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Publisher *Taylor & Francis*

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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

KINETICS AND CHELATE RING SIZE: REANALYSIS OF NICKEL(II)-AMINOMETHYLPYRIDINE ANALOGUES

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To cite this Article Jordan, Robert B.(1980) 'KINETICS AND CHELATE RING SIZE: REANALYSIS OF NICKEL(II)-AMINOMETHYLPYRIDINE ANALOGUES', *Journal of Coordination Chemistry*, 10: 4, 239 – 241

To link to this Article: DOI: 10.1080/00958978008079869

URL: <http://dx.doi.org/10.1080/00958978008079869>

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KINETICS AND CHELATE RING SIZE: REANALYSIS OF NICKEL(II)-AMINOMETHYLPYRIDINE ANALOGUES

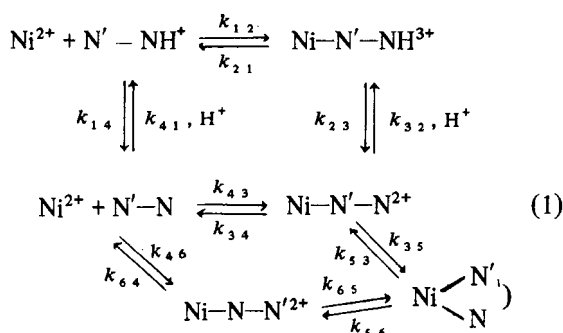
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(Received November 15, 1979; in final form April 29, 1980)

In a recent study Hubbard and Palaitis¹ reported the pH dependence of the complexing of nickel(II) by 2-(methylaminomethyl)pyridine (MAP). The authors noted that their rate law does not fit 40% of the results, specifically those in the low pH range, but derived rate constants for neutral ligands were compared to previous work on 2-(aminomethyl)pyridine (AMP)² and 2-(2-aminoethyl)pyridine (AEP).³

It is the purpose of this communication to show that the rate constant comparisons and rationalizations given by Hubbard and Palaitis¹ are not valid because the proper rate law was not used in the kinetic analysis of the MAP and AEP systems. A more complete rate law for AMP has been published in a recent study,⁴ and there seems to be no reason that these very similar ligands should have different rate laws. The results for AMP⁴ were analysed in terms of the reaction scheme shown in Eq. (1).



where N'— and —N represent the pyridine and amine nitrogen respectively. The aquo ligands on nickel(II), and ion pair precursor complex formation have been omitted for clarity. If the dissociative ion pair mechanism⁵ is applicable, then k_{12} , k_{43} and k_{46} are products of a specific rate constant and an ion pair formation constant. The pseudo-first order rate

constants for proton transfer are given by

$$\begin{aligned}
 k_{23} &= k_1 [\text{H}_2\text{O}] + k_2 [\text{Bu}] + k_3 [\text{OH}^-] \\
 k_{32} &= k_{-1} [\text{H}_3\text{O}^+] + k_{-2} [\text{BuH}^+] + k_{-3} [\text{H}_2\text{O}]
 \end{aligned} \quad (2)$$

where [Bu] and [BuH⁺] represent the concentrations of the basic and acidic forms of the buffer, and the equilibrium constant is $K_{23} = k_{23}(\text{H}^+)/k_{32}$. The kinetic solution of the scheme with $k_{53} = k_{56} = 0$ was discussed previously⁴ and the full equilibrium system has been published recently.⁶ For systems such as AMP, MAP and AEP the pseudo-first order rate constant for complex formation with $[\text{Ni}^{2+}] \gg [\text{ligand}]$ is given by

$$k_{\text{obsd}} = \frac{k_{23} \left(\frac{k_{12}}{k_{21}} \right) \left\{ \frac{(\text{H}^+)[\text{Ni}^{2+}]}{K_{14} + (\text{H}^+)} + \frac{(\text{H}^+)}{K_f K_{14}} \right\}}{1 + k_{23} \left(\frac{k_{12}}{k_{21}} \right) \left(\frac{1}{k_{12}} + \frac{k_{21}(\text{H}^+)}{k_{12}k_{35}K_{23}} \right)} \quad (3)$$

where

$$k_{23} = \frac{k_2 K_{\text{Bu}} [\text{Bu}]_{\text{T}}}{K_{\text{Bu}} + (\text{H}^+)} + \frac{k_3 K_{\text{w}}}{(\text{H}^+)},$$

and $[\text{Bu}]_{\text{T}} = [\text{Bu}] + [\text{BuH}^+]$, K_{Bu} is the acid dissociation constant of the buffer, and K_f is the formation constant of the nickel(II) complex. It may be noted that Eq. (3) simplifies to Eq. (15) of Ref. 4 if $K_f = \infty$, except that k_{obsd} was defined as the second order rate constant previously. This rate law was confirmed for AMP⁴ in that it correctly predicted the variation with (H⁺), buffer concentration, and value of K_{Bu} for three buffers over the pH range 4.7 to 6.9.

The variation of k_{obsd} with cacodylic acid buffer concentration was not investigated in the MAP system.¹ Since the $\text{p}K_{\text{a}}$ of cacodylic acid (6.2),

is between that of the two buffers, PIPES (6.61) and MES (6.06), studied with AMP⁴ a simple interpolation can be used to estimate that $k_2(k_{12}/k_{21}) = 2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$. This also involves the reasonable assumption that the equilibrium constant for complexation at pyridine (k_{12}/k_{21}) is the same for MAP and AMP. This assumption is not very critical because changing $k_2(k_{12}/k_{21})$ by $\pm 50\%$ has less than a 10% effect on the calculated k_{obsd} at the buffer concentrations used. The results show a similar insensitivity to $k_3K_w(k_{12}/k_{21})$, and in fact are almost independent of this value at low pH. Therefore the results with AMP⁴ have been used to estimate $k_3K_w(k_{12}/k_{21}) = 2.8 \times 10^{-5} \text{ s}^{-1}$. The formation constant (K_f) of the nickel(II)-MAP complex is $8.13 \times 10^6 \text{ M}^{-1}$.^{7,8}

With these values fixed all of the results of Hubbard and Palaitis can be fitted to Eq. (3) with $k_{12} = 300 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{35}K_{23}(k_{12}/k_{21}) = 6 \times 10^{-5} \text{ s}^{-1}$. The calculated values of k_{obsd} are compared to the experimental and calculated values of Hubbard and Palaitis in Table I. The new fit is marginally better for $\text{pH} > 5.83$, but is the only one of the two fits consistent with the results for $\text{pH} < 5.83$. A discussion of these results will be deferred until the AEP system has been reanalysed.

A comparison of the kinetic parameters for AEP and AMP provides an opportunity to assess the effect of chelate ring size on the rate constants for ring

TABLE I
Kinetic Data for Reaction of Nickel(II) and 2-methylamino-methylpyridine (25° , $\mu = 0.3 \text{ M}$)

| pH | exptl | $k_{\text{obsd}}/[\text{Ni}^{2+}], \text{ s}^{-1}$ | |
|------|-------|--|-------------------|
| | | calcd ref. 1 | eq 3 ^a |
| 6.92 | 128 | 144 | 128 |
| 6.80 | 110 | 112 | 112 |
| 6.80 | 97 | 116 | 111 |
| 6.75 | 108 | 102 | 105 |
| 6.58 | 87.1 | 75 | 85 |
| 6.4 | 61 | 56 | 65 |
| 6.28 | 47.5 | 47 | 55 |
| 6.11 | 40.1 | 38 | 40 |
| 6.10 | 39 | 38 | 42 |
| 5.91 | 29.2 | 31 | 29 |
| 5.83 | 30 | 29 | 25 |
| 5.83 | 22 | 29 | 24 |
| 5.61 | 15.5 | 25 | 16 |
| 5.51 | 12 | 24 | 13 |
| 5.26 | 6.8 | 22 | 7.7 |
| 5.20 | 7.99 | 21 | 7.1 |
| 4.99 | 4.30 | 20 | 4.4 |

^aCalculated with parameters given in the text and at the average value of $[\text{Ni}^{2+}]$ given at each pH in Table I of Ref. 1.

TABLE II
Kinetic Data for the Reaction of Nickel(II) and 2-aminoethylpyridine (25° , $\mu = 0.1 \text{ M}$, $[\text{Ni}^{2+}] = 1.6 \times 10^{-2} \text{ M}$).

| pH | $k_{\text{obsd}}/[\text{Ni}^{2+}], \text{ s}^{-1}$ | |
|------|--|--------------------|
| | exptl ^a | calcd ^b |
| 7.38 | 52 | 52 |
| 7.10 | 39 | 37 |
| 6.81 | 24 | 25 |
| 6.50 | 13.5 | 16.5 |
| 6.21 | 10.5 | 12 |
| 5.80 | 8.5 | 8.8 |
| 5.60 | 8.2 | 8.0 |
| 5.40 | 7.5 | 7.5 |
| 5.19 | 7.6 | 7.2 |

^aValues taken from Figure 1 of Ref. 3.

^bCalculated from Eq. (3) and parameters given in the text.

closing (k_{35}) and for ring opening (k_{53}). The observations of Hubbard and Palaitis³ on this system are difficult to interpret however. Calculations based on the formation constant for the Ni^{2+} -AEP system ($K_f = 1.58 \times 10^5 \text{ M}^{-1}$, $\mu = 0.1 \text{ M}$)⁷ indicate that as little as 10% complex formation should occur under some of the experimental conditions, yet it is claimed³ that "the data are best described by an overall second order reaction". It must be that this fact was checked only at relatively high pH where complexation would be essentially complete.

The published results for AEP ($[\text{Ni}^{2+}] = 1.6 \times 10^{-2} \text{ M}$, $\text{pH} 5.19-7.38$, $\mu = 0.10$, 25°) can be fitted to eq 3 if $k_2(k_{12}/k_{21})$ and $k_3K_w(k_{12}/k_{21})$ are estimated as before.⁹ The best fit, obtained with $k_{12} = 110 \text{ M}^{-1} \text{ sec}^{-1}$, and $k_{35}K_{23}(k_{12}/k_{21}) = 3.9 \times 10^{-6} \text{ s}^{-1}$, is compared to the experimental results in Table II. The fit is essentially as good as that obtained by Hubbard and Palaitis.³

The kinetic parameters for AMP, MAP and AEP are compared in Table III. Since $K_{23}(k_{12}/k_{21}) = K_{14}(k_{43}/k_{34})$ the known value of K_{14} can be used

TABLE III
Summary of Kinetic Results

| | AMP ^a | MAP ^a | AEP ^a |
|-------------------------------|----------------------|----------------------|----------------------|
| $\text{p}K_{14}$ | 8.6 | 9.29 | 9.65 |
| $\log K_f$ | 7.11 | 6.91 | 5.37 |
| k_{12} | 630 | 300 | 110 |
| $k_{35}K_{23}(k_{12}/k_{21})$ | 2.7×10^{-4} | 6.0×10^{-5} | 3.9×10^{-6} |
| $k_{35}(k_{43}/k_{34})$ | 1.1×10^5 | 1.2×10^5 | 1.7×10^4 |
| $10^2 \times k_{53}$ | 0.83 | 1.44 | 11 |

^aValues at 25° and $\mu = 0.5, 0.3$ and 0.1 for AMP, MAP and AEP respectively.

to calculate $k_{35}(k_{43}/k_{34})$, and since $K_f = (k_{43}k_{35}/k_{34}k_{53})$, then k_{53} can be calculated from the value of K_f .

The values of k_{12} are of the expected magnitude for a unipositive ligand reacting with nickel(II). For example, the analogous values for $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_3^{+1}$ and $\text{H}_2\text{N}(\text{CH}_2)_2\text{-N}(\text{CH}_3)_3^{+1.2}$ are $3.1 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Since k_{12} contains the ion pair formation constant (K_f) the variation in k_{12} values could be attributed to an ionic strength variation of K_f . However, Lin and Rarabacher did not find such an effect with $\text{H}_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3^+$. Internal hydrogen bonding may also affect the value of k_{12} , and has been suggested¹⁰ to explain the different rate constants for the systems mentioned above.

The values of $k_{35}(k_{43}/k_{34})$ for AMP and MAP are essentially the same. As noted previously⁴ one can estimate $k_{43}/k_{34} \approx 10$, based on the formation constant of the 2-methylpyridine complex.¹³ Then $k_{35} \approx 1 \times 10^4 \text{ s}^{-1}$, similar to the value of $3 \times 10^4 \text{ s}^{-1}$ for the water exchange rate constant of $\text{Ni}(\text{OH}_2)_6^{2+}$.¹⁴ This similarity is expected because coordinated pyridine ligands only slightly labilize coordinated water.¹⁴ It is noteworthy that $k_{35}(k_{43}/k_{34})$ for AEP is about 10 times smaller than for AMP and MAP. There is no reason to expect (k_{43}/k_{34}) to be less with AEP so that it appears that the increased ring size has caused k_{35} to decrease significantly.

The k_{53} value for MAP is larger than that of AMP. This is consistent with the N-CH₃ group causing some steric acceleration of ring opening. There is a more substantial increase in k_{53} with AEP. It appears that ring opening of the 6 membered ring is more favourable than with a 5 membered ring.

The kinetic results indicate that the greater formation constant of AMP compared to AEP lies about equally in a smaller ring closing rate constant and a larger ring opening rate constant. These observations confirm some longstanding suspicions about the kinetic origin of the chelate effect.¹⁵ As the ring size increases ring closing becomes a less probable event relative to each time a water molecule is exchanged. At the same time the larger ring

provides less restriction on movement of the ligand coordinating atom away from the metal center. Thus the ring opening rate constant will approach that of dissociation of its monodentate analogue as the ring size increases.

The kinetic behavior of these systems is consistent with the normally assumed dissociative ion pair mechanism.⁵ They follow the general reaction scheme discussed recently⁶ in that first bond formation (k_{12}) is rate determining at higher pH, while chelate ring closing (k_{35}) is rate limiting at lower pH.

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9. These estimates for the lutidine buffer are $k_2(k_{12}/k_{21}) = 8 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ and $K_w k_3(k_{12}/k_{21}) = 2.8 \times 10^{-5} \text{ s}^{-1}$. In fact these values are of little significance because the second term in the denominator of eq 3 is much greater than one, and k_{23} cancels between numerator and denominator.
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