Metal-exchange Reactions between Cobalt(II) and Lead(II) Complexes of Nitrilotriacetic Acid and Copper(II)

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The reactions between the cobalt(II) and lead(II) complexes of nitrilotriacetic acid (H_3nta) and the copper(II) ion have been studied using the stopped-flow technique over the concentration ranges $[M(nta)]_0 = 5 \times 10^{-4}$, $[Cu^{II}]_0 = (2.5—20) \times 10^{-3}$, and $[H^+] = (3—100) \times 10^{-6}$ mol dm^{-3}. The kinetics are found to agree with rate law (i). Values of $k^{M(nta)} = 1.1 \times 10^{-2}$ and 4.0×10^{-2} s^{-1}, $k_H^{M(nta)} = 7.8 \times 10^2$ and 2.6×10^3 dm^3 mol^{-1} s^{-1},

$$d[Cu(nta)^-]/dt = \{k^{M(nta)} + k_H^{M(nta)}[H^+] + k_{Cu}^{M(nta)}[Cu^{2+}]\}[M(nta)^-] \qquad (i)$$

and $k_{Cu}^{M(nta)} = 2.6$ and 35 dm^3 mol^{-1} s^{-1} are found for M = Co^{II} and Pb^{II} respectively, at 25 °C. The mechanism of these exchange reactions is discussed with reference to the relative stability of the intermediate binuclear mixed complexes, the labilities of the metal ions investigated, and the stabilities of the metal–ligand complexes involved in each of the different reaction pathways.

METAL or ligand exchange reactions in aminopolycarboxylato-complexes show a range of very different

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

$$ML + L' \rightleftharpoons ML' + L \qquad (2)$$

kinetic behaviour: a multistep dissociation of the ligand from the metal centre of the reacting complex is followed either by (i) the ligand's association with the incoming metal [reaction (1)] [1] or (ii) by the association of the new ligand with the metal [reaction (2)].[2,3] During this complex interaction, certain factors play important roles: sometimes the reactions go through an intermediate binuclear mixed complex whose stability, relative to the reacting species, has a strong influence on the reactivity.[4] In other cases, the ligand structure and rigidity does not allow the formation of a mixed complex and therefore complete dissociation of the reacting complex determines the reaction rate.[5]

Water exchange rates at the metal centres involved can also be relevant,[6] as well as the rates of single ligand–metal bond dissociations,[7] which depend, in turn, on the lability of the co-ordinated species. Outer-sphere association effects, steric effects, protonation of the ligand, partial dissociation of the co-ordinated ligands, pH of the solution, and the concentration of the reagents [8] all affect the location of the rate-determining step in the numerous steps that together represent the overall exchange reaction.

The combination of various metal ions with ethylenediaminetetra-acetate (edta) [8] according to exchange reaction (1) has been extensively studied. The relative reactivity of each metal was interpreted and predicted in terms of the relative stability constant of the metal–ligand complexes formed during the intermediate stages of the reaction.

The reactions studied here are given by equation (1) where ML is the nitrilotriacetato-complex (nta) of Co^{II} and Pb^{II} and M′ is Cu^{II}. The availability of data concerning the displacement by Pb^{II} and Ni^{II} of the complex $[Co^{II}(nta)]^-$,[9] and the displacement of the nta complex of Zn^{II} by Cu^{II},[10] enables us to make a series of interesting comparisons on the behaviour of metal ions with differing lability and whose complexes with the ligand itself, or with portions of it, have different stabilities.

EXPERIMENTAL

Reagents.—Reagent grade nitrilotriacetic acid (H_3nta) was obtained from E. Merck and used as such. Cobalt(II), lead(II), and copper(II) perchlorates were obtained from the corresponding carbonates and perchloric acid (E. Merck) and recrystallized from water. Stock solutions of the reagents were analyzed by means of standard methods.

Solutions of $[Co^{II}(nta)]^-$ and $[Pb^{II}(nta)]^-$ were obtained by adding a 5% molar excess of each metal perchlorate to a standard solution of the ligand. The pH was then raised to 10—10.5, the excess of metal was removed as the hydroxide, and the solutions were acidified to pH *ca.* 5.

Procedure.—Reaction rates were followed by means of a stopped-flow spectrophotometric technique at 760 nm for the reaction of $[Pb(nta)]^-$ and at 350 nm for the reaction of $[Co(nta)]^-$, by monitoring in each case the formation of the reaction product, $[Cu(nta)]^-$. At these wavelengths the greatest change in absorption between reagents and products was found. Kinetic runs were performed by mixing a $[Pb(nta)]^-$ or $[Co(nta)]^-$ solution (final concentration 5×10^{-4} mol dm^{-3}) with different copper(II) solutions (2.5×10^{-3}—20×10^{-3} mol dm^{-3}). All rate measurements were carried out in the presence of an excess of displaced metal (2×10^{-4}—5×10^{-4} mol dm^{-3}) in order to minimize complex dissociation; this excess had 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—4%. For lower concentrations of Cu^{2+}, the early part of the reactions was followed. Runs were performed at 25 ± 0.1 °C. Both reactant solutions contained sodium perchlorate, in order to maintain an ionic strength of 0.10 mol dm^{-3}, and acetate buffer. The buffer concentration was low with respect to $[Cu^{2+}]$ $\{c_{buffer}[\Sigma([MeCO_2H] + [MeCO_2^-])] = 2 \times 10^{-3}$ mol dm$^{-3}\}$ in order to avoid acetate catalysis.

RESULTS AND DISCUSSION

The reactions were found to be first order in displaced complex as shown by the linearity of plots of $\ln(A_\infty -$

A_t) against time {where A_∞ and A_t represent the absorbance at equilibrium and at time t, due to the product $[Cu(nta)]^-$ formation} and from their slopes the corresponding $k_{obs.}$ values collected in Table 1 were obtained. Figure 1 shows the effect that a change in copper(II) concentration has upon $k_{obs.}$, at different pH values. Since the reactions investigated are displaced to the right {log $K_1 = 2.6$ and 1.6 for $[Co(nta)]^-$ and $[Pb(nta)]^-$ respectively, see Table 2}, no contribution from the reverse reaction affects the $k_{obs.}$ values. Therefore, the rate of the reaction, regardless of copper concentration (intercepts of Figure 1), depends on rate-determining dissociative steps which involve the reacting complex. The functional form for $k_{obs.}$ is therefore that of equation (3) where k_a, the associative term, represents

$$k_{obs.} = k_a[Cu^{2+}] + k_b \qquad (3)$$

a direct composite interaction between the reactants, whereas k_b represents the contribution from the substitution which is independent of the incoming metal concentration, *i.e.* the decomposition of the reacting complex.

TABLE 1

Variation of the observed first-order rate constants, $k_{obs.}/s^{-1}$, with pH and excess of copper ion concentration for the reaction of cobalt(II) and lead(II) complexes of nitrilotriacetic acid with copper(II) ions; [nta] = 5.0×10^{-4}, $[Co^{2+}]$ or $[Pb^{2+}] = 1.0 \times 10^{-3}$, $\Sigma([MeCO_2H] + [MeCO_2^-]) = 2.0 \times 10^{-3}$ mol dm^{-3}, $I = 0.1$ mol dm^{-3}, 25.0 °C

	pH					
$10^3[Cu^{2+}]$	4.0	4.3	4.6	4.9	5.2	5.5
(*a*) Cobalt(II)						
2.50	0.095	0.057	0.035	0.027		
5.00	0.108	0.066	0.043	0.033	0.027	0.026
7.50	0.109	0.069	0.050	0.041	0.035	0.033
10.0	0.119	0.077	0.056	0.042	0.041	0.040
12.5	0.130	0.084	0.066	0.051	0.051	0.048
15.0	0.140	0.089	0.068	0.058	0.053	0.052
20.0	0.148	0.102	0.082	0.067	0.065	0.065
(*b*) Lead(II)						
2.50	0.382	0.242	0.163	0.135	0.123	0.130
5.00	0.562	0.389	0.297	0.237	0.217	0.249
7.50	0.651	0.555	0.366	0.307	0.273	0.327
10.0	0.793	0.626	0.454	0.336	0.357	0.399
12.5	0.939	0.681	0.525	0.407	0.414	0.484
15.0	0.947	0.759	0.595	0.449	0.495	0.527
17.5	1.101	0.896	0.743	0.587	0.531	0.672
20.0	1.236	0.993	0.796	0.620	0.654	0.750

TABLE 2

Stability constants (log values) used *

Ligand [b]	Co	Pb	Cu	Zn	Ni	H^+
$MeCO_2^-$	1.5	2.1	1.9	1.0	1.0	4.7
ida^{2-}	7.1	7.6	10.6	7.3	8.4	
nta^{3-}	10.4	11.4	13.0	10.7	11.5	

* Data have been taken from the literature to be as close to the investigated conditions as possible (25.0 °C, $I = 0.10$ mol dm^{-3} $Na[ClO_4]$). (L. G. Sillèn and A. E. Martell, *Special Publ.*, The Chemical Society, London, 1964, no. 17; no. 25, 1971; A. E. Martell and R. M. Smith, ' Critical Stability Constants,' Plenum, New York, 1974, vol. 1.)

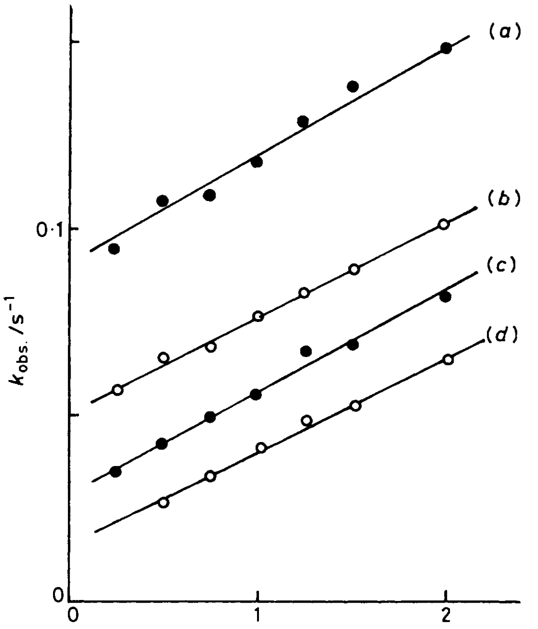


FIGURE 1 Variation of $k_{obs.}$ with copper concentration for the substitution reaction of $[Co(nta)]^-$ with Cu^{2+}, at different pH values: pH = 4.0 (*a*), 4.3 (*b*), 4.6 (*c*), and 5.5 (*d*)

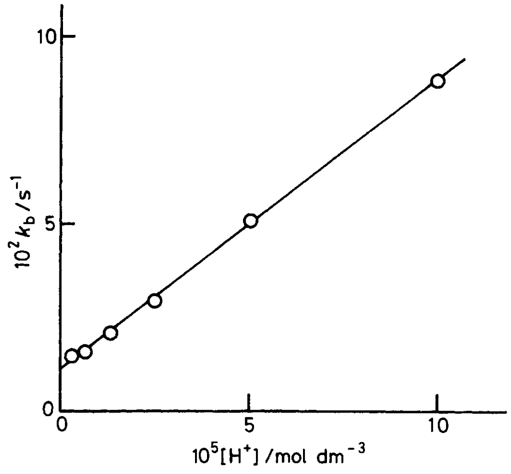


FIGURE 2 Direct acid dependence of the acid-catalysed reaction rate for the dissociative pathways of the reaction of $[Co(nta)]^-$ with Cu^{2+}

Figure 2 shows that the dependence of k_b on acidity is of the form (4) whereas the term k_a is independent of

$$k_b = k' + k''[H^+] \qquad (4)$$

acidity. Three competitive reaction pathways are therefore present. The dissociative paths k' and k'' (acid-catalyzed) are given by equations (5)—(8), where $k' = k^{M(nta)}$ and $k'' = k_H{}^{M(nta)} = K_H k^{M(Hnta)}$. The slow

$$[M(nta)]^{-} \xrightleftharpoons{k^{M(nta)}} M^{2+} + nta^{3-} \qquad (5)$$

$$[M(nta)]^- + H^+ \xrightleftharpoons{K_H} [M(Hnta)] \qquad (6)$$

$$[M(Hnta)] \xrightleftharpoons{k^{M(Hnta)}} M^{2+} + Hnta^{2-} \qquad (7)$$

$$nta^{3-}(Hnta^{2-}) + Cu^{2+} \xrightarrow{\text{fast}} [Cu(nta)]^-(+ H^+) \qquad (8)$$

steps (5) and (7) give rise to the free-ligand species nta^{3-} (and Hnta^{2-}) which react in a fast step (8) with Cu^{2+} to give the reaction products. The location of the rate-determining step before combination with copper makes the rates of these pathways independent of $[\mathrm{Cu}^{2+}]$.

The copper-dependent term is independent of acidity and can be ascribed to reaction (9) through the binuclear

$$\underset{(\mathrm{A})}{[\mathrm{M(nta)}]^-} + \mathrm{Cu}^{2+} \rightleftharpoons \underset{(\mathrm{B})}{\mathrm{M{-}nta{-}Cu}} \rightleftharpoons \mathrm{M} + \underset{(\mathrm{C})}{[\mathrm{Cu(nta)}]^-} \qquad (9)$$

intermediate (B).

Table 3 contains the data for the reactions studied here together with those for reactions previously investigated.

TABLE 3

Kinetic parameters of the different pathways for the substitution reactions of $[\mathrm{Co(nta)}]^-$ and $[\mathrm{Pb(nta)}]^-$ with Cu^{2+} and for related reactions

Reaction	$k^{\mathrm{M(nta)}}$/ $\mathrm{s^{-1}}$	$k_{\mathrm{H}}^{\mathrm{M(nta)}}$/ $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$	$k_{\mathrm{M'}}^{\mathrm{M(nta)}}$/ $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$	Ref.
$[\mathrm{Co(nta)}]^- + \mathrm{Cu}^{2+}$	1.1×10^{-2}	7.8×10^{2}	2.6	This work
$[\mathrm{Pb(nta)}]^- + \mathrm{Cu}^{2+}$	4.0×10^{-2}	2.6×10^{3}	35	This work
$[\mathrm{Zn(nta)}]^- + \mathrm{Cu}^{2+}$	3.0×10^{-2}	4.0×10^{3}	9.0	10
$[\mathrm{Co(nta)}]^- + \mathrm{Pb}^{2+}$	4.0×10^{-2}	1.1×10^{3}	1.65	9
$[\mathrm{Co(nta)}]^- + \mathrm{Ni}^{2+}$	4.0×10^{-4}	4.1×10^{1}	3.0×10^{-2}	9

In order to clarify the detailed reaction mechanism, the Scheme opposite can be considered. This Scheme outlines the multistep mechanism of successive partial dissociation of nta from the outgoing metal and association with the incoming one. It is debatable what type of bonds are present in the intermediate complex, (III), but increased co-ordination to Cu^{2+} would involve either (*i*) the nitrogen atom or (*ii*) other carboxylato-groups. In the latter case, highly unfavourable eight-membered chelation rings would be present, whereas a possible structure with a simple acetate bond to the outgoing metal implies that the rate-determining step, k_3, involves a metal–acetato-bond dissociation which occurs much more readily than the dissociation of a metal–nitrogen bond.

Application of the steady-state approximation to species (III) of the Scheme (see Appendix) gives equation (10) for the overall second-order rate constant k_{a}.[8] It

$$k_{\mathrm{a}} = k_{\mathrm{Cu}}^{\mathrm{M(nta)}} = k_1k_2k_3/k_{-1}(k_{-2} + k_3) \qquad (10)$$

can be seen that the rate-determining step in the forward direction will depend on the ratio $k_2k_3/(k_{-2} + k_3)$. If $k_{-2} \gg k_3$, the rate is governed by the k_3 term, whereas if $k_3 \gg k_{-2}$, the rate-determining step involves k_2. The rate constants k_3 and k_{-2} represent, respectively, the rate of dissociation of M from an iminodiacetic (ida) portion of the ligand [see structure (III)] and the rate of dissociation of Cu^{2+} from an acetato-ligand [see structure (III)]. These dissociation rates can be obtained from the formation rates (which in turn are related to the water exchange rates in the co-ordination sphere of the metals) and the equilibrium constants of the corresponding complexes (the outer-sphere complex formation constants should also be taken into account, but they are disregarded here since relative comparisons, only, will be made), by equations (11) and (12). Table 4 reports

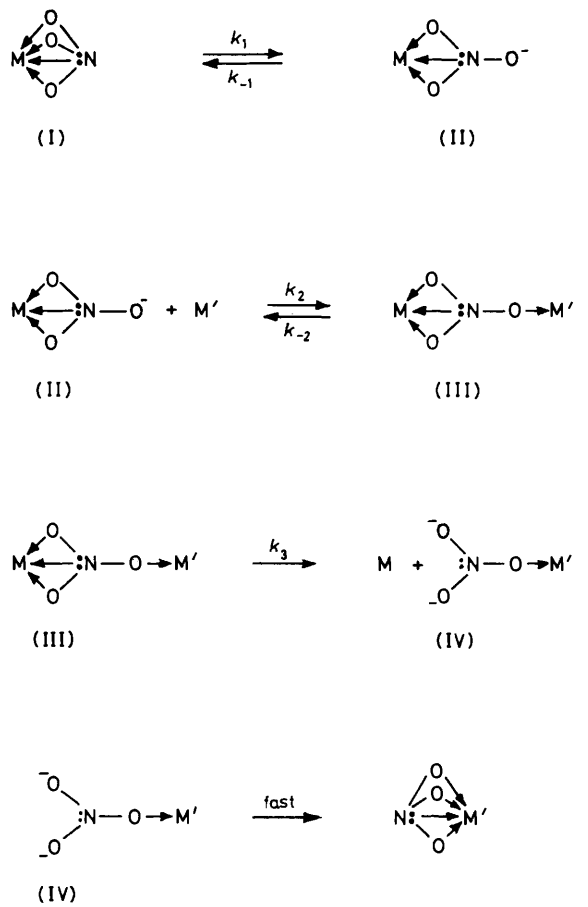
$$k_{-2} = k^{\mathrm{Cu(OH_2)}}/K_{\mathrm{Cu(O_2CMe)}} \qquad (11)$$

$$k_3 = k^{\mathrm{M(OH_2)}}/K_{\mathrm{M(ida)}} \qquad (12)$$

the values of k_{-2} and k_3 so determined and the ratio k_{-2}/k_3 for the reactions investigated. The data show that $k_{-2} \gg k_3$ for all the reactions and therefore that the release of the ida segment from the displaced metal ion is in all cases rate determining. The experimental second-order rate constant is therefore given by equation (13). The values of the individual rate factors which

$$k_{\mathrm{Cu}}^{\mathrm{M(nta)}} = k_1k_2k_3/(k_{-1}k_{-2}) \qquad (13)$$

contribute to the overall rate constant in equation (13) cannot be evaluated from the Scheme nor the available theories on the mechanism of substitution at labile aquametal species. However, an estimate of the relative magnitudes of the rates of the presently investigated substitution reactions, as well as for strictly



SCHEME

related reactions, can be obtained by the following considerations. The quantity k_1/k_{-1} is the equilibrium quotient between species (I) and (II) of the Scheme and therefore represents the stability constant of the complex of M with the iminodiacetato-portion of the ligand [structure (II)] relative to the complex containing the entire nta ligand [species (I)]. Hence, a good approximation is $k_1/k_{-1} \propto K_{M(ida)}/K_{M(nta)}$. Similarly, k_2/k_{-2} represents the equilibrium constant for formation of species (III) from the incoming metal ion, M′, and species (II); therefore it can be assumed that $k_2/k_{-2} \propto K_{M'(O_2CMe)}$. Rate constant k_3 represents the rate of release of M from the ida portion of nta in species (III), as described previously. Therefore a relative estimate of $k_{M'}^{M(nta)}$ can be obtained from equation (14).

TABLE 4

Evaluation and comparison of k_{-2} and k_3 for the systems investigated and related reactions [for details see text and equations (11) and (12)]

Parameter	Ni	Cu	Co	Zn	Pb
$\log[K_{M(ida)}]$ [a]	8.4	10.6	7.1	7.3	7.6
$\log[k^{M(OH_2)}]$ [b]	4.5	9.0	6.3	7.8	9.3
$\log[k^{M(OH_2)}/K_{M(ida)}]$	−3.9	−1.6	−0.8	0.5	1.7
$\log[K_{M(O_2CMe)}]$ [a]	1.0	1.9	1.5	1.0	2.1
$\log[k^{M(OH_2)}/K_{M(O_2CMe)}]$	3.5	7.1	4.8	6.8	7.2

Reaction M–nta + M′	$\log\{[k^{M'(OH_2)}/K_{M'(O_2CMe)}][k^{M(OH_2)}/K_{M(ida)}]^{-1}\}$
$[Co(nta)]^- + Cu^{2+}$	8.0
$[Pb(nta)]^- + Cu^{2+}$	5.5
$[Zn(nta)]^- + Cu^{2+}$	6.7
$[Co(nta)]^- + Pb^{2+}$	8.0
$[Co(nta)]^- + Ni^{2+}$	4.3

[a] See Table 2. [b] Ref. 8, pp. 4, 8, 13.

$$k_{M'}^{M(nta)} \propto [K_{M(ida)}/K_{M(nta)}]K_{M'(O_2CMe)}[k^{M(OH_2)}/K_{M(ida)}] = (k_{M'}^{M(nta)})_{computed} \quad (14)$$

Certain approximations are of course introduced, since, for example, co-ordination of M′ in species (III) cannot simply be assumed to be the same as that in the M′–acetate complex, likewise M, in species (II) or (III), cannot be assumed to be in the same environment as in the M–iminodiacetato-complex. In addition, electrostatic effects, due to the presence of neighbouring charged groups, are present and structural constraints, for example in species (III), are operative. If, however, on the one hand, all these effects alter the value of $k_{M'}^{M(nta)}$ determined by equation (14), on the other, they are cancelled out when relative reactivities are computed for different metal substitution reactions with nta.

Table 5 lists the computed $k_{M'}^{M(nta)}$ values together with the derived relative reactivities. The agreement with experimental relative reactivities supports the proposed mechanism and intermediate structures and enables the following features to be pointed out: (*i*) the dissociation step k_{-2} is faster than k_3 which appears to be the rate-determining step; (*ii*) the factor which influences the magnitude of $k_{M'}^{M(nta)}$ and therefore determines the observed rate constants is k_3, which, in turn, is proportional to the lability of the displaced metal ion.

In the present reactions no shift from first to zero order and again to first order was observed as a function of the copper concentration, as was found for other metal substitution reactions.[11,12] However, it is not possible to exclude that at very high concentrations of copper the rate of the reaction approaches a zero-order condition; this would imply a complete saturation of the free acetato-group by Cu^{2+}, in structure (III), with complete displacement to the right of the equilibrium (II) + $Cu^{2+} \rightleftharpoons$ (III). A second pathway first order in $[Cu^{2+}]$ after the above saturation has been reached would seem highly improbable though. In fact this could only appear if a different rate-determining step were present before the above equilibrium, but this seems unrealistic, if as discussed above the nitrogen atom must be bound to the leaving metal and if co-ordination of two carboxylato-groups to Cu^{2+} is unfavourable.

TABLE 5

Evaluation of $(k_{M'}^{M(nta)})_{computed}$ from equation (14) and comparison between experimental and computed relative reactivities {with reference to the faster reaction, $[Co(nta)]^- + Cu^{2+}$}

Parameter	Co	Pb	Cu	Zn	Ni
$k_1/k_{-1} \propto K_{M(ida)}/K_{M(nta)}$	−3.3	−3.8	−2.4	−3.4	−3.1
$k_2/k_{-2} \propto K_{M(O_2CMe)}$	1.5	2.1	1.9	1.0	1.0
$k_3 = k^{M(OH_2)}/K_{M(ida)}$	−0.8	1.7	−1.6	0.5	−3.9

		Relative reactivities $\{[Pb(nta)]^- = 1\}$	
Reaction	$\log[k_{M'}^{M(nta)}]_{computed}$	Comput.	Expt.
$[Co(nta)]^- + Cu^{2+}$	−2.2	1×10^{-2}	7×10^{-2}
$[Pb(nta)]^- + Cu^{2+}$	−0.2	1	1
$[Zn(nta)]^- + Cu^{2+}$	−1.0	0.16	0.26
$[Co(nta)]^- + Pb^{2+}$	−2.0	1.6×10^{-2}	4.7×10^{-2}
$[Co(nta)]^- + Ni^{2+}$	−3.0	1.6×10^{-3}	0.9×10^{-3}

Multiple-order reactions are expected as the concentration of the attacking metal is increased, as more co-ordination sites become free and bind the copper ion; the presence of two nitrogen atoms as in the case of ethylenediamine derivatives, such as ethylenediaminediacetic acid,[12] or edta,[11] makes this feature even more probable. The present interpretation supports previous observations of an acetato-arm as the bridging group for the nta ligand in substitution reactions between two bivalent transition-metal ions.[9,10] This can be further discussed with reference to the magnitude of the rates for the different pathways of the same reaction. Each pathway involves different intermediate mixed-complex species or protonated species that are formed prior to the rate-determining step. If the slowest step, in all these pathways, involves a bond dissociation between the displaced metal and portions of the ligands, as generally found in these cases, the same rate-determining bond rupture must be active for all the pathways and the rate of the overall processes will be governed by the stability of the intermediate prior to the rate-determining step. Absolute stabilities for these intermediate species cannot be obtained but their relative values can readily be determined by comparing the stability of the complexes M–P and M′–P′ with the stability of the starting complex using equation (15) † where P and P′ represent

$$K_{\text{relative}} = K_{\text{M-P}}K_{\text{M}'\text{-P}'}/K_{\text{M-L}} \qquad (15)$$

the portions of the ligand, L, bound to the leaving, M, and entering, M′, metal respectively. Statistical factors, when there are several possible routes to the intermediate complex, as well as electrostatic interactions between non-bound charged groups within a complex species must be computed and accounted for.

TABLE 6

Comparison of the relative stabilities [computed using equation (15)] for the intermediates and relative reactivities of the different pathways for the substitution reactions of Co^{2+}, Pb^{2+}, and Zn^{2+} complexes of nta with Cu^{2+}

Intermediate structure * Pathway	(II) $k^{\text{M(nta)}}$	(III; M′ = H) $k_{\text{H}}^{\text{M(nta)}}$	(III; M′ = Cu) $k_{\text{Cu}}^{\text{M(nta)}}$
log $K_{\text{rel.}}$ M = Co^{2+}	−3.3	1.4	−1.4
log $K_{\text{rel.}}$ M = Pb^{2+}	−3.8	0.9	−1.9
log $K_{\text{rel.}}$ M = Zn^{2+}	−3.4	1.3	−1.5
Relative ractivities	$k^{\text{M(nta)}}$	$10^2k_{\text{H}}^{\text{M(nta)}}/k^{\text{M(nta)}}$	$10^{-2}k_{\text{Cu}}^{\text{M(nta)}}/k^{\text{M(nta)}}$
Theor. (from log $K_{\text{rel.}}$)	1	1	6
Exptl. {for $[Co(nta)]^-$ + Cu^{2+}}	1	0.5	3
Exptl. {for $[Pb(nta)]^-$ + Cu^{2+}}	1	0.1	0.7
Expt. {for $[Zn(nta)]^-$ + Cu^{2+}}	1	0.3	4

* See Scheme for structures.

In the case of the reaction of M–nta + Cu^{2+} (M = Co^{2+}, Pb^{2+}, or Zn^{2+}), the structures reported in Table 6 are considered and their relative stabilities, computed with equation (15), are listed. Table 6 also lists the experimental and computed (from the relative stabilities) reactivity ratios between the steps of each reaction and the direct copper-dependent substitution. The agreement confirms that the method of computing the relative stabilities of the binuclear intermediate species can be applied to the present systems and that the proposed intermediate structures and rate-determining step conform to the experimental reactivities. Therefore, it can be concluded that an acetato-arm is the active group towards copper and that the dissociation of the nitrogen–leaving metal bond is the rate-determining step.

APPENDIX

From the Scheme, application of the steady-state approximation to (III) gives equation (A1). Assuming

$$\mathrm{d}[(\text{III})]/\mathrm{d}t = k_2[(\text{II})][\text{M}'] + k_{-3}[(\text{IV})][\text{M}] - k_3[(\text{III})] - k_{-2}[(\text{III})] \qquad (\text{A1})$$

that equilibrium (I) $\rightleftharpoons$ (II) must be fast (aquation and anation reactions for the displaced metal ions are fast compared to the observed rate constants) and that the last step of the Scheme is also fast for the same reason (chelation ring closure around Cu^{2+}), equations (A2) and (A3) can be derived, by neglecting the k_{-3} term in equation (A1). From these we obtain equation (A4) which represents

$$[(\text{III})] = k_2[(\text{II})][\text{M}']/(k_{-2} + k_3) \qquad (\text{A2})$$

$$[(\text{II})]/[(\text{I})] = k_1/k_{-1} \qquad (\text{A3})$$

$$\text{Rate} = k_3[(\text{III})] = [k_1k_2k_3/k_{-1}(k_{-2} + k_3)][(\text{I})][\text{M}'] \qquad (\text{A4})$$

the second-order rate law, designated by $k_{\text{a}} = k_{\text{Cu}}^{\text{M(nta)}}$ in equation (10).

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† For the derivation of equation (15) see ref. 4*a* and for examples of its applications see refs. 1, 2, 4*b*, and 9—11.