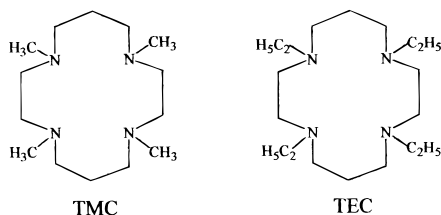
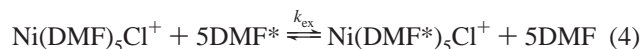


$\text{Ni}^{2+}/\text{Br}^-/\text{DMF}$ (DMF = *N,N*-dimethylformamide). On one hand, the reaction of nickel ions with the macrocyclic ligands $L = \text{TMC}$ (tetra-*N*-methylated cyclam) and $L = \text{TEC}$ (tetra-*N*-ethylated cyclam) in DMF according to eq 3 is investigated by stopped-flow spectrophotometry in the absence and in the presence of chloride and bromide ions, respectively, to obtain information about the kinetics and mechanism of macrocyclic complex formation with the mono halo species $\text{Ni}(\text{DMF})_5\text{Cl}^+$ and $\text{Ni}(\text{DMF})_5\text{Br}^+$, as compared to the fully solvated cation $\text{Ni}(\text{DMF})_6^{2+}$.



This reaction is investigated by stopped-flow spectrophotometry in the absence and in the presence of chloride and bromide ions, respectively, to obtain information about the kinetics and mechanism of macrocyclic complex formation with the mono halo species $\text{Ni}(\text{DMF})_5\text{Cl}^+$ and $\text{Ni}(\text{DMF})_5\text{Br}^+$, as compared to the fully solvated cation $\text{Ni}(\text{DMF})_6^{2+}$. On the other hand, the rate of solvent exchange in the mono halo species $\text{Ni}(\text{DMF})_5\text{Cl}^+$ and $\text{Ni}(\text{DMF})_5\text{Br}^+$ according to eq 4 is studied by the variable-temperature ^{13}C NMR technique and compared to the hexa solvated cation $\text{Ni}(\text{DMF})_6^{2+}$.



Experimental Section

Chemicals. TBAClO₄ (tetra-*n*-butylammoniumperchlorate), TBABr (tetra-*n*-butylammoniumbromide), TBACl·H₂O (tetra-*n*-butylammoniumchloride monohydrate), ⁴BuM (4-isobutylmorpholin), and DMF (*N,N*-dimethylformamide) were commercially available in reagent grade quality and were used without further purification. [¹³C₂]DMF (*N,N*-dimethyl[¹³C₂]formamide; 99%) was obtained from Isotec. $\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2$ was prepared on the basis of the procedure described by Fee et al.⁴

Warning! Perchlorate salts and organic solutions of such salts are potentially explosive. They should be handled in small quantities and with caution.

Ligands. TMC (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)^{5a} and TEC·4HBr (1,4,8,11-tetraethyl-1,4,8,11-tetraazacyclotetradecane tetrahydrobromide)⁶ were prepared as described in the literature. Treatment of the hydrobromide with NaOH, extraction with CHCl₃, and distillation in vacuo led to the free ligand TEC (slightly yellow oil).

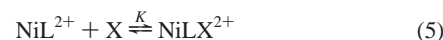
Complexes. Trans I–Ni(TMC)(ClO₄)₂, obtained by the reaction of an aqueous solution of nickel perchlorate with a solution of TMC in methanol, was recrystallized in methanol/water. Trans III–Ni(TMC)(ClO₄)₂ was prepared as described in the literature.^{5b} The preparation of Ni(TEC)(ClO₄)₂ according to the literature procedure⁶ led to the violet form of this complex as the major product.

Solutions. The solutions for NMR work were prepared by weighing, and their concentration is therefore given in molality *m* (mol kg⁻¹).

The concentration of the solutions used in kinetic work is given in molarity *M* (mol L⁻¹).

Instrumentation. UV/vis spectra were recorded on a diode array spectrophotometer (Zeiss, type Specord S10), and UV/vis/NIR spectra were recorded on a double-beam spectrophotometer (Perkin-Elmer, type Lambda 900). Complex formation kinetics measurements were performed on a diode array spectrophotometer with a two-chamber quartz cell (*t*_{1/2} > 10 min) and on a rapid-scan stopped-flow spectrophotometer⁷ (*t*_{1/2} < 1 min). ¹³C NMR spectra were recorded on a Bruker spectrometer (type Avance 400).

Spectrophotometric Titration. Equilibrium constants *K* for addition reactions according to eq 5 with X = DMF, Cl⁻, or Br⁻ were determined by spectrophotometric titration.



The absorbance/[X] data were computer-fit to eq 6 to obtain *K*.

$$A = (A_0 + A_\infty K[X]) / (1 + K[X]) \quad (6)$$

The symbols *A*₀ and *A*_∞ refer to the absorbance of the species $\text{Ni}L^{2+}$ and $\text{Ni}LX^{2+}$, respectively, at $[\text{Ni}L^{2+}]_0$.

Kinetic Investigation of Complex Formation. Complex formation according to eq 3 was studied spectrophotometrically in DMF at 298 K and *I* = 0.6 M (TBAClO₄). The experiments were carried out either under 1:1 conditions ($[\text{metal}]_0 = [\text{ligand}]_0$) or under pseudo-first-order conditions ($[\text{metal}]_0 \gg [\text{ligand}]_0$ or vice versa). Rate constants were obtained by multiwavelength analysis in the range *l* = 320–620 nm. The absorbance/time data, as obtained for the fast stage of complex formation, were computer-fit to either eq 7 (1:1 conditions), eq 7a (mild excess of nickel or ligand), or eq 8 (pseudo-first-order conditions) to obtain the corresponding rate constant *k* (second-order) or *k*_{obsd} (pseudo-first-order).

$$A = \{(A_0 - A_\infty) / (1 + k[\text{metal}]_0 t)\} + A_\infty \quad (7)$$

$$A = \{(A_0 - A_\infty)(z - 1) \exp(-\beta t)\} / \{z - \exp(-\beta t)\} + A_\infty \quad (7a)$$

$$A = (A_0 - A_\infty) \exp(-k_{\text{obsd}} t) + A_\infty \quad (8)$$

Equation 7a was used to fit the absorbance/time data obtained under moderate excess conditions [*z* = $[\text{nickel}]_0 / [\text{ligand}]_0$ or $[\text{ligand}]_0 / [\text{nickel}]_0$, respectively, with *z* in the range 1–10 and $\beta = k[\text{excess partner}]_0(1 - z^{-1}) = k_{\text{obsd}}(1 - z^{-1})$]. Under certain conditions (see Results), the time dependence of the absorbance was biphasic or triphasic so that the data had to be fit to the sum of two (*m* = 2) or three (*m* = 3) exponentials according to eq 9 (*A*₀ and *A*_∞ refer to *t* = 0 and *t* = ∞, respectively).

$$A = \left[\sum_{i=1}^m A_i \exp(-k_{\text{obsd},i} t) \right] + A_\infty \quad (9)$$

NMR Investigation of Solvent Exchange. Solutions for ¹³C NMR spectroscopy were prepared using [¹³C₂]DMF diluted with normal DMF to 27% ¹³C enrichment. A stock solution was prepared by adding 214.50 mg (0.308 mmol) of $\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2$ to 3.014 g of DMF, resulting in a solution 0.102 *m* in $\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2$ (Sol. 1). Two solutions containing chloride anions were prepared as follows: (i) 27.17 mg (0.098 mmol) of TBACl was added to 1.087 g of the stock solution, giving a solution 0.10 *m* in TBACl (Sol. 2), and (ii) 83.52 mg (0.03 mmol) of TBACl was added to 1.074 g of stock solution, giving a solution 0.30 *m* in TBACl (Sol. 3). One solution containing bromide anion was prepared by adding 32.08 mg (0.01 mmol) of TBABr to 0.969 g of stock solution, giving a solution 0.11 *m* in TBABr (Sol. 4). Benzene (1%) was added to all of the solutions as a chemical shift standard.

The kinetics of DMF exchange on $\text{Ni}(\text{DMF})_6^{2+}$ and $\text{Ni}(\text{DMF})_5\text{Cl}^+$ were followed by ¹³C NMR as a function of temperature (¹³C resonance frequency = 100.61 MHz). The acquisition parameters for the variable-

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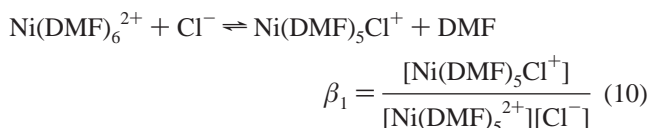
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temperature measurements were as follows: pulse length of 8 ms, quadrature detection mode with 64K data points resulting from 2500 scans accumulated over a spectral width of 150 kHz. No ^1H decoupling was applied. Chemical shifts were measured with respect to the high-field part of the apparent benzene doublet, fixed to +127.205 ppm. The temperature was controlled within ± 0.2 K using a Bruker B-VT 3000 digital instrument and was measured before and after spectral accumulation by substituting the sample with a calibrated platinum resistance fit into an NMR tube.⁸ Standard 5-mm NMR tubes were used.

Results

Formation of Nickel Halo Complexes in the Systems $\text{Ni}^{2+}/\text{Cl}^-/\text{DMF}$ and $\text{Ni}^{2+}/\text{Br}^-/\text{DMF}$. The calorimetric and spectrophotometric study of Ishiguro et al.^{9a} on the formation of chloro complexes of nickel(II) in the system $\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2/\text{Et}_4\text{NCl}/\text{DMF}$ showed that stepwise coordination of one, two, three, and finally four Cl^- ions to the nickel takes place, the overall formation constants being $\log \beta_1 = 2.85$ ($\beta_1 = 708 \text{ M}^{-1}$), $\log \beta_2 = 3.76$, $\log \beta_3 = 5.53$, and $\log \beta_4 = 7.40$ (298 K; $I = 0.4 \text{ M Et}_4\text{NClO}_4$). Pilarczyk and Klinszporn^{9b} reported $\beta_1 = 1380 \text{ M}^{-1}$ for the formation of the octahedral monochloro species $\text{Ni}(\text{DMF})_5\text{Cl}^+$ according to eq 10 at 298 K.



One calculates that, for $\beta_1 = 708 \text{ M}^{-1}$, $[\text{nickel}]:[\text{chloride}] = 1:2$ and $[\text{nickel}]_{\text{tot}} = 1 \times 10^{-3} \text{ M}$, 53% of the nickel is present in the form of the cation $\text{Ni}(\text{DMF})_5\text{Cl}^+$, approximately 46% in the form of the cation $\text{Ni}(\text{DMF})_6^{2+}$, and 1% in the form of the species $\text{Ni}(\text{DMF})_4\text{Cl}_2$. One should note that the formation of the species $\text{Ni}(\text{DMF})_5\text{Cl}^+$ according to eq 10 is a fast process, as controlled by the rate of solvent exchange in the cation $\text{Ni}(\text{DMF})_6^{2+}$.

The equilibrium constant β_1 for the formation of the monobromo species $\text{Ni}(\text{DMF})_5\text{Br}^+$ in the system $\text{Ni}^{2+}/\text{Br}^-/\text{DMF}$ is reported to be 631 M^{-1} at 298 K.^{9b} Spectrophotometric titration of $\text{Ni}(\text{DMF})_6^{2+}$ with TBABr in DMF led to the considerably smaller value of $\beta_1 = 133 \pm 10 \text{ M}^{-1}$.¹⁰

^{13}C NMR Investigation of Solvent Exchange at Variable Temperature. The ^{13}C NMR spectra of the cation $\text{Ni}(\text{DMF})_6^{2+}$ (Sol. 1) were recorded between 193 and 395 K. At lower temperatures ($< 294 \text{ K}$), a doublet was observed at 161.9/162.9 ppm that was assigned to the formyl carbon of bulk DMF. Two quartets centered at 35.0 and 29.4 ppm were assigned to the *cis*- and *trans*-methyl groups of bulk DMF, respectively. In the temperature range 193–294 K, signals of the methyl carbons of coordinated DMF were visible (at 116.2 and 77.7 ppm at 193 K). These signals do not show a multiplet structure because of the strong relaxation enhancement of the methyl protons caused by the paramagnetic Ni^{2+} cation. The transverse relaxation enhancement and chemical shift of bulk DMF, both as a function of temperature, were analyzed simultaneously using the standard Swift and Connick formalism.¹¹ The results as

Table 1. Kinetic Parameters Obtained from the Variable-Temperature ^{13}C NMR Data for Solutions of the Cations $\text{Ni}(\text{DMF})_6^{2+}$ and $\text{Ni}(\text{DMF})_5\text{Cl}^+$ in DMF

	$\text{Ni}(\text{DMF})_6^{2+}$		$\text{Ni}(\text{DMF})_5\text{Cl}^+$
	$^1\text{H}/^{17}\text{O}$ NMR literature results	this work ^d	this work ^e
$k_{\text{ex}}^{298}, \text{s}^{-1}$	3.8×10^3 ^a 6.9×10^3 ^b 7.7×10^3 ^c	$(3.7 \pm 0.4) \times 10^3$	$(5.3 \pm 1) \times 10^5$
$\Delta H^\ddagger, \text{kJ mol}^{-1}$	62.9 ^a 54.4 ^b 39.3 ^c	59.3 ± 5	42.4 ± 4
$\Delta S^\ddagger, \text{J mol}^{-1} \text{K}^{-1}$	+33.5 ^a +25.0 ^b −37.7 ^c	$+22.3 \pm 14$	$+6.7 \pm 15$

^a Ref 12. ^b Ref 13. ^c Ref 14. ^d Solution that is 0.102 m in $\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2$. ^e Mean value of two solutions that are 0.026 m (0.004 m) in $\text{Ni}(\text{DMF})_6^{2+}$, 0.076 m (0.098 m) in $\text{Ni}(\text{DMF})_5\text{Cl}^+$, and 0.024 m (0.202 m) in Cl^- in DMF.

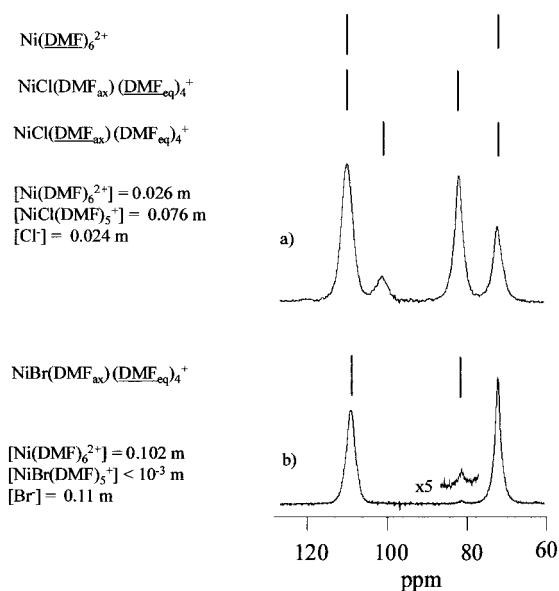


Figure 1. Part of ^{13}C NMR spectra of solutions that are 0.102 m $\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2$ in DMF with added (a) chloride (0.100 m) and (b) bromide (0.110 m) recorded at 215 K. The equilibrium concentrations obtained by integration are provided on the left. Solid bars represent the ^{13}C shifts of the *trans*- and *cis*-methyl carbons of the corresponding species.

presented in Table 1 agree very well with those obtained previously by ^1H NMR.^{12,13–14}

In addition to the resonances attributable to bulk DMF and to $\text{Ni}(\text{DMF})_6^{2+}$, the ^{13}C NMR spectra of the cation $\text{Ni}(\text{DMF})_5\text{Cl}^+$ (Sols. 2 and 3) show two additional signals at 108.1 and 87.9 ppm. The coordinated DMF in the species $\text{Ni}(\text{DMF})_5\text{Cl}^+$ can be classified as one axial and four equatorial DMF molecules. Keeping in mind that the *cis*- and *trans*-methyl carbons have different chemical shifts, one should observe two resonance pairs with a ratio of 4:1. Furthermore, a certain amount of $\text{Ni}(\text{DMF})_6^{2+}$ is always present in Sols. 2 and 3, leading to two $^{13}\text{CH}_3$ resonances as described above. Figure 1a shows the spectral region of the coordinated methyl in Sol. 2 at 215 K. Only four resonance lines are found instead of six, as theoretically predicted. It follows from integration that we can attribute the signal at 117.3 ppm to the superposition of the

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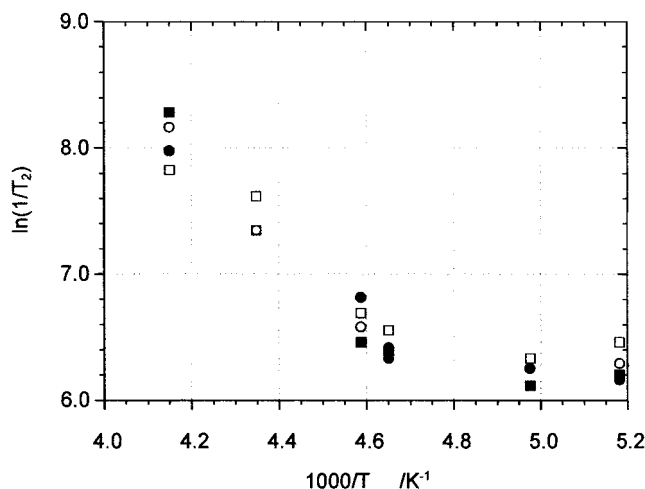


Figure 2. Temperature dependence of the transverse relaxation rates of methyl groups: (●, ○) *trans*-CH₃ of equatorial DMF in Ni(DMF)₅Cl⁺ and (■, □) *cis*-CH₃ of axial DMF in Ni(DMF)₅Cl⁺. Solid (open) symbols correspond to Sol. 2 (Sol. 3).

cis-CH₃ of DMF in Ni(DMF)₆²⁺ and the *cis*-CH₃ of the equatorial DMF in Ni(DMF)₅Cl⁺. Likewise, we attribute the peak at 77.6 ppm to the *trans*-CH₃ of DMF in Ni(DMF)₆²⁺ and the *trans*-CH₃ of the axial DMF in Ni(DMF)₅Cl⁺. The resonances at 108.1 and 87.9 ppm are due to the *cis*-CH₃ of axial DMF in Ni(DMF)₅Cl⁺ and the *trans*-CH₃ of equatorial DMF in Ni(DMF)₅Cl⁺, respectively. Sol. 4, containing bromide ions, shows primarily two ¹³CH₃ resonances that are due to Ni(DMF)₆²⁺ (Figure 1b). A small peak at 80.6 ppm can be attributed to the equatorial DMF of *trans*-Ni(DMF)₅Br⁺.

Raising the temperature results in a broadening of the ¹³CH₃ resonances and a shift toward bulk DMF signals because of the chemical exchange of DMF molecules. At temperatures above 294 K, the signals of the coordinated DMF disappear in the baseline because of the large broadening caused by exchange.

Equilibrium constant β_1 for the formation of the chloro complex according to eq 10 was obtained from the integration of the ¹³CH₃ resonances of the spectra recorded at 193–218 K. Because of the uncertainty in the integration and the small temperature range covered, a significant temperature dependence of β_1 could not be found. The best nonlinear least-squares fit of all of the data resulted in a value of $\beta_1 = 116 \pm 22 \text{ m}^{-1}$, independent of temperature. The concentrations of the species Ni(DMF)₆²⁺, Ni(DMF)₅Cl⁺, and Cl⁻ in Sol. 2 (Sol. 3) are 0.026 *m* (0.004 *m*), 0.076 *m* (0.098 *m*), and 0.024 *m* (0.202 *m*), respectively. The concentration of the cation Ni(DMF)₅Br⁺ is estimated to be $< 10^{-3} \text{ m}$.

Figure 2 shows the transverse relaxation rates of the unique resonances attributed to the *cis*-CH₃ of axial DMF and to the *trans*-CH₃ of equatorial DMF in the chloro complex. At temperatures above 217 K ($1000/T \approx 4.6 \text{ K}^{-1}$), these relaxation rates are directly related to the lifetimes of DMF molecules in the equatorial and the axial positions, respectively. The observed lifetimes are the same within experimental error, and we conclude that the exchange rate constants of equatorial and axial DMF in Ni(DMF)₅Cl⁺ are the same. We can therefore treat coordinated DMF in Ni(DMF)₅Cl⁺ as one single exchanging species. Furthermore, the concentration of Ni(DMF)₅Cl⁺ is much larger than that of Ni(DMF)₆²⁺ (at least for Sol. 3), and the exchange of DMF on Ni(DMF)₅Cl⁺ is about 500 times faster (at 250 K) than that of DMF on the hexacoordinated cation Ni(DMF)₆²⁺. We therefore analyzed the transverse relaxation

enhancements and chemical shifts of bulk DMF resonances using a simultaneous nonlinear least-squares fit with the simple Swift and Connick approach.¹¹ One can further expect that the exchange rate of Ni(DMF)₄Cl₂ is much faster than that of Ni(DMF)₅Cl⁺. Therefore, even small amounts of Ni(DMF)₄Cl₂ could contribute to the line broadening of the bulk DMF signals. The contribution of this process can be excluded, however, because of the fact that the Swift and Connick data obtained in a large temperature range are consistent with those observed at low temperatures on the bound DMF signals (Figure 2). The results are summarized in Table 1 (the error limits correspond to one standard deviation).

Because the concentration of the species Ni(DMF)₅Br⁺ in the temperature range covered is $< 10^{-3} \text{ m}$, DMF exchange on this complex could not be measured. The transverse relaxation enhancements and chemical shifts of the bulk DMF resonances of Sol. 4 can therefore be fit in fair approximation by parameters obtained for solutions of the cation Ni(DMF)₆²⁺.

State of Coordination of the Complexes NiL₂²⁺ (L = TMC, TEC) in DMF and in the Presence of Halide Ions. Nickel(II) complexes of cyclam and derivatives of cyclam with a more or less square-planar N₄ coordination geometry tend to increase their coordination number from four to five or six. Titration of the complexes *trans* I–Ni(TMC)²⁺ and Ni(TEC)²⁺ with DMF in nitromethane leads to the equilibrium constants $K = 3.9$ and 0.23 m^{-1} , respectively, for the addition of one molecule of DMF according to eq 5 (see Table 2). The addition of a second molecule of DMF (that is, the formation of octahedrally coordinated complexes) is not observed. A comparison of the UV/vis spectra of the complexes in nitromethane and in DMF confirms that, in DMF, the five-coordinate species prevails [98% *trans* I–Ni(TMC)(DMF)²⁺ vs 2% *trans* I–Ni(TMC)²⁺ and 75% Ni(TEC)(DMF)²⁺ vs 25% Ni(TEC)²⁺].

Titration of the complexes with halide ions in DMF shows that there is a strong tendency to form the five-coordinate halo species NiLX⁺ (Table 2). Chloride ions are bound more firmly than bromide ions, and the five-coordinate halo TMC complexes are several orders of magnitude more stable than the corresponding TEC complexes. The analogous behavior of the complexes *trans* I–Ni(TMC)(DMF)²⁺ and Ni(TEC)(DMF)²⁺ upon addition of nucleophiles suggests that the cation Ni(TEC)²⁺ has the *trans*-I configuration in DMF.

Kinetics of Nickel Complex Formation with TMC. As part of a systematic study,¹⁵ we reported earlier that the reaction of the cation Ni(DMF)₆²⁺ with TMC in DMF is biphasic according to eq 11, with an initial second-order incorporation step (rate constant k_1) followed by a first-order isomerization step (rate constant k_2).



In this earlier investigation, the kinetic data were based on absorbance/time measurements recorded at 20 wavelengths (494–509 nm) lying within one of the absorption bands ($\lambda_{\text{max}} = 512 \text{ nm}$) of the product *trans* I–Ni(TMC)(DMF)²⁺.

The kinetic analysis of the absorbance/time data of the present study is based on multiwavelength analysis in the wide range of 320–620 nm. Application of this more extensive analytical procedure to the renewed study of reaction 11 confirmed the final first-order isomerization step (rate constant k_2) but surpris-

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Table 2. Equilibrium Constants K (M^{-1}) for the Addition of Nucleophiles X to Complexes NiL^{2+} According to Equation 5 at 298 K

complex	X = DMF ^a	X = Cl ^{-b}	X = Br ^{-b}
trans III-Ni(TMC) ²⁺	0.47 ± 0.06	(8.4 ± 0.8) × 10 ³	(2.5 ± 0.3) × 10 ³
trans I-Ni(TMC) ²⁺	3.9 ± 0.4	>10 ⁶	(3.1 ± 0.3) × 10 ⁵
Ni(TEC) ²⁺ (violet form)	0.23 ± 0.02	(3.5 ± 0.4) × 10 ³	(4.9 ± 0.4) × 10 ³

^a Solvent nitromethane. ^b Solvent DMF.

Table 3. Rate Constants for the Reaction of Nickel(II) with the Ligands L = TMC and TEC in DMF at 298 K and $I = 0.6$ M (TBAClO₄) According to Equation 11 in the Absence and in the Presence of Chloride Ions

system	[Ni(DMF) ₆ (ClO ₄) ₂] ₀ , M	[L] ₀ , M	[TBACl], M	[4 ⁱ BuM] ₀ , M	k_{1a} , M ⁻¹ s ⁻¹	$k_1 (= k_{1b})$, M ⁻¹ s ⁻¹	$k_2 \times 10^4$, s ⁻¹
L = TMC							
1	0.01–0.1	0.001			240 ± 19	99 ± 5	15 ± 1 ^a
2	0.001	0.001		0.02		99 ± 9 ^b	5 ± 0.8
3	0.001	0.001	0.00001–0.1			(23 ± 3) × 10 ³ ^c	11 ± 1 ^d
L = TEC							
4	0.001	0.001				230 ± 10	410 ± 21 (k_{2a}) ^e 64 ± 5 (k_{2b}) ^e
5	0.005–0.05	0.001				237 ± 12	420 ± 24 (k_{2a}) ^e 64 ± 6 (k_{2b}) ^e
6	0.001	0.005–0.05				237 ± 13	480 ± 30 (k_{2a}) ^e 63 ± 5 (k_{2b}) ^e
7	0.001	0.001	0.0001–0.05			(11 ± 1) × 10 ³ ^c	405 ± 20 (k_{2a}) ^e 63 ± 5 (k_{2b}) ^e

^a Mean of k_2 as obtained at five different concentrations of nickel perchlorate. ^b Mean of k_2 as obtained at five different concentrations of the base 4ⁱBuM. ^c As obtained from the saturation value of $k_{obsd,1}$ (see Figure 3 and Discussion). ^d Mean of k_2 as obtained at 11 different concentrations of TBACl. ^e The slow isomerization stage of the reaction consists of two consecutive steps, as characterized by first-order rate constants k_{2a} and k_{2b} ; the data listed are the mean of k_{2a} and k_{2b} as obtained at four different concentrations of the excess partner nickel and ligand, respectively.

ingly showed two parallel second-order processes ($k_{1a} = 240 \pm 19$ M⁻¹ s⁻¹ and $k_{1b} = 99 \pm 5$ M⁻¹ s⁻¹ at 298 K; see system 1 in Table 3 and Table S11) for the initial stage of the reaction. It followed from some additional experiments¹⁶ that the faster second-order reaction (k_{1a}) is obviously caused by residual water in DMF. In the presence of the nearly noncoordinating base 4-isobutylmorpholin (4ⁱBuM), the k_{1a} path disappeared, and $k_{1b} = k_1 = 99 \pm 8.5$ M⁻¹ s⁻¹ remained as a second-order rate constant describing the initial reaction of nickel with TMC (see system 2 in Table 3 and Table S12). The various rate constants and reaction conditions are summarized in Table 3.

In the presence of chloride ions, complex formation according to eq 11 is substantially accelerated (see system 3 in Table 3 and Table S13). As shown in Figure 3 for the condition [TMC]₀ = [nickel]₀, the experimental rate constant $k_{obsd,1}$, obtained by fitting the absorbance/time data to eq 7a with $z = [TMC]_0/[Ni(DMF)_5Cl^+]_0$,¹⁷ increases approximately linearly¹⁸ with [TBACl]₀ to arrive at a plateau for [TBACl]₀/[Ni(DMF)₅Cl⁺]₀ ≥ 20 at which $k_{obsd,1} = 23 \pm 3$ s⁻¹, which corresponds to $k_1 = 23 \times 10^3$ M⁻¹ s⁻¹ (see Table 3). This means that, at an approximately 20-fold or higher excess of chloride over nickel, the rate of formation of the intermediate nickel complex with TMC is a factor of approximately 230 faster than the rate in the absence of chloride.

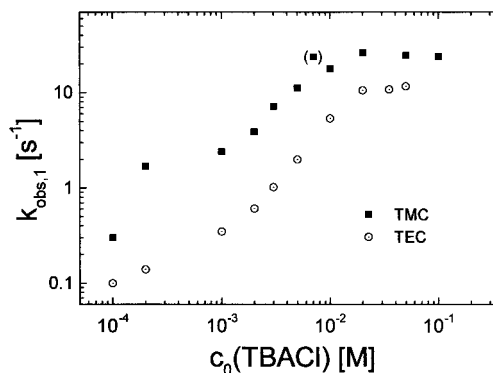


Figure 3. Dependence of the first-order rate constants $k_{obsd,1}$ (s⁻¹) on the concentration of TBACl for the reactions of nickel(II) perchlorate (10⁻³ M) with (■) TMC (10⁻³ M) and (○) TEC (10⁻³ M) in DMF according to reaction 11 at 298 K (the value for $k_{obsd,1}$ at [TBACl] = 7 × 10⁻³ M was neglected; see Discussion).

In the presence of chloride, the spectrum of the intermediate is clearly different from the spectrum of the intermediate Ni(TMC)_{int}⁺ obtained in the absence of chloride, and the spectrum of the product corresponds to the spectrum of Ni(TMC)Cl⁺, as obtained from titration studies (see Table S17). These findings are in line with the interpretation that the species Ni(DMF)₅Cl⁺ reacts with TMC to form the intermediate Ni(TMC)Cl_{int}²⁺, which isomerizes to form the complex Ni(TMC)Cl²⁺.

It should be mentioned that chloride ions, admixed *after* the formation of the intermediate Ni(TMC)_{int}²⁺,¹⁹ led to rate constant of $k_2 = (11 \pm 1) \times 10^{-4}$ s⁻¹, which is in fair agreement with the data obtained for k_2 with chloride present from the beginning. The final absorption spectrum obtained in this experiment with delayed admixing of chloride corresponded to the species Ni(TMC)Cl⁺.

(16) As controlled by Karl Fischer titration, the commercial reagent grade DMF had a mean water content corresponding to [H₂O] = 1.5 × 10⁻² M. In dried DMF (CaH₂) the k_{1a} path disappeared, as it also did in commercial DMF after the addition of the base 4ⁱBuM as a sponge for the water at a concentration of [4ⁱBuM] ≥ 10⁻² M. We think that the residual water interacts with the base TMC, but we do not have a convincing interpretation at hand that explains the mechanistic details of the k_{1a} path. For the kinetic comparison of the species Ni(DMF)₆²⁺ and Ni(DMF)₅Cl⁺ reacting with TMC, the base 4ⁱBuM was added to suppress the water-initiated pathway.

(17) The calculation of $z = [TMC]_0/[Ni(DMF)_5Cl^+]_0 = 1.9$ was based on $\beta_1 = 708$ m⁻¹ and $\beta_2 = 5750$ m⁻¹ (see ref 9).

(18) The initial increase of $k_{obsd,1}$ with [TBACl]₀ is approximately linear. Computer fitting of the data obtained for $k_{obsd,1}$ in the range [TBACl]₀ = 1 × 10⁻⁴ M to [TBACl]₀ = 7 × 10⁻³ M leads to a slope of $m = 1.0 \pm 0.3$.

(19) This experiment was performed with a four-syringe stopped-flow unit (Biologic, type SFM-4). After generation of the intermediate Ni(TMC)_{int}²⁺ within approximately 90 s, the third syringe was used to conduct a stopped-flow experiment with the intermediate and a solution of chloride ions in DMF.

Compared to chloride ions, bromide ions enhance the rate of complex formation between nickel and TMC much less effectively. Under comparable conditions, rate enhancement by bromide is a factor of approximately 10 smaller than that for chloride. The kinetic effect of bromide appears to be more complex²⁰ and was therefore not studied in detail.

Kinetics of Nickel Complex Formation with TEC. To our knowledge, complex formation of nickel with TEC has not been studied so far. The results obtained confirm that formation of the complex Ni(TEC)²⁺ follows the reaction pattern shown in eq 11 for TMC, in that fast, second-order nickel incorporation is followed by slow, first-order isomerization of the initially formed intermediate Ni(TEC)_{int}²⁺. In contrast to the intermediate Ni(TMC)_{int}²⁺, the species Ni(TEC)_{int}²⁺ isomerizes in two consecutive steps (see first-order rate constants k_{2a} and k_{2b} in Table 3).

Complex formation with TEC was studied under 1:1 conditions {[nickel]_o = [TEC]_o; see system 4 in Table 3}, as well as with an excess of either nickel (see system 5 in Table 3 and Table S14) or TEC (see system 6 in Table 3 and Table S15). The data obtained for k_1 , k_{2a} , and k_{2b} under these various conditions agree very satisfyingly (see Table 3). It follows from the comparison of k_1 (TMC) with k_1 (TEC) that intermediate formation with TEC is approximately 2.4 times faster than with TMC. Both of the consecutive steps describing the first-order isomerization of the intermediate formed with TEC are faster than the one isomerization step observed for Ni(TMC)_{int}²⁺.

In the presence of chloride ions, complex formation with TEC according to eq 11 is significantly accelerated (see system 7 in Table 3 and Table S16). As shown in Figure 3 for the condition [TEC]_o = [nickel]_o, the experimental rate constant $k_{\text{obsd},1}$, obtained by fitting the absorbance/time data to eq 7a with $z = [\text{TEC}]_o/[\text{Ni}(\text{DMF})_5\text{Cl}^+]_o$,¹⁷ increases approximately linearly²¹ with [TBACl]_o to arrive at a plateau for [TBACl]_o/[Ni(DMF)₅Cl⁺]_o ≥ 20 at which $k_{\text{obsd},1} = 11 \pm 1 \text{ s}^{-1}$, which corresponds to $k_1 = 11 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (see Table 3). This means that, at a 20-fold or higher excess of chloride over nickel, the rate of formation of the intermediate nickel complex with TEC is a factor of approximately 47 faster than the rate in the absence of chloride.

Discussion

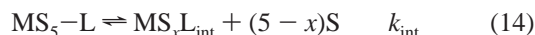
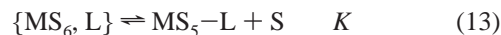
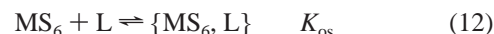
Lability of Coordinated DMF in the Cation Ni(DMF)₅Cl⁺. The rate constant at room temperature k_{ex} ²⁹⁸ for solvent exchange in the cation Ni(DMF)₆²⁺, as determined by ¹³C NMR in the present study, agrees well with the results obtained earlier by ¹H NMR¹² (see Table 1). Relative to the chloride position, the species Ni(DMF)₅Cl⁺ has four equatorial (cis) DMF positions and one axial (trans) position. The ¹³C NMR data obtained do not support the expectation that there is preferential lability of the trans-orientated DMF molecule. The data suggest instead that the rate of exchange of DMF is the same in all five of the DMF positions. The results presented in Table 1 for 298 K show that the replacement of one of the six DMF ligands in the octahedral ligand field of the cation Ni(DMF)₆²⁺ by chloride enhances the rate of DMF exchange by a factor of 143.

The Eigen–Wilkins mechanism implies that second-order rate constants k , describing complex formation reactions with monodentate ligands, are composite parameters according to $k = k_i K_{\text{os}}$. Fast initial formation of an outer-sphere complex (equilibrium constant K_{os}) is followed by rate-controlling interchange (first-order rate constant k_i). In the interchange step, a coordinated solvent molecule is replaced by the incoming ligand. It is well documented³ that solvent exchange on the solvated nickel(II) cation follows the I_d mechanism. If so, the rate of complex formation of the cation Ni(DMF)₆²⁺ with monodentate ligands should correlate with the rate of solvent exchange on this cation, as characterized by $k_{\text{ex}} = 3.7 \times 10^3 \text{ s}^{-1}$ (see Table 1). This means that the size of the experimentally obtained second-order rate constant k for complex formation reactions with monodentate ligands is expected to lie in the range from $0.6 \times 10^3 \text{ s}^{-1}$ ($K_{\text{os}} = 0.15 \text{ M}^{-1}$)²² to $4 \times 10^3 \text{ s}^{-1}$ ($K_{\text{os}} = 1.0 \text{ M}^{-1}$)²² at 298 K, according to $k = k_{\text{ex}} K_{\text{os}}$. For the more labile cation Ni(DMF)₅Cl⁺, the range expected for k is from $0.8 \times 10^5 \text{ s}^{-1}$ ($K_{\text{os}} = 0.15 \text{ M}^{-1}$) to $5 \times 10^5 \text{ s}^{-1}$ ($K_{\text{os}} = 1.0 \text{ M}^{-1}$).

Kinetics of Complex Formation: The Comparison of TMC with TEC and the Kinetic Effect of Chloride Ions.

The results obtained for the tetra-*N*-ethylated cyclam derivative TEC confirm the general experience¹ that (i) complex formation with N₄ macrocycles of the cyclam type takes place in two stages according to eq 1, and (ii) both stages can comprise several steps. First, TEC incorporates the nickel(II) cation 2.4 times faster than TMC (see data for k_1 in Table 3), which indicates a somewhat greater flexibility of TEC. Second, in contrast to complex formation with TMC, the slow, first-order isomerization of the intermediate Ni(TEC)_{int}²⁺ is biphasic. The similarity in kinetic behavior and absorption spectra (see Table S17) suggests that, as in the case of TMC,^{1,15a} the configuration of the intermediate Ni(TEC)_{int}²⁺ is trans-II and that of the product Ni(TEC)₂₊ (violet form) trans-I. The stereochemistry of the species formed in the first isomerization step (rate constant $k_{2a} = 437 \times 10^{-4} \text{ s}^{-1}$) is not known.

Depending on the estimated size of K_{os} (see above), second-order rate constants $k_1 = 99 \text{ M}^{-1} \text{ s}^{-1}$ and $k_1 = 235 \text{ M}^{-1} \text{ s}^{-1}$ for nickel incorporation with TMC and TEC, respectively, are approximately 1 order of magnitude smaller than expected for complex formation with monodentate ligands according to the Eigen–Wilkins mechanism. In line with earlier work,^{1,15} it is reasonable to assume for both TMC and TEC that the rate constant k_1 describes the rate-controlling formation of the second Ni–N bond according to eqs 12–14 with $k_1 = K_{\text{os}} K k_{\text{int}}$ ($\text{M} = \text{Ni}^{2+}$, $\text{S} = \text{DMF}$, and $\text{L} = \text{TMC}$ or TEC). In the species MS₅–L the tetradentate ligand L is singly bonded.



The monochloro species Ni(DMF)₅Cl⁺ is more than 100-fold more labile (see Table 1) and hence more reactive than the cation Ni(DMF)₆²⁺. When the macrocyclic ligand L is exposed to a mixture of Ni(DMF)₅Cl⁺ and Ni(DMF)₆²⁺, as generated by

(20) The rate constant $k_{\text{obsd},1}$ for the initial incorporation step increases linearly with [Cl[−]]_o (see ref 18). In the case of bromide, admixed in the concentration range 0.0001–0.18 M, the slope of the plot of $k_{\text{obsd},1}$ vs [Br[−]]_o is approximately 0.5 instead of 1.0.

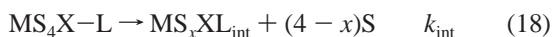
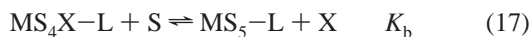
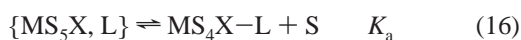
(21) The initial increase of $k_{\text{obsd},1}$ with [TBACl]_o is approximately linear. Computer fitting of the data obtained for $k_{\text{obsd},1}$ in the range [TBACl]_o = 1×10^{-4} M to [TBACl]_o = 2×10^{-2} M leads to a slope of $m = 1.1 \pm 0.1$.

(22) One can estimate, on the basis of theoretically deduced expressions (see ref 3), that $K_{\text{os}} = 0.15 \text{ M}^{-1}$ for a divalent cation such as Ni²⁺ interacting with an uncharged species in water. In organic solvents, K_{os} can be on the order of approximately 1 M^{-1} (see ref 23).

(23) Wilkins, R. G. *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*; Allyn & Bacon: Boston, MA, 1974; p 183.

chloride ions according to the equilibrium in eq 10, it will therefore react preferentially with the cation $\text{Ni}(\text{DMF})_5\text{Cl}^+$. Again, it is found that second-order rate constants $k_1 = 23 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (TMC) and $k_1 = 11 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (TEC) for the incorporation step in the presence of chloride are approximately 1 order of magnitude smaller than expected for the reaction of the monochloro species $\text{Ni}(\text{DMF})_5\text{Cl}^+$ with monodentate ligands according to the Eigen–Wilkins mechanism. From the mechanistic point of view, it is therefore reasonable to assume that, in the case of $\text{Ni}(\text{DMF})_5\text{Cl}^+$ instead of $\text{Ni}(\text{DMF})_6^{2+}$, the reaction sequence in eqs 12–14 applies analogously with $\text{MS}_x\text{LCl}_{\text{int}}$ being the intermediate formed in reaction 14.

As a matter of fact, the rate constants $k_{\text{obsd},1}$ plotted in Figure 3 were obtained by fitting the absorbance/time data to eq 7a with $z = [\text{ligand}]_o/[\text{Ni}(\text{DMF})_5\text{Cl}^+]_o$. This means that the variation of $[\text{Ni}(\text{DMF})_5\text{Cl}^+]_o$ with $[\text{TBACl}]_o$ was taken into account for the determination of $k_{\text{obsd},1}$. The approximately linear increase of $k_{\text{obsd},1}$ with $[\text{TBACl}]_o$ (see Figure 3) indicates the participation of a chloride-dependent equilibrium. As shown in the reaction sequence in eqs 15–18 ($\text{M} = \text{Ni}^{2+}$, $\text{S} = \text{DMF}$, $\text{X} = \text{Cl}^-$, and $\text{L} = \text{TMC}$ or TEC), we suggest that the species $\text{MS}_4\text{X}-\text{L}$ with singly bonded L is subject to dissociation according to eq 17.



Second-order rate constant k_1 would thus also depend on the size of K_{b} according to $k_1 = K_{\text{os}}K_{\text{a}}K_{\text{b}}k_{\text{int}}$. The reaction sequence in eqs 15–18 postulates that the rate-controlling formation of the second Ni–N bond occurs with the species $\text{MS}_4\text{X}-\text{L}$, the concentration of which is affected by chloride ions according to the equilibrium in eq 17. At adequate excess concentrations of chloride, this equilibrium is shifted to the left, and the dependence of $k_{\text{obsd},1}$ on $[\text{TBACl}]_o$ arrives at saturation (see Figure 3).

The sum of the experimental data confirms for both ligands that both the intermediate formed in the first, fast stage of the reaction and the final product contain chloride bound to the nickel.

To our knowledge, there are no reports so far on the kinetic effect of coordinating anions or other ligands on complex formation reactions of transition metals with macrocyclic N-donor or S-donor ligands in nonaqueous media. Wu and Kaden studied the kinetics of complexation reactions of nickel(II)^{24a} and copper(II)^{24b} with cyclam in the presence of additional ligands in aqueous solution. They found that the rate of the reaction of the partially complexed, hydrated metal species NiX^z and CuX^z with monoprotonated cyclam increases by a factor of ap-

proximately 10 upon going from $z = +2$ ($\text{X} = \text{water}$) to $z = +1$ ($\text{X} = \text{acetate}$), 0 ($\text{X} = \text{oxalate}$), and -1 ($\text{X} = \text{tricarallylate}$). This rate enhancement was explained on electrostatic grounds. For the series of nickel species $\text{NiX}^{2+} = \text{Ni}(\text{H}_2\text{O})_6^{2+}$, $\text{Ni}(\text{H}_2\text{O})_5\text{-NH}_3^{2+}$, $\text{Ni}(\text{H}_2\text{O})_4\text{en}^{2+}$, and $\text{Ni}(\text{H}_2\text{O})_3\text{dien}^{2+}$, the change in complexation rate with cyclam was found to be quite minimal. The authors correlated the reactivity of MX^z toward monoprotonated cyclam with the thermodynamic stability of MX^z . In comparison with the dipolar aprotic solvent DMF, though, the medium water is very different, in that protonation of the macrocyclic ligand occurs, a fact that complicates the comparison of data.

Conclusions

The formation of complexes of nickel(II) with tetra-*N*-ethylated cyclam (TEC) in DMF follows the general reaction pattern observed for cyclam and other cyclam derivatives, in that fast, second-order nickel incorporation leads to an intermediate with full N_4 coordination, which rearranges slowly to form a thermodynamically more stable nickel TEC complex. The formation of the intermediate with TEC and also its two-step rearrangement are somewhat faster than in the case of tetra-*N*-methylated cyclam (TMC) studied earlier. Mechanistically, formation of the second Ni–N bond controls the rate of intermediate formation. The results obtained suggest that the complex formed, $\text{Ni}(\text{TEC})^{2+}$, has the trans-I configuration.

Compared to that of the fully solvated cation $\text{Ni}(\text{DMF})_6^{2+}$, solvent exchange of the DMF molecules coordinated in the monochloro nickel(II) species $\text{Ni}(\text{DMF})_5\text{Cl}^+$ is more than 100-fold faster at 298 K. The ¹³C NMR data obtained are in line with the interpretation that the rate of DMF exchange is the same for equatorially and axially coordinated DMF in the cation $\text{Ni}(\text{DMF})_5\text{Cl}^+$.

The reactions of $\text{Ni}(\text{DMF})_5\text{Cl}^+$ with TMC and TEC lead to the macrocyclic chloro complexes $\text{Ni}(\text{TMC})\text{Cl}^+$ and $\text{Ni}(\text{TEC})\text{-Cl}^+$, respectively. For both TMC and TEC, the rate of intermediate formation with $\text{Ni}(\text{DMF})_5\text{Cl}^+$ is considerably higher than that with $\text{Ni}(\text{DMF})_6^{2+}$. The rate enhancement by factors of 230 (TMC) and 47 (TEC) is on the order of the increased lability of coordinated DMF in $\text{Ni}(\text{DMF})_5\text{Cl}^+$ compared to $\text{Ni}(\text{DMF})_6^{2+}$. Mechanistically, formation of the second Ni–N bond controls the rate of intermediate formation with the species $\text{Ni}(\text{DMF})_5\text{Cl}^+$.

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Supporting Information Available: Material concerning solvent exchange: calculation of equilibrium constant, Tables S1 and S2, equations used for treatment of ¹³C NMR relaxation and chemical shift data with fitting results, Figure S1 and Tables S3–S10. Material concerning the kinetics of complex formation and spectroscopic data: Tables S11–S17. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(24) (a) Wu, Y.; Kaden, T. A. *Helv. Chim. Acta* **1984**, *67*, 1868. (b) Wu, Y.; Kaden, T. A. *Helv. Chim. Acta* **1985**, *68*, 1611.