

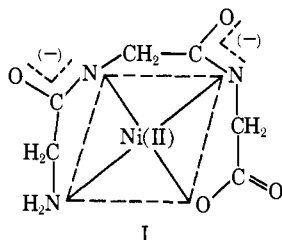
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Reaction of Cyanide Ion with Nickel Triglycine. An Example of the Kinetic Trans Effect in Low-Spin Nickel(II)

Sir:

There have been many reported examples of the trans effect in Pt(II) and Pd(II) substitution reactions;¹ however, the same cannot be said for low-spin nickel(II). Triglycine forms a yellow, low-spin complex with nickel(II) in which the deprotonated nitrogen atoms are coordinated.²⁻⁴ This complex, NiH₂L⁻ (shown in structure I), reacts with cyanide ion through a series



of mixed complexes to form Ni(CN)₄²⁻. It is through the formation of the mixed complex NiH₂L(CN)₂³⁻ that cyanide is capable of labilizing the trans imide groups and thus increasing the rate of the substitution reaction.

The rate equation for the formation of Ni(CN)₄²⁻ at pH 11 is shown in eq 1. The mixed complex NiH₂L-

$$\frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} = \left\{ k_{1,0}[\text{CN}^-] + \frac{K_2[\text{CN}^-]}{1 + K_2[\text{CN}^-]} k_{2,0}[\text{CN}^-] \right\} [\text{NiH}_2\text{L}(\text{CN})_2^{3-}] \quad (1)$$

(CN)₂³⁻ forms rapidly and completely as evidenced by the fact that no Ni(CN)₄²⁻ is produced when the molar ratio of CN⁻ to NiH₂L⁻ is equal to or less than 1. The visible spectra of NiH₂L⁻ and NiH₂L(CN)₂³⁻ also exhibit an isosbestic point at 406 nm. Cyanide probably replaces the coordinated carboxylate group. The reaction was studied under pseudo-first-order conditions and the observed rate constant is shown in eq 2.

$$k_{\text{obsd}} = k_{1,0}[\text{CN}^-] + \frac{K_2[\text{CN}^-]k_{2,0}[\text{CN}^-]}{1 + K_2[\text{CN}^-]} \quad (2)$$

At [CN⁻] < 9 × 10⁻⁴ M the value of K₂[CN⁻] is negligible compared to 1 and thus k_{obsd} = k_{1,0}[CN⁻] + K₂k_{2,0}[CN⁻]². This equation indicates that a plot of k_{obsd}/[CN⁻] vs. [CN⁻] should be linear with a slope of K₂k_{2,0} and an intercept of k_{1,0}. From a plot of this

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(2) R. B. Martin, M. Chamberlin, and J. T. Edwall, *J. Amer. Chem. Soc.*, **82**, 495 (1960).

(3) H. C. Freeman, J. M. Guss, and R. L. Sinclair, *Chem. Commun.*, 485 (1968).

(4) M. K. Kim and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 5138 (1967).

Table I. Rate Constants for the Reaction of Cyanide Ion with Nickel(II) Triglycine^a

10 ⁶ [NiH ₂ L ⁻], M	10 ⁴ [CN ⁻], M	pH	10 ³ k _{obsd} , sec ⁻¹
9.59	1.63	10.94	0.93
9.57	3.25	10.99	1.98
9.54	6.39	10.98	4.20
9.49	9.56	10.98	6.79
9.24	31.3	11.09	29.8
9.17	37.3	11.04	39.1
9.06	46.1	11.06	49.7

^a Temperature, 25.0°; μ = 0.10 M NaClO₄.

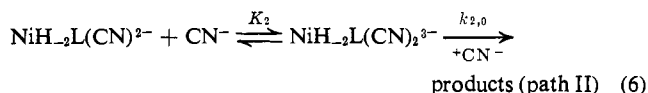
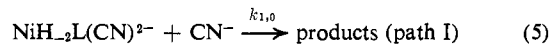
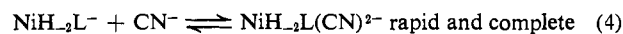
type, the value of k_{1,0} = 5.9 M⁻¹ sec⁻¹ and K₂k_{2,0} = 1.3 × 10³ M⁻² sec⁻¹. The relevant kinetic data are summarized in Table I.

At [CN⁻] > 9 × 10⁻⁴ M the value of K₂[CN⁻] is not small compared to 1. Equation 2 can be rearranged to the form shown in eq 3. This equation indicates

$$\frac{[\text{CN}^-]}{(k_{\text{obsd}} - k_{1,0}[\text{CN}^-])} = \frac{1}{k_{2,0}} + \frac{1}{K_2 k_{2,0}[\text{CN}^-]} \quad (3)$$

that a plot of [CN⁻]/(k_{obsd} - k_{1,0}[CN⁻]) vs. 1/[CN⁻] should be linear with a slope of 1/K₂k_{2,0} and an intercept of 1/k_{2,0}. From a plot of this type, k_{2,0} = 25 M⁻¹ sec⁻¹ and K₂ = 52 M⁻¹. The relevant kinetic data are summarized in Table I.

The reaction of cyanide with NiH₂L⁻ at pH 11 proceeds through a two-path mechanism (see eq 4-6).



However, the rate-determining step for each path involves the breakage of the first nickel-imide bond. The difference between the two paths lies in the degree of the mixed complex formed prior to the rate-determining step. Path I carries the reaction at low cyanide concentration, requiring a total of two cyanide molecules in the activated complex. The first cyanide adds to NiH₂L⁻ rapidly and completely to form NiH₂L(CN)²⁻. The second cyanide then reacts with concurrent breakage of the imide bond near the carboxylate end of triglycine. This is the step that is rate determining and has a rate constant k_{1,0} = 5.9 M⁻¹ sec⁻¹. Previous studies with NiH₂L⁻ and CuH₂L⁻ indicate that the carboxylate coordination is more labile than the imide coordination.^{5,6} Cyanide is not capable of exerting any trans labilization in this path since the imide bond trans to the coordinated cyanide does not break during the rate-determining step.

At high cyanide concentration path II carries the reaction through the formation of a second mixed complex, NiH₂L(CN)₂³⁻, which is believed to have cyanide occupying both of the planar positions trans to the imide coordination sites. This complex reacts with another cyanide during the rate-determining step. Since cyanide is trans to both of the imide bonds it is capable of labilizing these bonds. This labilization is

(5) E. J. Billo, G. F. Smith, and D. W. Margerum, *ibid.*, **93**, 2635 (1971).

(6) G. K. Pagenkopf and D. W. Margerum, *ibid.*, **92**, 2683 (1970).

evidenced in the rate constant $k_{2,0}$ ($k_{2,0} = 25 M^{-1} \text{sec}^{-1}$) which is a factor of 4 greater than $k_{1,0}$. This difference is significant and definitely shows that substitution rates in low-spin nickel(II) are sensitive to the nature of the ligands coordinated in the other square-planar positions. The difference is probably much greater than 4 but because of electrostatic repulsions it is significantly reduced.

Other ligand exchange reactions with NiH_2L^- and CuH_2L^- are proton-transfer limited.^{7,8} The rates observed in this work at pH 11 are less than what would be expected for a proton-transfer mechanism and thus indicating that the presence of cyanide in NiH_2L^- (CN^{2-}) and $\text{NiH}_2\text{L}(\text{CN})_2^{3-}$ has a very pronounced effect upon the lability of the nickel-imide bonds. There is no hydrogen ion dependence in the pH 11–12 region; however, there is a significant contribution to path II from hydrogen cyanide at pH 9. Boric acid has no effect upon the observed rate and thus the reaction is not subject to general acid catalysis.

(7) E. J. Billo and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 6811 (1970).

(8) G. K. Pagenkopf and D. W. Margerum, *ibid.*, **90**, 6963 (1968).

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Electron Transfer through Organic Structural Units. XIII. Radical-Cation Intervention

Sir:

Radical species bound both to Co(III) and Cr(III) have been suggested as intermediates in the Cr(II) reductions of heterocyclic¹ and unsaturated carboxylato² derivatives of cobalt(III). The present communication describes a strongly absorbing intermediate appearing during the reduction of pyrazinecarboxylato-pentaamminecobalt(III)^{1b} (I) with Cr^{2+} ; the behavior of this species corresponds to that of the suspected cation-radical intermediate.

Addition of excess Cr^{2+} (0.005–0.05 M) to oxidant I (7×10^{-5} M) in 1.2 M HClO_4 results in a very marked increase in absorbance throughout the range 400–660 nm during the first 0.01 sec after mixing, followed by a fading, during the next 1.4 sec, to an absorbance characterizing Co^{2+} and the chelated Cr(III) product V.^{1b} Both changes are cleanly first order. Absorption maxima for the intermediate lie at 625 nm (ϵ 2400) and 430 (5100).³ The maximum concentration of the absorbing species, its rate of formation, and its rate of disappearance are independent of (Cr^{2+}) in the range studied. The measured specific rates (25° , $\mu = 1.22$) for these reactions, 263 ± 12 and $2.39 \pm 0.06 \text{ sec}^{-1}$, are many orders of magnitude below known⁴ substitution rates at Cr^{2+} ($\sim 10^9 \text{ sec}^{-1}$) and Co^{2+} ($\sim 10^6 \text{ sec}^{-1}$) centers; neither observed reaction can then reasonably be taken as the formation of the binuclear precursor

(1) (a) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964); (b) E. S. Gould, *ibid.*, **87**, 4730 (1965); (c) F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968).

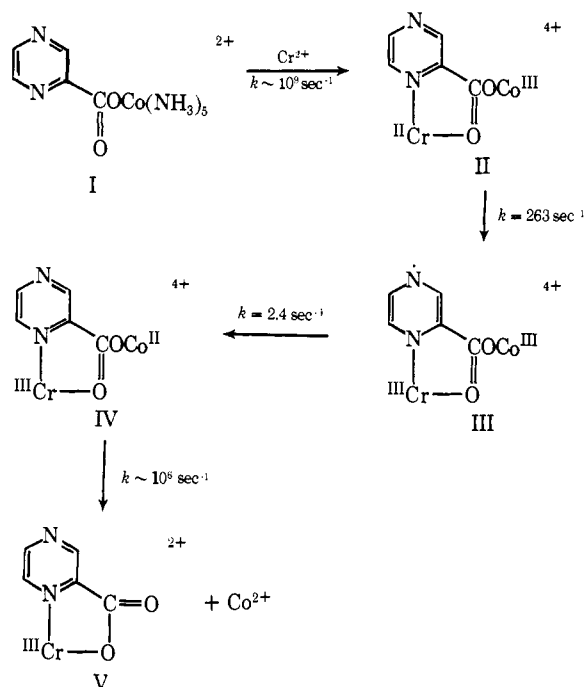
(2) H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970).

(3) Extinction coefficients are calculated assuming complete conversion of complexes I and VI to the absorbing species.

(4) See, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968, pp 152–155.

complex II or the collapse of successor complex IV. Instead, it is suggested (Scheme I) that the increase in

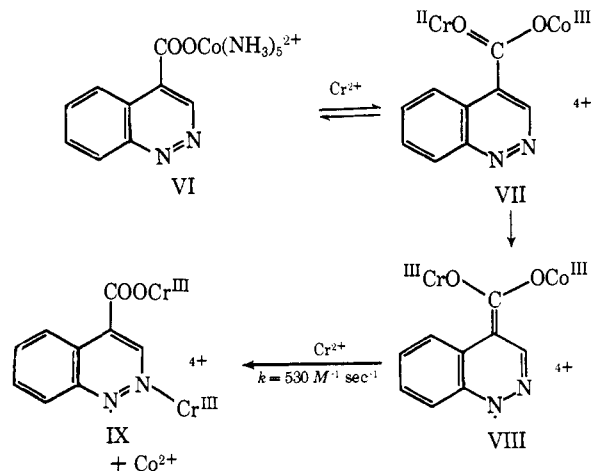
Scheme I



absorbance reflects internal electron transfer in precursor II to form radical-cation III and that the fading is due to further conversion to successor IV, which undergoes very rapid aquation. If this scheme is correct, the absence of (Cr^{2+}) dependency in the conversions $\text{II} \rightarrow \text{III}$ and $\text{III} \rightarrow \text{IV}$ demands that conversion of I to a Cr^{II} chelate be virtually complete, even in 1.2 M HClO_4 .

A strongly absorbing intermediate intervenes also during the Cr^{2+} reduction of a 2.6×10^{-4} M solution of the 4-cinnolinecarboxylato derivative VI.^{1b} The degree of conversion to this intermediate (ϵ_{360} 3400, ϵ_{580} 420, sh)³ is again independent of (Cr^{2+}) when the latter exceeds 0.005 M, but in this case both formation ($k = 2.4 \pm 0.3 \times 10^5 M^{-1} \text{sec}^{-1}$) and disappearance ($k = 530 \pm 30 M^{-1} \text{sec}^{-1}$) are first order in Cr^{2+} . The implications here (Scheme II) are different, and more

Scheme II



tentative, from those pertaining to the reduction of complex I. If the strongly absorbing intermediate is