Table II. ^1H NMR Chemical Shift Data[a]

$H_2XB_3N_3$-H_2CH_3	Ortho isomer			Para isomer	
	p-NH[b]	*o*-NH[b]	*o*-CH_3[b]	*o*-NH[b]	*p*-CH_3[b]
F	5.05	4.50	2.85	4.50	2.99
Cl	5.17	5.17	3.00	5.17	3.00
Br	5.44	5.44	3.05	5.44	3.08
$N(CH_3)_2$	4.78	4.16	3.00	4.16	2.93

[a] Chemical shifts (δ) are given in ppm downfield from Me_4Si.
[b] Positions in a given isomer are relative to the boron substituent.

the coordination number about the central atom of the chlorinating agent increases, the percentage of para isomer formed increases. The reagent BCl_3 which has a coordination number of 3 yields more ortho than para isomer, whereas $SnCl_4$ with tetrahedral symmetry gives a slight excess of the para isomer. The reagent $HgCl_2$ which gives a large predominance of the para isomer must be reacting as a higher coordinated species rather than the simple linear triatomic molecule. A simple linear $HgCl_2$ species would have been expected to give more ortho then para isomer. The most reasonable explanation is that $HgCl_2$ is reacting as the solid in which the coordination number about mercury is six, a distorted octahedron.[10] This conclusion is consistent with the experimental conditions, *n*-pentane as reaction solvent. Since none of the reactions produce the statistical distribution expected from random attack on $H_3B_3N_3H_2CH_3$, the *N*-methyl group exerts some type of directive effect. The most probable directive effect is a steric effect but an electronic effect cannot be discounted.

It is of interest to compare the relative amounts of different isomers from the BCl_3 and BBr_3 reactions. The yield of the para isomer is larger for BBr_3, as expected. However, the difference is almost within the experimental error. Thus, these results would suggest that the coordination number about the central atom is more important than the size of the halogen atom. However, other data demonstrate that the nature of the particular halogen atom can have a very significant effect on reactivity. For example, $HgBr_2$ does not react with $H_3B_3N_3H_3$ under the identical conditions used for $HgCl_2$ reactions.[4] All of our data are consistent with the hypothesis that these reagents react with the borazine by a polar mechanism.[4,11] Steric effects are very important in determining the specific site of reaction. However, we do not have sufficient data to ascertain the influence of electronic effects due to substituents on nitrogen.

The ^1H NMR spectra of the compounds $H_2FB_3N_3H_2CH_3$, $H_2ClB_3N_3H_2CH_3$, $H_2BrB_3N_3H_2CH_3$, and $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ are interesting to compare (Table II). The most important feature of these spectra is that the ortho and para isomers can be distinguished by the ring $N-CH_3$ resonances in each case, except for the chloro derivative. It should be realized that the only pure isomers which have been isolated and whose spectra have been recorded are the para isomers[6] of $H_2ClB_3N_3H_2CH_3$ and $H_2[N(CH_3)_2]B_3N_3H_2CH_3$. Only mixtures of isomers of $H_2FB_3N_3H_2CH_3$ and $H_2BrB_3N_3H_2CH_3$ have been studied. The chemical shift data for both ortho and para isomers are also consistent with an additivity effect per substituent as previously observed for B-disubstituted borazine derivatives.[3] These data would suggest that both N and B substitutents interact with the π system by means of a resonance effect to alter chemical shifts of protons around the ring. However, the limitations on the nature of the possible nitrogen substituents preclude a definitive conclusion. Other factors might also influence ^1H NMR chemical shifts in partially delocalized systems such as borazines.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. Solvents were dried and purified by conventional means. The preparation[6,12] of $H_3B_3N_3H_2CH_3$ and its reaction[6] with $HgCl_2$ in C_5H_{12} as well as product isolation[6] and isomer identification[6] using $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ have been previously described. The reactions of $H_3B_3N_3H_2CH_3$ with BCl_3, $SnCl_4$, and BBr_3 were run neat at 25 °C. The reaction times for best results were 5 h (BCl_3), 2 h ($SnCl_4$), and 1 h (BBr_3). In the case of the BBr_3 reaction, the products have not been previously described. The compound $H_2BrB_3N_3H_2CH_3$, which was obtained from both −46 and −78 °C traps in a fractionation train using −23, −46, −78, and −196 °C trap temperatures, was a liquid at room temperature with a vapor pressure of 4.0 mm at 24 °C. The solid product, $HBr_2B_3N_3H_2CH_3$, was isolated with the −23 °C trap and had a vapor pressure of 0.8 mm at 24 °C.

Compound $H_2FB_3N_3H_2CH_3$ was prepared from $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ by the analogous reaction and techniques used for $H_2FB_3N_3H_3$.[1] The product $H_2FB_3N_3H_2CH_3$ was isolated in a −78 °C trap by very careful repeated fractionations and had a vapor pressure of 47 mm at 24 °C. The product was identified by mass spectral analysis and ^1H NMR data. Since BCl_3 and BBr_3 reacted with $H_3B_3N_3H_2CH_3$, the analogous reaction using BF_3 was attempted. There was no observed reaction after the mixture was allowed to stand at room temperature for 12 h. Both the BF_3 and $H_3B_3N_3H_2CH_3$ were recovered unchanged.

Nuclear Magnetic Resonance Spectra. The ^1H NMR spectra were recorded at 100 MHz by means of a Jeolco Model MH-100 spectrometer. In all cases the solvent was $Si(CH_3)_4$ for the 10% solutions.

Registry No. $H_2FB_3N_3H_2CH_3$ (ortho isomer), 63325-10-0; $H_2FB_3N_3H_2CH_3$ (para isomer), 63325-11-1; $H_2ClB_3N_3H_2CH_3$ (ortho isomer), 37053-90-0; $H_2ClB_3N_3H_2CH_3$ (para isomer), 36953-63-6; $H_2BrB_3N_3H_2CH_3$ (ortho isomer), 52920-79-3; $H_2BrB_3N_3H_2CH_3$ (para isomer), 52920-81-7; $H_2N(CH_3)_2B_3N_3H_2CH_3$ (ortho isomer), 37013-94-8; $H_2N(CH_3)_2B_3N_3H_2CH_3$ (para isomer), 37133-10-1; $HCl_2B_3N_3H_2CH_3$ (ortho,ortho isomer), 63325-12-2; $HCl_2B_3N_3H_2CH_3$ (ortho,para isomer), 63325-13-3; $HBr_2B_3N_3H_2CH_3$ (ortho,ortho isomer), 63325-14-4; $HBr_2B_3N_3H_2CH_3$ (ortho,para isomer), 63325-15-5; $HgCl_2$, 7487-94-7; $SnCl_4$, 7646-78-8; BCl_3, 10294-34-5; BBr_3, 10294-33-4.

References and Notes

(1) O. T. Beachley, Jr., *J. Am. Chem. Soc.*, **92**, 5372 (1970).
(2) O. T. Beachley, Jr., *J. Am. Chem. Soc.*, **93**, 5066 (1971).
(3) O. T. Beachley, Jr., *Inorg. Chem.*, **12**, 2503 (1973).
(4) O. T. Beachley, Jr., and B. Washburn, *Inorg. Chem.*, **14**, 120 (1975).
(5) O. T. Beachley, Jr., and T. R. Durkin, *Inorg. Chem.*, **13**, 1768 (1974).
(6) O. T. Beachley, Jr., *J. Am. Chem. Soc.*, **94**, 4223 (1972).
(7) P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).
(8) A. Grace and P. Powell, *J. Chem. Soc. A*, 673 (1966).
(9) P. Powell, *Inorg. Chem.*, **12**, 913 (1973).
(10) A. F. Wells, "Structural Inorganic Chemistry", 3rd ed, Oxford University Press, London, 1962, p 357.
(11) J. W. Wiggins and G. E. Ryschkewitsch, *Inorg. Chim. Acta*, **4**, 33 (1970).
(12) O. T. Beachley, Jr., *Inorg. Chem.*, **8**, 981 (1969).

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Influence of Internal Hydrogen Bonding on the Kinetics of Complex Formation with Nickel(II). 2. Alizarin Yellow G

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When internally hydrogen-bonded acids act as ligands in the formation of labile metal ion complexes, the reaction takes place with rate constants which are considerably below those typical for the cation in question.[1-4] These acids are also known to lose their proton to bases at rates far below the usual, diffusion controlled value.[5]

In continuation of our program of investigating the correlation between these effects we have now studied the reaction between Ni(II) and alizarin yellow G (4-(*m*-nitrophenylazo)salicylate; its monoprotonated form will be abbreviated HL^-). This enables us to draw comparisons between Ni(II) and Mg^{2+} on the one hand[4] and between alizarin yellow G and substituted phenylazoresorcinols,[1] that is to say, between an OH···O and an OH···N bond, on the other.

Experimental Section

Most of the kinetic experiments were again carried out by the temperature jump method, as described in our previous papers[1,4] where details are also given about the sources of the substances used, the calculation of $[OH^-]$ from the measured pH, and the reproducibility of the results. Some experiments were also carried out by the stopped-flow technique, using an Aminco-Morrow apparatus.

The temperature was again 25 °C. The ionic strength was 0.2 M. No buffer was added, the pH being regulated as described before.[1]

The formation constant of the complex was measured in the pH range 6.01–7.16. The stoichiometric concentration of Ni(II), *a*, was varied between 4×10^{-3} and 5×10^{-2} M, and that of the ligand, *b*, between 1.5×10^{-5} and 2×10^{-4} M. The metal ion was thus always in large excess.

The T-jump experiments were carried out in the pH range 5.95–6.77, with *a* between 4×10^{-2} and 7×10^{-2} M and *b* between 5×10^{-5} and 2×10^{-4} M. In the stopped-flow experiments higher values of pH could be used—up to 7.14. Solutions containing 6×10^{-2} M Ni(II) and 5×10^{-5} M ligand were mixed with equal volumes of solutions containing 10^{-4} M ligand.

Results

Equilibrium Constant. In the wavelength range between 340 and 450 nm the absorbance *A* of a solution containing Ni(II) and ligand is significantly higher than corresponds to the sum of the constituents. Ascribing this to the formation of a complex NiL, we can write[1,3]

$$\frac{b}{A - \epsilon_{HL}b - \bar{\epsilon}_{Ni}a} = \frac{1}{\epsilon_{NiL} - \epsilon_{HL}} + \frac{1}{\epsilon_{NiL} - \epsilon_{HL}}\,\frac{[H^+]}{K_2 a} \qquad \text{(I)}$$

where $\bar{\epsilon}_{Ni}$ is a weighted extinction coefficient[1] which changes with pH owing to the presence of $NiOH^+$, albeit in small concentration. It was determined experimentally at each pH and wavelength.[6] The constant K_2 is

$$K_2 = [NiL]\,[H^+]/[Ni^{2+}]\,[HL^-] \qquad \text{(II)}$$

A plot of the left-hand side of eq I vs. $[H^+]/a$ should yield a straight line with a ratio between intercept and slope equal to K_2. In order to check the assumption that the complex is indeed NiL, we carried out separate evaluations for five constant values of pH, 6.02, 6.42, 6.62, 6.80, and 6.93. The value of K_2 was found to be independent of pH. (The standard deviations around the mean value obtained at a given pH and three to four different wavelengths were on the average ~15% and were equal to the standard deviations around the mean value obtained at the same wavelength and different values of pH.) This confirms our assumption that the complex is NiL. We subsequently used all results (including those at pH 7.02 and 7.15, where only a small number of points were taken) to minimize the sum of squares of $\{b/(A - \epsilon_{HL}b - \bar{\epsilon}_{Ni}a) - [1/(\epsilon_{NiL} - \epsilon_{HL}) + [H^+]/K_2a(\epsilon_{NiL} - \epsilon_{HL})]\}/[b/(A - \epsilon_{HL}b - \bar{\epsilon}_{Ni}a)]$ in order to obtain the value of K_2 which best fits our data. We found[7] $K_2 = 1.29 \times 10^{-5}$.

Kinetic Results. The reciprocal relaxation times decreased with increasing pH to a flat trough, increasing slightly at still higher values of pH. The rate increased with increasing values of *a* and, to a lesser extent, with increasing values of *b*. Examples of the influence of pH and of *a* are shown in Figure 1. (The full curves in this figure are synthesized from the constants obtained as described below.)

Reaction Mechanism and Evaluation of Rate Constants. A reaction scheme which fits our results is given by eq 1–3 where

$$\begin{array}{ll}
Ni^{2+} + L^{2-} \rightleftharpoons NiL & \qquad (1) \\
\qquad\quad \upharpoonleft\downharpoonright & \\
Ni^{2+} + HL^- \rightleftharpoons NiL + H^+ & \qquad (2) \\
\upharpoonleft\downharpoonright & \\
NiOH^+ + HL^- \rightleftharpoons NiL + H_2O & \qquad (3)
\end{array}$$

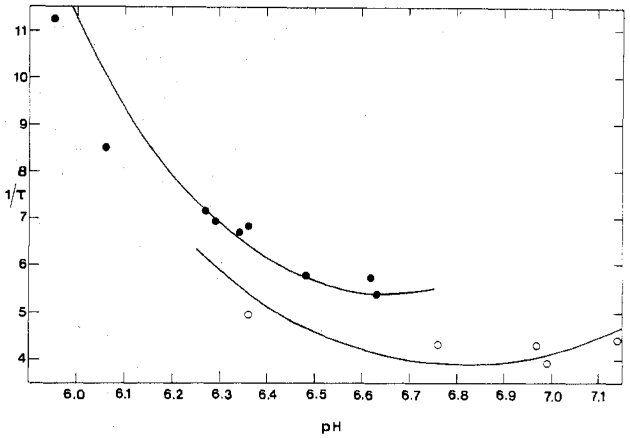

Figure 1. Two examples of the dependence of $1/\tau$ on pH: solid circles, $b = 10^{-4}$ M and $a = 6 \times 10^{-2}$ M (T-jump); open circles, $b = 7.5 \times 10^{-5}$ M and $a = 3 \times 10^{-2}$ M (stopped flow). The curves are synthesized from parameters obtained from *all* experiments.

the vertical equilibria are rapid in comparison with reactions 1–3, and we expect to see only one relaxation time. Reactions involving H_2L can be neglected. With $pK \leq 3$, this species constitutes at most 0.1% of the total ligand, whereas its rate constant can be expected to be considerably below that of HL^-.

After linearization of the rate equation, this scheme leads to the following expression for the reciprocal relaxation time[8,9]

$$1/\tau = [\vec{k}_{Ni,HL} + (\vec{k}_{NiOH}K_{NiOH}K_w + \vec{k}_{Ni,L}K_c)/[H^+]]B \qquad \text{(III)}$$

where[10–12]

$$K_{NiOH} = [NiOH^+]/[Ni^{2+}]\,[OH^-] = 2 \times 10^4\ M^{-1} \qquad \text{(IV)}$$

K_w is the autoprotolysis constant of water, K_c the second dissociation constant of our ligand at $I = 0.2$ M, and *B* is given by

$$\begin{aligned} B &= a + (\overline{[H^+]} + \overline{[NiL]}\,\delta_H/\delta_{NiL})/K_2 \\ &= a + \overline{[H^+]}/K_2 + b\overline{[H^+]}^2/K_{NiOH}K_w(\overline{[H^+]} + K_2a) \end{aligned} \qquad \text{(V)}$$

In the derivation of *B* we have made use of the fact that $a >> b$. The bar denotes equilibrium concentration, and δ_i is the difference between actual and equilibrium concentration of substance i. Since the solutions are to some extent buffered by the system Ni^{2+}–$NiOH^+$, the ratio $\overline{\delta_H/\delta_{NiL}}$ is small (to a good approximation, equal to $\overline{[H^+]}/\overline{[NiOH^+]}$) but not sufficiently small for $\overline{[NiL]}(\delta_H/\delta_{NiL})$ to be completely negligible in comparison with $\overline{[H^+]}$.

When the concentration changes during the reaction are not sufficiently small for linearization of the rate equation to be justified, the multiplier of δ_H/δ_{NiL} in eq V changes as the reaction proceeds. Therefore, in the stopped-flow experiments, solutions which already contained some NiL were mixed with solutions of HL^- to form further NiL at concentrations which were small in comparison with both $[NiL]_0$ and $[HL]_0$, though not very small, because otherwise the observed signal would become too small. In order to decrease still further the time-dependent term in our expression for $1/\tau$—to less than 7% of the total—we therefore also had to choose values of pH sufficiently high (≥6.36) for δ_H/δ_{NiL} to be very small.

Equation III shows that a plot of $1/\tau B$ as a function of $1/[H^+]$ should be a straight line; from its intercept and slope we can evaluate $\vec{k}_{Ni,HL}$ and the sum of the contributions of reactions 1 and 3.

The appropriate plot is shown in Figure 2. The deviations from the straight line are within the expected experimental

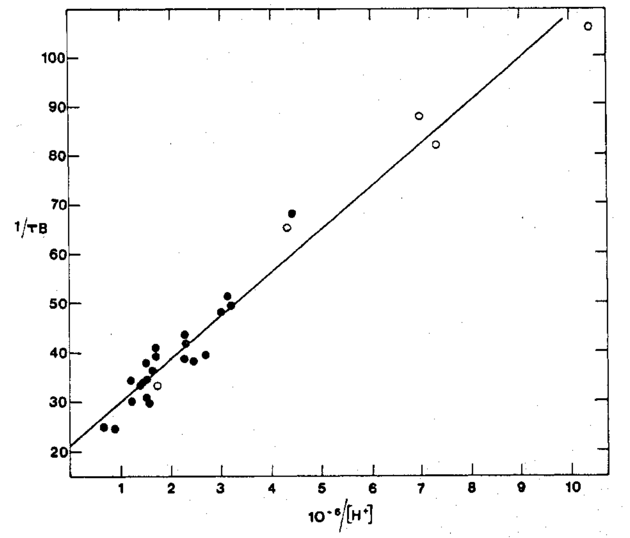

Figure 2. The dependence of $1/\tau B$ on $1/[H^+]$ (see eq III and V): solid circles, T-jump; open circles, stopped flow.

error and are completely random with respect to changes in *a*. An ordinary least-squares treatment yields[12]

$$\overrightarrow{k}_{\mathrm{Ni,HL}} = 21.5 \pm 1.1\ \mathrm{M^{-1}\,s^{-1}}$$

and

$$\overrightarrow{k}_{\mathrm{NiOH}}K_{\mathrm{NiOH}}K_{\mathrm{w}} + k_{\mathrm{Ni,L}}K_{\mathrm{c}} = (8.7 \pm 0.3) \times 10^{-6}\ \mathrm{s^{-1}}$$

Making use of our value for K_2, we get

$$\overleftarrow{k}_{\mathrm{Ni,HL}} = 1.67 \times 10^{6}\ \mathrm{M^{-1}\,s^{-1}}$$

Discussion

Equilibrium Constant. Not surprisingly, the chelate formation constant of Ni^{2+} is higher than that of Mg^{2+} by a factor of ~150. It is interesting to note, however, that the complex MHL in which the chelate has not yet been formed[4] is weaker—or in any case cannot be significantly stronger—with Ni^{2+} than with Mg^{2+}, because otherwise its presence would have made itself felt in a pH dependence of the formation constant.[4] On the other hand, comparison of our results with those concerning substituted phenylazoresorcinols shows that the nickel(II) ion is able to form a chelate, dislodging the phenolic proton adjacent to the CO_2^- group at a pH approximately five units below the p*K*, but under similar circumstances is not able to dislodge the phenolic proton adjacent to the azo group.

Rate Constants. Let us first consider reaction 2. With a distance of approach of 5 Å, the Fuoss equation[13] yields an ion pair constant of a dimonovalent pair of $K_{\mathrm{IP}} = 1.67$ M at $I = 0.2$ M. Combining this result with[14] $3.4 \times 10^4\ \mathrm{s^{-1}}$, the exchange rate of water between the bulk and the inner-coordination shell (a more recent value than that used in our previous paper[1,15]), and multiplying by a statistical factor of 0.75,[16] we find $\overrightarrow{k}_{\mathrm{Ni,HL}}$ predicted from the Eigen mechanism[17,18] to be $\sim 4.3 \times 10^4\ \mathrm{M^{-1}\,s^{-1}}$. Although experimental values are frequently lower than those calculated on this basis,[16] an inspection of the table compiled by Kustin and Swinehart[18] shows our present value of $\overrightarrow{k}_{\mathrm{Ni,HL}}$ to be several hundred times smaller than that for a "normal" monovalent ligand.

We have previously estimated[19] that a fraction of ~1/300 of the total HL^- is present in the non-hydrogen-bonded form. This fraction, reacting with a normal rate constant, suffices to sustain the observed rate, as it does in the reaction between alizarin yellow G and bases.[19] In this respect, our present system differs from the reactions between Ni^{2+} and substituted phenylazoresorcinols,[1] and between Mg^{2+} and alizarin yellow G,[4] where the rate constant is less drastically reduced below its normal value. The observed rate was explained by assuming an additional reaction path, namely, the direct attack of the metal ion on the hydrogen-bonded oxygen. The reactivity of internally hydrogen-bonded ligands toward unhydrolyzed metal ions thus varies from one system to the other.

More regularity is observed for the $[H^+]^{-1}$-dependent path in our expression of $1/\tau B$—the slope in Figure 2. This is composed of the contributions of two reactions which have the same pH dependence. If reaction 1 proceeds at a normal rate, then, again on the basis of the Eigen mechanism, $\overrightarrow{k}_{\mathrm{Ni,L}}$ should be $\sim 2.2 \times 10^5\ \mathrm{M^{-1}\,s^{-1}}$, but most divalent ligands have rate constants toward Ni^{2+} considerably lower than that.[18] With $K_{\mathrm{c}} = 1.4 \times 10^{-11}\ \mathrm{M^{-1}}$, calculated from the literature[19,20] for $I = 0.2$ M, the contribution of reaction 1 should thus be $\leq 3.3 \times 10^{-6}\ \mathrm{s^{-1}}$. This reaction *alone* therefore cannot explain the observed $[H^+]^{-1}$-dependent path. The chief contribution (at least $5.4 \times 10^{-6}\ \mathrm{s^{-1}}$) must come from reaction 3. With[21] $K_{\mathrm{w}} = 1.8 \times 10^{-14}\ \mathrm{M^2}$ this leads to $\overrightarrow{k}_{\mathrm{NiOH}} \geq 1.5 \times 10^4\ \mathrm{M^{-1}\,s^{-1}}$, higher than our $\overrightarrow{k}_{\mathrm{Ni,HL}}$ by a factor of ~700; the lowered charge on the cation would lead us to expect the opposite. A possible explanation would be that $NiOH^+$, too, reacts chiefly with the non-hydrogen-bonded form, but with a rate constant very much higher than that of Ni^{2+}, because of a strong labilizing influence of OH^- on the remaining water molecules.[11] This effect is well known[17] for Fe(III), but for Ni(II) it has been reported only when the reaction site is blocked by a proton.[1,11] We therefore assume that with $NiOH^+$ the reaction involving the non-hydrogen-bonded form is of minor importance, and the dominant path is the attack of the cation on the hydrogen-bonded oxygen. In this attack the efficiency of the strong base[10] $NiOH^+$ can exceed[19] that of Ni^{2+} by several orders of magnitude and, in contrast with Ni^{2+}, the unblocking of the reaction site is no longer rate determining.

In the present case, as well as in the reaction[4] between Mg(II) and alizarin yellow G, no labilizing effect of OH^- on the remaining water molecules is needed to explain the observed rate, whereas in the reaction between Ni(II) and substituted resorcinols some such effect—though far less pronounced than for Fe(III)—must be assumed.

We suggest that the dramatically enhanced reactivity of the hydrolyzed form of a cation toward internally hydrogen-bonded ligands—a kind of inverted "internal hydrolysis"[17]—should really be a very common feature. As explained before,[1] unless the acid is extremely weak, the effect necessarily escapes notice, since reaction 3 would be swamped by the much higher contribution of reaction 1.

Registry No. NiL, 63393-81-7; alizarin yellow G, 584-42-9; Ni^{2+}, 14701-22-5.

References and Notes

(1) Part 1: B. Perlmutter-Hayman and R. Shinar, *Inorg. Chem.*, **15**, 2932 (1976).
(2) R. G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1970).
(3) R. Koren, B. Perlmutter-Hayman, and R. Shinar, *Int. J. Chem. Kinet.*, **6**, 39 (1974).
(4) B. Perlmutter-Hayman and R. Shinar, *Inorg. Chem.*, **16**, 385 (1977).
(5) M. Eigen, *Angew. Chem.*, **75**, 489 (1963); *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).
(6) Although $\bar{\epsilon}_{\mathrm{Ni}} << \epsilon_{\mathrm{HL}}, \epsilon_{\mathrm{NiL}}$, the product $\bar{\epsilon}_{\mathrm{Ni}}a$ is not negligible in comparison with $\epsilon_{\mathrm{HL}}b$.
(7) A slightly higher result would be obtained on the basis of an ordinary, nonweighted, least-squares treatment; the standard deviation given by that program is ~8%.
(8) F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965).
(9) B. Perlmutter-Hayman, *Adv. Mol. Relaxation Processes*, in press.
(10) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964); **No. 25** (1971).
(11) S. Funahashi and M. Tanaka, *Inorg. Chem.*, **8**, 2159 (1969).
(12) The value of $K_{\mathrm{NiOH}} = 2 \times 10^4\ \mathrm{M^{-1}}$ seems to us more reliable than the $5 \times 10^4\ \mathrm{M^{-1}}$ we used previously.[1] The latter value would yield an intercept of 32.7. The slope would be little changed and $\overrightarrow{k}_{\mathrm{NiOH}}$ would become $\leq 5.5 \times 10^3\ \mathrm{M^{-1}\,s^{-1}}$. Our mechanistic conclusions would not be affected.
(13) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
(14) J. W. Neely and R. E. Connick, *J. Am. Chem. Soc.*, **94**, 3419, 8646 (1972).

(15) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); see also R. E. Connick and D. Fiat, *ibid.*, **44**, 4103 (1966).
(16) J. Neely and R. Connick, *J. Am. Chem. Soc.*, **92**, 3476 (1970).
(17) M. Eigen and G. Wilkins, *Adv. Chem. Ser.*, **No. 49**, 55 (1965).
(18) K. Kustin and J. Swinehart, *Prog. Inorg. Chem.*, **13**, 107 (1970).
(19) B. Perlmutter-Hayman and R. Shinar, *Int. J. Chem. Kinet.*, **9**, 1 (1977).
(20) M. C. Rose and J. E. Stuehr, *J. Am. Chem. Soc.*, **94**, 5532 (1972).
(21) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed, Reinhold, New York, N.Y., 1950, p 485.

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A Comparative Study of Steric Effects of Nickel(II) Complexes Containing 12-Membered Macrocyclic Ligands

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Substitution on the nitrogen atoms on a polyamine ligand has been shown to have a major effect on the stoichiometry, the geometry, and the electronic configuration of nickel(II) complexes.[1,2] For example, by employing diamine ligands, one to three bidentate ligands will coordinate to the nickel(II) depending on the bulkiness of the groups substituted on the nitrogen atoms. Square-planar, octahedral, and tetrahedral geometries have been observed for nickel(II) complexes as a function of the organic groups on the donor atoms and the counteranions.

We have made a comparative study on the effect of N substitution on 12-membered saturated cyclic tetradentate ligands coordinated to nickel(II). Because these are cyclic tetradentate ligands it is unlikely that substitution will alter the stoichiometry of the nickel(II) complexes. The expected nickel(II) to ligand ratio should be one to one. (The nickel(II) complexes of 1,4,7,10-tetrathiocyclododecane and 1,4,7,10-tetrathiacyclotridecane are exceptions and they form complexes with a nickel(II) to ligand ratio of two to three.[3]) A 12-membered cyclic tetradentate ligand should not coordinate coplanar with the nickel(II)[3-5] and therefore square-planar or trans octahedral geometries are not likely. A tetrahedral geometry is also unlikely because the small 12-membered cyclic ligand cannot span the large tetrahedron bond angles. Therefore, unlike saturated linear tetradentate ligands or larger saturated cyclic tetradentate ligands, the geometrical options available to the nickel(II) ion bonded to 12-membered saturated cyclic ligands are more limited. It is for these reasons we would like to compare the chemistry of nickel(II) complexes of 1,4,7,10-tetraazacyclododecane, cyclen,[6] with the nickel(II) compounds of 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane, tbcyclen.[6] The complexes of tbcyclen have been reported earlier;[7] those containing cyclen are first reported here.

We have observed that all the nickel(II)- or cobalt(II)-tbcyclen complexes containing monodentate counteranions have a trigonal-bipyramidal geometry, [M(tbcyclen)X]Y (where X is chloride, bromide, and thiocyanate, and Y is chloride, bromide, or perchlorate). However, complexes containing a planar, weak field counteranion such as nitrate or oxalate have a cis octahedral geometry.[7,8]

The five-coordinate geometry of all the nickel(II) complexes is believed to be due to the large benzyl groups limiting the space around the nickel(II) to only five donor atoms. To attain a six-coordinate complex, the counteranion must be a small weak field planar bidentate ligand. The tbcyclen bonded to the nickel(II) in a six-coordinate geometry has an unusually low *Dq* value for a tetradentate ligand. The *Dq* value for $[Ni(tbcyclen)NO_3]NO_3$ is 973 cm^{-1} and this value is between that found for $Ni(H_2O)_6^{2+}$ and $Ni(NH_3)_6^{2+}$.[7] This low *Dq* value was attributed both to the small size of the macrocycle imposing strained metal-to-donor bonds and to the steric strain imposed by the four benzyl groups.

Table I. Comparative Magnetic Moments (μ_B)

$Ni(cyclen)Cl_2$	3.06	$Ni(tbcyclen)(NO_3)_2$[7]	3.20
$Ni(cyclen)Br_2$	3.16	$Ni(cyclam)Cl_2$[11]	3.09
$Ni(cyclen)(NO_3)_2$	3.15	$Ni(tbcyclen)Cl_2$[7]	3.70

Table II. Electronic Spectral Data for Nickel(II) Complexes of Cyclen and Tbcyclen

Complex	Medium	nm (λ)
$Ni(cyclen)(NO_3)_2$	Solid	870, 545, 350
	CH_3CN	900 (33), 545 (28), 355 (45)
	C_2H_5OH	900 (30), 545 (25), 350 (45)
	CH_3OH	920 (28), 555 (19), 355 (29)
	H_2O	950 (27), 560 (10), 360 (13), 300 sh (16)
$Ni(tbcyclen)(NO_3)_2\cdot{}^1/_2H_2O$[7]	Solid	1025, 600, 380
	H_2O	650 (24), 480 (215), 400 sh (53)
	CH_3OH	1025 (25), 850 sh (5), 610 (30), 348 (70)
$Ni(cyclen)Br_2\cdot{}^1/_2C_2H_5OH$	Solid	945 br, 590, 375
	CH_3OH	945 (20), 545 (12), 340 (19)
$Ni(cyclen)Cl_2$	Solid	950 br, 585, 375
$Ni(tbcyclen)Cl_2\cdot{}^1/_2H_2O$[7]	Solid	710, 440
	H_2O	650 (150), 480 (320), 400 sh (120)
	CH_3OH	1560 sh (2.5), 1460 (5), 1090 (10), 715 (100), 440 (245)
	C_2H_5OH	710 (295), 440 (315)
	CH_3CN	710 (164), 440 (345)
$Ni(tbcyclen)ClClO_4\cdot H_2O$[7]	Solid	710, 440

We have prepared a variety of nickel(II)–cyclen complexes of the type $Ni(cyclen)X_2$ where X = Cl, Br, or NO_3. These complexes are purple in the solid state and in solution. In contrast all the nickel(II)–tbcyclen complexes which have a six-coordinate geometry are blue while the nickel(II)–tbcyclen complexes which have a five-coordinate geometry are green. All the $Ni(cyclen)X_2$ complexes have magnetic moments in the 3.06–3.20 μ_B range (Table I). (In contrast, the magnetic moment of [Ni(tbcyclen)Cl]Cl is 3.7 μ_B.[7]) These magnetic moments for the $Ni(cyclen)X_2$ complexes are within the range expected for nickel(II) in a six-coordinate geometry.[1] Also, the electronic spectra of all these complexes in the solid state and in solution are typical of six-coordinate nickel(II) (Table II). Therefore it can be concluded that the benzyl groups on the tbcyclen are responsible for the five-coordinate geometry of nickel(II)–tbcyclen complexes.

In the infrared spectra of $Ni(cyclen)(NO_3)_2$ the absorption peaks at 810, 1260, and 1490 cm^{-1} can be assigned to bidentate nitrate while the bands at 830 and 1325 cm^{-1} can be assigned to ionic nitrate.[9,10] These assignments confirm the similar assignments made on $Ni(tbcyclen)(NO_3)_2$.[7] The bidentate nitrate indicates that the cyclen and tbcyclen must be in a folded configuration around the nickel(II). The N–H stretching frequencies also suggest that all the nickel(II)–cyclen complexes are in a cis configuration. There are several N–H stretches between 3300 and 3100 cm^{-1} in contrast to $Ni(cyclam)Cl_2$ (cyclam is 1,4,8,11-tetraazacyclotetradecane) which has only one N–H stretch at 3145 cm^{-1}.[11] Since the cyclam coordinates coplanar with the nickel(II) all the hydrogens bonded to nitrogens are in essentially the same environment. In contrast, the cyclen is coordinated to the nickel(II) in a folded manner and therefore all the hydrogens bonded to the nitrogen are not in identical environments.