \mathrm{OH}^- \qquad (18)$$

In the cases of edta and egta the dependence of $k_{obs.}$ on the concentration of exchanged ligand varies from first down to

Table 3. Observed rate constants, $k_{obs.}$, and parameters A and B for the exchange reactions of edta and egta from Co^{II} to Cu^{II} at different copper concentrations and acidities; $[Co^{II}L] = 5.0 \times 10^{-4}$ mol dm^{-3}, 25.0 °C, $I = 0.10$ mol dm^{-3}. Values in parentheses are the computed observed rate constants obtained from the derived A and B values [a]

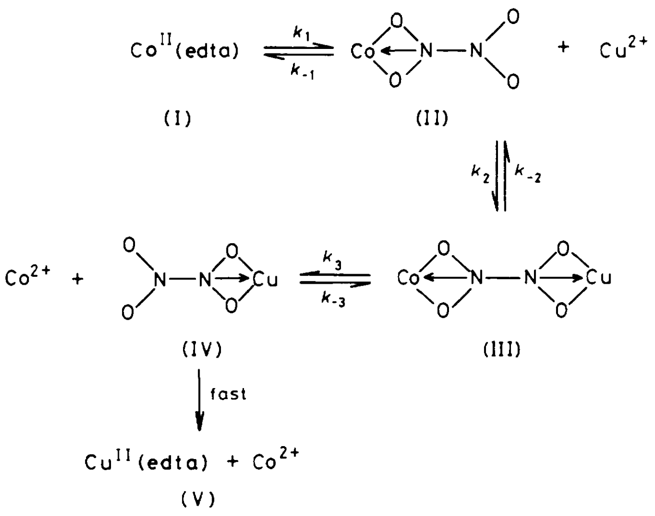
$10^3[Cu^{2+}]$/mol dm^{-3}	pH 4.0	4.3	4.6	4.9	5.2	5.5
edta ($10k_{obs.}$/s^{-1})						
2.50	0.41 (0.41)					
5.00	0.77 (0.76)	0.65 (0.64)	0.62 (0.59)	0.57 (0.57)	0.57 (0.56)	0.60 (0.60)
7.50	1.02 (1.06)	0.86 (0.88)	0.80 (0.80)	0.79 (0.79)	0.79 (0.78)	0.81 (0.83)
10.0	1.29 (1.32)	1.11 (1.10)	1.02 (0.98)	1.00 (0.98)	0.96 (0.95)	0.99 (1.02)
12.5	1.50 (1.54)	1.28 (1.29)	1.20 (1.13)	1.14 (1.14)		
15.0	1.72 (1.74)	1.43 (1.45)	1.40 (1.26)	1.23 (1.28)	1.25 (1.28)	1.34 (1.32)
20.0	2.06 (2.08)	1.69 (1.72)	1.56 (1.47)	1.55 (1.52)	1.47 (1.47)	1.66 (1.56)
egta ($k_{obs.}$/s^{-1})						
2.50	2.31 (2.17)	2.22 (2.08)	1.87 (1.47)	1.56 (1.26)	1.19 (1.01)	1.29 (1.14)
5.00	2.87 (2.63)		1.92 (1.92)	1.69 (1.69)	1.43 (1.49)	1.52 (1.56)
7.50	2.88 (2.83)	2.52 (2.68)	2.16 (2.14)	1.89 (1.91)	1.80 (1.78)	1.71 (1.79)
10.0	2.94 (2.94)	2.73 (2.78)	2.32 (2.27)	2.05 (2.04)	1.89 (1.96)	1.85 (1.92)
12.5	3.04 (3.01)	2.65 (2.84)	2.36 (2.36)	2.17 (2.13)	1.95 (2.09)	2.05 (2.02)
15.0	3.15 (3.06)	2.86 (2.88)	2.41 (2.42)	2.24 (2.19)	2.18 (2.19)	2.12 (2.08)
20.0	3.16 (3.13)	3.09 (2.94)	2.54 (2.50)	2.27 (2.27)	2.33 (2.32)	
A/s mol dm^{-3} [b]	0.056 (0.0004)	0.066 (0.0008)	0.068 (0.0008)	0.072 (0.001)	0.070 (0.0016)	0.068 (0.0012)
B/s [b]	2.0 (0.30)	2.5 (0.32)	3.4 (0.36)	3.0 (0.39)	3.3 (0.35)	3.0 (0.40)

[a] Each $k_{obs.}$ value was found reproducible to ±2—3%. [b] Values for edta, and (in parentheses) for egta.

Table 4. Kinetic parameters for the substitution reactions $Co^{II}L$ + Cu

Reaction	k^{CoL}/s^{-1}	$k_H^{CoL}K_H$/dm^3 mol^{-1} s^{-1}	k_{Cu}^{CoL}/dm^3 mol^{-1} s^{-1}	$k_{Cu(OH)}^{CoL}K_{hy}$*/s^{-1}
Co(edda) + Cu^{2+}	$(7.0 \pm 1.0) \times 10^{-2}$	$(5.6 \pm 0.5) \times 10^3$	17 ± 2	
Co(hedta) + Cu^{2+}		$(1.3 \pm 0.1) \times 10^2$	2.8 ± 0.3	$(1.4 \pm 0.2) \times 10^{-5}$
Co(edta) + Cu^{2+}	0.33 ± 0.04		15 ± 2	
Co(egta) + Cu^{2+}	3.0 ± 0.3		$(1.0 \pm 0.3) \times 10^3$	

* K_{hy} represents the equilibrium constant for $Cu(OH)^+$ formation.



Scheme.

zero order. For these ligands a partial unwrapping of one or more acetato-groups from Co^{II} allows binding of Cu^{II}; the intermediate complex thus formed then participates in the rate-determining step followed by complete release of Co^{II} and full co-ordination around Cu^{II} (Scheme, reaction steps written for edta apply also to egta). This last step is considered fast as compared to previous steps since the equilibrium (IV) $\rightleftharpoons$ (V) is mainly governed by the ease of substitution at copper (water-exchange rate, $k_{Cu}^{-H_2O} \approx 3 \times 10^8$ s^{-1}).[14]

By applying the steady-state approximation to species (III) and (IV), expression (19) may be obtained. Alternatively, with reference to equation (8), we can write equation (20) and hence expressions (21). If one considers equation (19), at

$$d[Cu(edta)]/dt = k_{obs.}[Co(edta)] = \frac{k_1k_2k_3[Cu^{2+}][Co(edta)]}{k_{-1}(k_{-2} + k_3) + k_2k_3[Cu^{2+}]} \quad (19)$$

$$\frac{[Cu^{2+}]}{k_{obs.}} = \frac{k_{-1}(k_{-2} + k_3)}{k_1k_2k_3} + \frac{[Cu^{2+}]}{k_1} \quad (20)$$

$$\frac{k_1k_2k_3}{k_{-1}(k_{-2} + k_3)} = A^{-1}, k_1 = B^{-1} \quad (21)$$

high copper(II) concentrations the dependence on $[Cu^{2+}]$ should level off, which is indeed experimentally observed, and the k_1 step becomes the rate-limiting process, while at low concentrations the rate is first order in both $[Cu^{2+}]$ and [Co(edta)] and the second-order rate constant is given by equation (22). In order to identify the rate-determining step

$$k_{Cu}^{CoL} = k_1k_2k_3/[k_{-1}(k_{-2} + k_3)] \quad (22)$$

under the latter conditions one must consider whether k_{-2} or k_3 is the predominant term in the denominator. Since k_{-2} and k_3 represent the rates of dissociation of Cu^{2+} and Co^{2+} from an iminodiacetate (ida) portion of the ligand, a relative comparison can be made on the basis of the water-exchange rates and equilibrium constants of the corresponding complexes:[13-15] $k_{-2} \approx k_{Cu}{}^{-H_2O}/K_{Cu(ida)} = 3 \times 10^8/3 \times 10^{10} = 1 \times 10^{-2}\ s^{-1}$; $k_3 \approx k_{Co}{}^{-H_2O}/K_{Co(ida)} = 2 \times 10^6/8 \times 10^6 = 2.5 \times 10^{-1}\ s^{-1}$. Thus, $k_{Cu}{}^{CoL} \approx k_2K_1$, and the rate-determining step is represented by (II) $\longrightarrow$ (III). The same behaviour has been found in the case of egta and all the derived kinetic parameters are collected in Table 4.

Now if one considers the associative path (k_a) for each ligand the rate of reaction is governed in one case (edda and hedta) by the stability of an intermediate binuclear complex [reaction (14)] and by the rate of its decomposition [equations (15) and (16)], and in the other (edta and egta) by the stability of an intermediate mononuclear complex species, where cobalt has a lower co-ordination number than the starting reactant [species (II) of the Scheme] and by the rate of its interaction with Cu. In both cases, knowledge of the structure of the intermediate allows one to postulate a mechanism on the basis of its relative stability which may be computed according to equation (23) where K_{CoL} is the stability constant of the starting complex taken as a reference, $K_{Co\text{-}segment}$

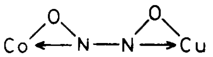
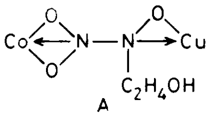
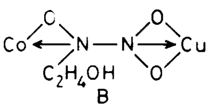
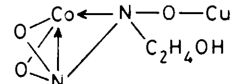
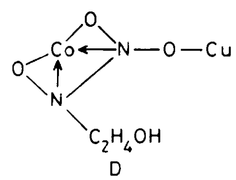
$$K_{rel} = \frac{K_{Co\text{-}segment}\,K_{Cu\text{-}segment}}{K_{CoL}} \cdot K_{stat}K_{el} \qquad (23)$$

and $K_{Cu\text{-}segment}$ are the stability constants of the metal complexes of Co and Cu bound to the segments of L in the intermediates, K_{el} accounts for the electrostatic stabilization from the charged unbound portions of L in the intermediate ($K_{el} \approx 10$ for a 1− group), and K_{stat} is a statistical factor which accounts for the number of equivalent ways in which the intermediate can be formed by interaction of the entering metal with equivalent sites of CoL.[2,3] Previous investigations on edda exchange reactions[11] have shown that the structure of the intermediate MLM′ comprises two glycinato (GlyO) segments bound to both leaving and entering metals, and that the rate-determining step is given by the dissociation of the M←N bond in the M–GlyO portion.

Substitution of Co with Cu in both edda and hedta complexes involves dissociation of a similar Co←N bond, therefore the overall rates of exchange are governed by the relative stabilities of the intermediates. Table 5 compares the structures of the intermediate Co(edda)Cu with a series of structures to be tested for the Co(hedta) + Cu^{2+} reaction. As can be seen the best agreement between the experimental relative reactivities and relative intermediate stabilities is obtained for structures A and B, of which A is favoured; on the contrary, structures C and D give much less stable intermediates which do not give satisfactory agreement with the experimental reactivities. Therefore copper attacks the more easily unwrapped end of the ligand and is bound through both CO_2^- and N.

If one now considers a series of M(edda) + Cu^{2+} reactions, the proposed mechanism can be tested by comparing the experimental reactivities and those computed from equation (16) where K_{eq} is obtained from equation (23) and k [the rate constant for equation (15), *i.e.* the rate of release of M^{2+} from a glycinato-ligand] is obtained from $k_M{}^{-GlyO} = K_{M(GlyO)}k_M{}^{GlyO}$ [where $K_{M(GlyO)}$ is the stability constant of the M(GlyO) complex and $k_M{}^{GlyO}$ is the rate of reaction of M^{2+} with GlyO, which in turn is given by the rate of water exchange at M^{2+}]. Table 6 lists all the kinetic parameters together with the ratio r between the experimental and computed values, which should be constant. A good agreement is observed for reactions of Co^{2+} and Zn^{2+}, while the exchange of Ni^{2+} from edda and its dimethyl-substituted derivative eddp shows a

Table 5. Comparison of reaction intermediates for Co(edda) + Cu^{2+} and Co(hedta) + Cu^{2+}

	Intermediate	Relative stability constants, $\log K_{rel}$	$\dfrac{k_{Cu}{}^{Co(edda)}}{k_{Cu}{}^{Co(hedta)}}$	$\dfrac{K_{rel}{}^{(edda)}}{K_{rel}{}^{(hedta)}}$
edda		+1.0 *	6.1	
hedta	 A	+0.2	6.1	3.2
	 B	+0.7 *	6.1	2.0
	 C	−0.7	6.1	25
	 D	−1.3 *	6.1	200

* Statistical factor of 0.5.

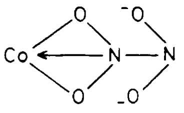
Table 6. Comparison of experimental and computed kinetic and equilibrium parameters for the exchange reactions of M^{II}(edda) + Cu^{2+}

Reaction	$k_{Cu}{}^{CoL}$ / $dm^3\ mol^{-1}\ s^{-1}$	$\log K_{rel}$	$\log k_M{}^{-H_2O}$ [a]	$\log K_{M(GlyO)}$ [b]	$k_M{}^{-GlyO}$ / s^{-1}	$K_{rel}k_M{}^{-GlyO}$ / $dm^3\ mol^{-1}\ s^{-1}$	$r\ (= K_{rel}k_M{}^{-GlyO}/k_{Cu}{}^{CoL})$	Ref.
Co^{II}(edda) + Cu^{2+}	80	1.00 [c]	6.30	4.6	50	500	29	This work
Zn^{II}(edda) + Cu^{2+}	17	1.40 [c]	7.50	5.0	32	7.9×10^3	99	3
Ni^{II}(edda) + Cu^{2+}	7.49×10^{-2}	0.30 [c]	4.50	5.6	0.079	0.16	2.1	11
Ni^{II}(eddp) [d] + Cu^{2+}	7.51×10^{-3}	−1.37 [e]	4.50	2.7 [f]	63	2.7	380	2

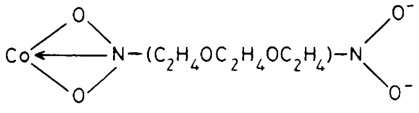
[a] From ref. 15. [b] From ref. 13. [c] Computed assuming a double-GlyO structure as in Table 5. [d] eddp = 2.2′-ethylenedi-iminodipropionate. [e] Relative to a Ni–eddp–Cu intermediate.[2] [f] Refers to the formation of a 1 : 1 Ni–NH_3 complex in order to take into account the different intermediate structure.

scatter below and above the values for Co^{2+} and Zn^{2+}, with moderate agreement.

If the intermediate structures in the reactions of edta and egta are taken into account the relative stabilities of the intermediates are governed [see equation (23)] by the stability of the Co–GlyO portion (which is the same for both complexes) and by the inverse of the stability of Co(edta) and Co(egta); in addition, electrostatic stabilization from the two released carboxylato-groups must be taken into account for edta (factor of 10 for each group) while, for egta, the dioxyethyl chain separates the dissociated portion of the ligand from the metal centre so that there is no stabilization from this source. Thus we obtain K_{rel} [Co(edta) intermediate] = $\frac{1}{2}K_{Co(GlyO)}10^2/K_{Co(edta)} = 1.3 \times 10^{-10}$ and K_{rel} [Co(egta) intermediate] = $\frac{1}{2}K_{Co(GlyO)}10^2/K_{Co(egta)} = 1.3 \times 10^{-8}$, where $\frac{1}{2}$ is a statistical factor accounting for the ability of CoL to give the intermediate by opening either side of the ethylenediamine skeleton. The agreement between the experimental reactivity ratio ($k_{Cu}{}^{Co(edta)}/k_{Cu}{}^{Co(egta)} = 1.5 \times 10^{-2}$) and that computed from the relative stabilities of the intermediate species [K_{rel}(edta)/K_{rel}(egta) = 1×10^{-2}] is very good and confirms the proposed mechanisms.



edta



egta

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Received 14*th March* 1983; *Paper* 3/397