

## Steric Effects on the Rates of Redox Reactions Involving Nickel(II/III) Macrocycles

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Several isomers of (5,12-dimethylcyclam)nickel(II) (cyclam = 1,4,8,11-tetraazacyclotetradecane) and one of the 5,12-diethyl macrocycle complex with nickel have been isolated. Characterization using  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy and comparison with a known crystal structure provide details of the conformations of the complexes. In the case of  $\alpha$ -[Ni( $M_m$ )] $^{2+}$  and [Ni( $E_m$ )] $^{2+}$  derived from the meso forms of the dimethyl and diethyl ligands, equatorial disposition of the substituent groups renders the nickel(II) center readily available for solvation. In the case of  $\beta$ -[Ni( $M_m$ )] $^{2+}$ , axial configurations of the methyl groups are indicated. Intermediate dispositions are found for a complex formed from the racemic form. Significant differences in solvation equilibria, redox potentials, and self-exchange rate constants ( $k_{11}$ ) of the Ni(II/III) macrocycle couples are observed. For the  $\alpha$ -[Ni( $M_m$ )] $^{3+/2+}$  couple,  $k_{11} = (8 \pm 1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  while, for  $\beta$ -[Ni( $M_m$ )] $^{3+/2+}$ ,  $k_{11} = 26 \pm 5 \text{ M}^{-1} \text{ s}^{-1}$ . Comparison with other nickel macrocycles indicates that, in the electron-transfer process, the inner-sphere reorganizational energy requirements lie in the range 90–100 kJ mol $^{-1}$  for octahedral species, [Ni(MAC)(OH) $_2$ ] $^{2+}$  and [Ni([9]aneN $_3$ )] $^{2+}$ , whereas for less solvated or axially crowded centers, the value is much larger, leading to lower self-exchange rates.

## Introduction

Although the ability of tetraaza macrocycles to stabilize trivalent nickel complexes has been well documented, $^{1-3}$  little work has been carried out on the effects of the stereochemistry of the macrocyclic ligands on electron-transfer reactions. Busch $^4$  has demonstrated the importance of ring size, ligand unsaturation, and substituent groups on the electrochemical behavior of these species in nonaqueous (principally acetonitrile) media. Differences in kinetic and thermodynamic stability of two isomers of (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)-nickel(III) in aqueous sulfate and perchlorate solutions have been reported by Meyerstein. $^5$  In the present study, we describe the preparation of several isomers of (5,12-dialkylcyclam)nickel(II) (cyclam = 1,4,8,11-tetraazacyclotetradecane). Differences in kinetic stability are observed between the trivalent *C-meso* and *C-rac* isomers. It is evident that the stereochemistry of the ligand contributes in an important way to the electron-transfer processes of the macrocyclic nickel complexes. Comparable work on the hexamethyl-substituted complexes is hindered (vide infra) first by the large numbers of isomers theoretically possible (10) in both the *C-rac* and *C-meso* series and second by the presence of two *gem*-dimethyl groups that contribute further to the steric effects.

The ligands under study are shown in Figure 1. Interconversion of conformation by nitrogen inversion was precluded by the maintenance of acid concentrations of  $[\text{H}^+] = 0.5 \text{ M}$ . It is shown that both the redox potentials and the electron self-exchange rates are sensitive to substituent orientation and ring conformation. Attempts have been made to rationalize this behavior in terms of axial steric interactions in the nickel complexes.

## Experimental Section

**Caution!** Perchloric acid and its salts are used in many of the syntheses described below. Care should be exercised in their handling and use.

**Preparation of Compounds.** All chemicals used were reagent grade except where otherwise stated. Nickel(II) perchlorate hexahydrate was obtained from G. F. Smith, and all organic starting materials were obtained from the Aldrich Chemical Co.

**(I) *C-meso* ( $M_m$ ) and *C-rac* ( $M_r$ ) Isomers of 5,12-Dimethylcyclam.** These isomers (Figure 1) were prepared by the sodium borohydride reduction $^6$  of 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate (1), which was prepared by the reaction $^7$  of methyl

vinyl ketone with 1,2-diaminoethane monohydroperchlorate in methanol at  $-5^\circ\text{C}$ . A 30-g (0.08-mol) sample of 1 was then suspended in  $\sim 30$  mL of methanol at  $40^\circ\text{C}$ , and reduction to the saturated macrocycle was achieved by slow addition of 15 g (0.44 mol) of sodium borohydride to the reaction mixture with continuous stirring. After addition of the  $\text{NaBH}_4$  (1 h), the methanol was removed under vacuum and the residue dissolved in 500 mL of 2 M sodium hydroxide. The aqueous solution was then extracted with  $\sim 400$  mL of chloroform by means of a continuous liquid-liquid extractor. At this point, the organic solvent was removed and the residue (12 g) was recrystallized from  $\sim 250$  mL of hot xylene. When the mixture was cooled in the refrigerator overnight, feathery white crystals (3 g) of the *C-meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane were obtained.

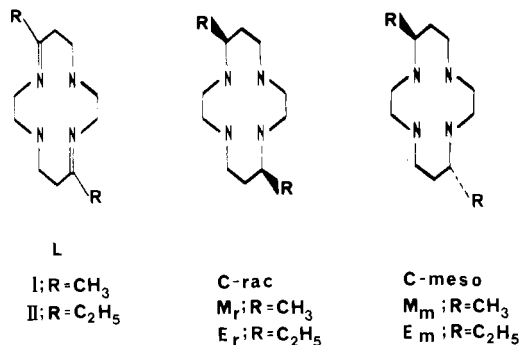
The filtrate volume was then reduced to  $\sim 150$  mL and the filtrate cooled to  $0^\circ\text{C}$  (12 h), whereupon a second crop (3 g) of feathery white crystals were obtained and removed by filtration. The two fractions were combined and recrystallized from a minimum of boiling xylene, collected on a glass frit, washed with a few milliliters of ice-cold xylene followed by diethyl ether, and finally dried in vacuo overnight. The white solid (mp  $136$ – $138^\circ\text{C}$  (lit. $^7$  mp  $144.5$ – $145.0^\circ\text{C}$ ) (Despite several recrystallizations a melting point of  $136$ – $138^\circ\text{C}$  was obtained, calibrated by using benzoic acid and benzil.);  $M^+$  228) was soluble in methanol but fairly insoluble in diethyl ether. The *C-rac* isomer was recovered from the filtrate above by removing all the xylene under vacuum and resuspending the residue in 200 mL of boiling diethyl ether on a steam bath. The cloudy suspension was then filtered while hot through a Whatman 1PS phase-separation paper and the filtrate allowed to cool in an ice bath for 6 h. A light powdery precipitate was obtained, which was filtered and dried under vacuum. The product (yield 4 g; mp  $106$ – $110^\circ\text{C}$ ;  $M^+$  228) was the *C-rac* isomer as characterized by Kolinski. $^7$

**(II) *C-meso* ( $E_m$ ) and *C-rac* ( $E_r$ ) Isomers of 5,12-Diethylcyclam.** A procedure similar to that used for the dimethyl isomes was used. 5,12-Diethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate (2) was synthesized by a modification of the method of Hay and Piplani. $^8$

To a solution of 7.2 g (0.12 mol) of 1,2-diaminoethane in 180 mL of anhydrous methanol was added dropwise with stirring 10.6 mL of 70%  $\text{HClO}_4$ . The mixture was maintained in a salt-ice bath and under a slow stream of nitrogen for the entire reaction, the internal temperature being maintained between  $-5$  and  $0^\circ\text{C}$ . After addition of the perchloric acid, the dropping funnel was washed with 20 mL of anhydrous methanol and then recharged with a solution of 10 g of ethyl vinyl ketone (0.12 mol) in 70 mL of anhydrous methanol (care should be exercised in handling this ketone as it has an extremely pungent odor and is a strong lachrymator). The ethyl vinyl ketone was added dropwise to the reaction mixture over a 1-h period. Stirring was continued, and after about 2 h, a copious white precipitate of the product appeared; this was filtered, washed with methanol and then diethyl ether, and finally dried under vacuum (yield 5 g (18%); mp  $114$ – $116^\circ\text{C}$ ; IR  $\nu(\text{NH}_2)$  3200 (br),  $\nu(\text{C}=\text{N})$  1660 (s),  $\nu(\text{ClO}_4^-)$  1100 (s), 630 (s)). The saturated macrocycles were obtained by the gradual addition of 2 g of sodium borohydride to a suspension of 5 g of the diene dihydroperchlorate in 100 mL of methanol at  $40^\circ\text{C}$ . After addition of the  $\text{NaBH}_4$  (1 h), the methanolic solution was reduced to dryness and redissolved in  $\sim 200$  mL of hot water. A 20-g sample of sodium hydroxide dissolved in 50 mL of  $\text{H}_2\text{O}$

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**Figure 1.** 5,12-Dialkyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienes and their reduction products.

was added, and on cooling, a white powdery precipitate was obtained. The product was collected and recrystallized from xylene (yield 700 mg; mp 137–139 °C;  $M^+$  256). By analogy to the behavior of both *C-meso*-5,12-dimethylcyclam and *C-meso*-5,7,7,12,14,14-hexamethylcyclam (tet *a*)<sup>9</sup> with respect to solubility, melting point, and other properties, this product was assigned a *C-meso* configuration, *C-meso*-5,12-diethyl-1,4,8,11-tetraazacyclotetradecane ( $E_m$ ). The *C-rac* diastereomer was obtained by extraction of the aqueous alkaline filtrate with 300 mL of chloroform by means of a continuous extractor for a 24-h period. The solvent was removed subsequently and the product recrystallized from 50 mL of xylene to yield a further 300 mg of the  $E_m$  isomer (mp 137–139 °C). The xylene was removed and the residue dissolved in 70 mL of boiling diethyl ether. Following filtration through a phase-separation paper and overnight cooling, a product of white needle crystals was obtained (yield 0.4 g; mp 104–110 °C;  $M^+$  256). Again, by analogy to other *C-rac* isomers of substituted cyclams, this compound was considered to be the *C-rac* isomer of 5,12-diethyl-1,4,8,11-tetraazacyclotetradecane ( $E_r$ ).

**(III) Nickel(II) Complexes of *C-meso*-5,12-Dimethylcyclam ( $M_m$ ).**  
**(a) [ $\alpha$ ]-*C-meso*-[Ni(5,12-Me<sub>2</sub>cyclam)](ClO<sub>4</sub>)<sub>2</sub> ( $\alpha$ -[Ni( $M_m$ )](ClO<sub>4</sub>)<sub>2</sub>).** A 1-g (4.3-mmol) sample of pure *C-meso* ligand was dissolved in 50 mL of methanol (1:1). To this was added a solution of 1.4 g (4 mmol) of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in 15 mL of methanol. The solution was heated on a steam bath for 45 min and then acidified to pH ~1 with dropwise addition of 3 M HClO<sub>4</sub>. On cooling, red crystals of the  $\alpha$  isomer formed. These were collected, washed with propan-2-ol and diethyl ether, and finally dried under vacuum. A further crop may be obtained by reducing the filtrate volume to ~20 mL and refrigerating for several days.

**(b) [ $\delta$ ]-*C-meso*-[Ni(5,12-Me<sub>2</sub>cyclam)](ClO<sub>4</sub>)<sub>2</sub> ( $\delta$ -[Ni( $M_m$ )](ClO<sub>4</sub>)<sub>2</sub>).** The filtrate obtained from the second crop of the  $\alpha$  isomer was reduced to dryness and the resulting solid redissolved in 30 mL of boiling propan-2-ol (containing 1 mL of 3 M HClO<sub>4</sub>). The solution was filtered, and on cooling, light yellow needles of the  $\delta$  isomer were obtained. These were filtered, washed with diethyl ether, and dried under vacuum.

**(c) [ $\beta$ ]-*C-meso*-[Ni(5,12-Me<sub>2</sub>cyclam)](ClO<sub>4</sub>)<sub>2</sub> ( $\beta$ -[Ni( $M_m$ )](ClO<sub>4</sub>)<sub>2</sub>).** The filtrate from the above reaction was reduced to dryness and redissolved in a minimum of hot ethanol-water (1:1). A few drops of concentrated HClO<sub>4</sub> were added, and when the reaction mixture was allowed to stand for several days at room temperature, small yellow prisms of the  $\beta$  isomer formed, which were collected by filtration.

**(IV) A Nickel(II) Complex of *C-meso*-5,12-Diethylcyclam: [Ni( $E_m$ )](ClO<sub>4</sub>)<sub>2</sub>.** A mixture of 700 mg of NiClO<sub>4</sub>·6H<sub>2</sub>O (2 mmol) and 500 mg (2 mmol) of the ligand  $E_m$  was dissolved in 30 mL of methanol. The solution was heated on a steam bath for 10 min and filtered while hot, and the filtrate was allowed to cool in an ice bath for 2 h after the addition of 1 mL of 3 M HClO<sub>4</sub>. A light orange precipitate of the product was obtained. No attempt was made to isolate other isomers from the filtrate.

**(V) A Nickel(II) Complex of *C-rac*-5,12-Dimethylcyclam ( $M_r$ ): [Ni( $M_r$ )](ClO<sub>4</sub>)<sub>2</sub>.** A 500-mg sample of the free ligand ( $M_r$ ) was dissolved in ~30 mL of methanol, and to this solution was added 700 mg of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O dissolved in 20 mL of methanol. The solution was heated for 30 min on the steam bath, after which it was filtered and allowed to cool following addition of 3–4 drops of concentrated HClO<sub>4</sub>. When the reaction mixture was left overnight in the refrigerator, golden orange flakes of the product were precipitated. The crude product was redissolved in ~15 mL of 10<sup>-2</sup> M HClO<sub>4</sub> and loaded onto a C-25 Sephadex column (2 × 20 cm, pre-equilibrated with 10<sup>-2</sup> M HClO<sub>4</sub>). The column was then eluted with an aqueous solution 0.3 M in sodium per-

**Table I.** <sup>1</sup>H or <sup>13</sup>C NMR Spectra of Ni(II) Complexes in CD<sub>3</sub>NO<sub>2</sub><sup>a</sup>

compd	$\delta(^1\text{H})$ (J, Hz)	$\delta(^{13}\text{C})^b$
$\alpha$ -[Ni( $M_m$ )] <sup>2+</sup>	1.23 (5.27)	23.11, 36.05, 48.23, 48.62, 50.40, 55.32
$\beta$ -[Ni( $M_m$ )] <sup>2+</sup>	1.74 (6.85)	16.26, 33.71, 44.33, 48.78, 51.11, 52.84
$\delta$ -[Ni( $M_m$ )] <sup>2+</sup>	1.12 (8.32)	19.05, 36.20, 49.17, 49.65, 52.31, 55.52
[Ni( $M_r$ )] <sup>2+</sup>	1.75 (6.52), 1.19 (6.07)	16.33, 19.55, 33.72, 35.83, 44.51, 49.35, 49.99, 50.07, 51.22, 52.36, 53.03, 56.78
[Ni( $E_m$ )] <sup>2+</sup>	0.94 (7.0), <sup>c</sup> 112 (7.0) <sup>c</sup>	9.04, 9.22, 25.14, 30.14, 32.73, 45.71, 48.61, 50.45

<sup>a</sup> Chemical shifts relative to Me<sub>4</sub>Si; solvent identified at  $\delta$  4.33 for <sup>1</sup>H NMR and  $\delta$  63.79 for <sup>13</sup>C NMR. <sup>b</sup> See Figure 3. <sup>c</sup> Ethyl triplets.

chlorate containing 10<sup>-2</sup> M HClO<sub>4</sub>. Three bands were discernible: a rapidly moving bright yellow band followed by a much less intense light orange fraction and very faint, very slowly moving brown band, visible 2 cm from the origin as the first band was eluting. The fastest moving yellow band was collected and after several recrystallizations from slightly acidic propan-2-ol, a crop of light orange crystals was obtained. This product was considered an isomer of [Ni( $M_r$ )](ClO<sub>4</sub>)<sub>2</sub>.

C, H, and N analyses of all compounds were found to be satisfactory and were carried out by Canadian Microanalytical Services, Vancouver, B.C.

**Characterization of Metal Complexes.** UV/visible spectra were recorded on a Beckman DU-8 instrument. Equilibrium studies were performed by using a Pye-Unicam SP1800 fitted with a circulating-water thermostat ( $T = 25 \pm 0.2$  °C). Infrared spectra were run as KBr disks on a Perkin-Elmer 283 spectrophotometer. Electrochemical measurements were made under a stream of nitrogen on a PAR Model 370 cyclic voltammetry apparatus using aqueous sodium perchlorate ( $I = 1.0$  M,  $[H^+] = 0.5$  M (HClO<sub>4</sub>)) as supporting electrolyte and a saturated calomel electrode (+0.245 V vs. NHE) as reference electrode with two platinum wires as working and sensing electrodes.

Kinetic measurements were made at 25 °C with a stopped-flow spectrometer described previously.<sup>10</sup> Aqueous solutions ( $I = 1.0$  M (NaClO<sub>4</sub>),  $[H^+] = 0.5$  M (HClO<sub>4</sub>)) were used throughout. Data points (500) were collected and processed by an IBM PC microcomputer interfaced to the spectrophotometer via a Techmar Incorporated PC-Mate Lab Master module. First-order reactions were linear to more than 3 half-lives.

<sup>13</sup>C and <sup>1</sup>H NMR spectra were run in proton-decoupled FT mode on a Bruker WM-250 instrument in 10-mm tubes. Deuterated nitromethane was used as solvent with external Me<sub>4</sub>Si as reference for both proton and carbon-13 NMR spectra.

Melting points were determined in a Buchi SMP-20 apparatus running parallel calibrant samples of benzoin (mp 132–134 °C) and benzil (mp 94–95 °C). Mass spectra were run on a Finnigan GC/MS 3300 by using electron-impact techniques.

## Results

**(a) NMR Studies.** As is seen from Figure 1, reduction of the 5,12-dialkyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienes (I and II) yields two isomers of the 5,12-dialkylcyclams. On complexation of the reduced species with a metal ion, the secondary nitrogen centers become optically active and several isomeric forms may result. Hay<sup>6</sup> has pointed out that in the *C-meso* series there are six *N-rac* and four *N-meso* forms, while in the *C-rac* isomers ten *N-rac* forms are possible. Ligand L may thus give rise to a maximum of 20 diastereoisomers of the square-planar nickel(II) complex of a 5,12-dialkylcyclam. Kolinski<sup>7,11</sup> has isolated four forms of the nickel(II) species of the *C-meso* series of the dimethyl ligand. These he defined as  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  isomers. They exhibit differences in both chelate ring conformation and nitrogen configuration. <sup>1</sup>H NMR spectroscopy has been applied successfully to elucidate the stereochemistry of methyl substituents on the macrocyclic rings in similar systems.<sup>12,13</sup> Expected resonances

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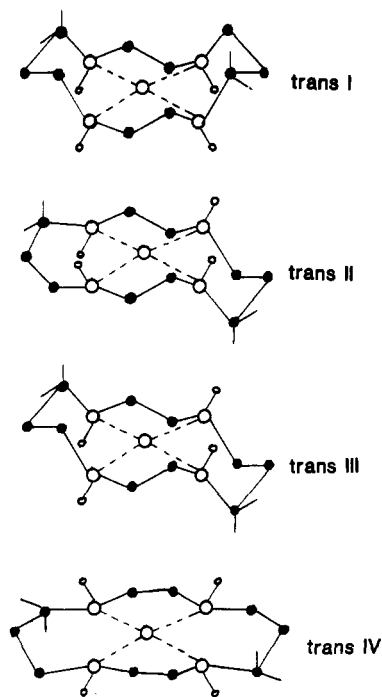


Figure 2. Thermodynamically favored macrocyclic ring conformations from ref 15.

for equatorial methyl groups are  $\delta \sim 1.3$  and those for axial substituents  $\delta \sim 1.7$ .

Studies on the three species isolated from the reaction of nickel(II) perchlorate with *C-meso*-5,12-Me<sub>2</sub>cyclam ( $\alpha$ -[Ni(M<sub>m</sub>)]<sup>2+</sup>,  $\beta$ -[Ni(M<sub>m</sub>)]<sup>2+</sup>, and  $\delta$ -[Ni(M<sub>m</sub>)]<sup>2+</sup>) (Table I) demonstrate that the  $\alpha$  isomer exhibits only equatorial methyl resonances, as does the  $\delta$  isomer, while the  $\beta$ -[Ni(M<sub>m</sub>)]<sup>2+</sup> methyl groups are axially disposed. The crystal structure of the  $\beta$  isomer has been determined by Krajewski et al.<sup>14</sup>

In the case of the single racemic isomer studied ([Ni(M<sub>r</sub>)]<sup>2+</sup>), axial and equatorial doublets of equal intensity were found, as might be expected for a *C-rac* complex with the same chelate ring conformation as the  $\beta$ -[Ni(M<sub>m</sub>)]<sup>2+</sup> isomer. The <sup>1</sup>H NMR spectrum of the *C-meso*-5,12-Et<sub>2</sub>cyclam exhibited the expected spectrum with two triplets, assigned to the CH<sub>3</sub> moiety of the ethyl groups at  $\delta$  0.94 and 1.12 ( $J = 7$  Hz in both cases). The associated quartets were found at  $\delta$  3–4 but were difficult to assign since they were obscured by proton resonances from the chelate rings. No similar Et<sub>2</sub>cyclam complexes have been prepared, and assignment to axial or equatorial positions was not pursued. However, after consideration of both the electrochemical and chemical behavior of [Ni(E<sub>m</sub>)]<sup>2+</sup> (vide infra), the ethyl groups were considered to be in equatorial configurations.

Correlations may also be made between solid-state conformation and that in solution. Paramagnetic NMR studies<sup>15</sup> have shown that in solution nickel(II) macrocycles take up the thermodynamically preferred *trans*-III conformation<sup>16</sup> (see Figure 2) if a facile kinetic path exists for the molecule to adopt the preferred structure. Energy barriers to conformational change are high, and there is consequently no rapid interconformational change if such reactions are inhibited kinetically. We have observed that under conditions of  $>0.2$  M H<sup>+</sup> in solution, nitrogen conversion, which is facile at pH  $\sim 10$ , is prevented completely.

<sup>13</sup>C NMR spectroscopy provides further information as to the conformations of the various species studied in solution. The results are presented in Table I, and some of the spectra obtained are shown in Figure 3. <sup>13</sup>C NMR has proved to be useful in assigning chelate ring conformations<sup>17,18</sup> and has been employed

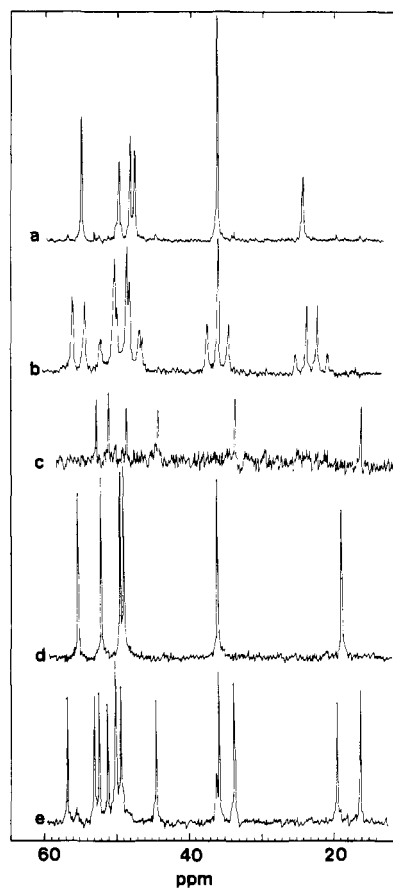


Figure 3. <sup>13</sup>C NMR spectra of Ni macrocyclic complexes: (a)  $\alpha$ -[Ni(M<sub>m</sub>)]<sup>2+</sup>; (b)  $\alpha$ -[Ni(M<sub>m</sub>)]<sup>2+</sup> (off resonance); (c)  $\beta$ -[Ni(M<sub>m</sub>)]<sup>2+</sup>; (d)  $\delta$ -[Ni(M<sub>m</sub>)]<sup>2+</sup>; (e) [Ni(M<sub>r</sub>)]<sup>2+</sup>.

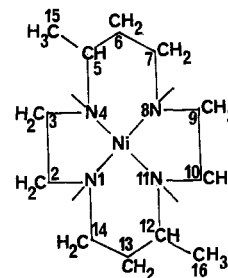
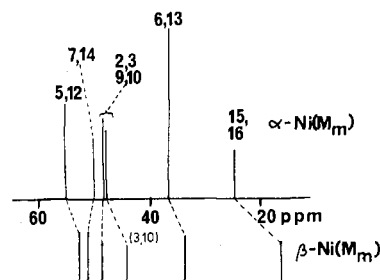


Figure 4. <sup>13</sup>C NMR assignments for  $\alpha$ -[Ni(M<sub>m</sub>)]<sup>2+</sup> and  $\beta$ -[Ni(M<sub>m</sub>)]<sup>2+</sup>.

successfully in elucidation of related nickel(II) macrocyclic complexes.<sup>19</sup>

Assignments of resonances for  $\alpha$ -[Ni(M<sub>m</sub>)]<sup>2+</sup> are shown in Figure 4. This has been aided by consideration of the <sup>13</sup>C NMR spectra of [Ni(M<sub>m</sub>)]<sup>2+</sup> (Figure 3a,b) in both proton-decoupled and off-resonance modes and by comparison with standard

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spectra.<sup>20</sup> The resonance(s) at about  $\delta$  20 are attributable to the methyl groups in the  $\text{Me}_2\text{cyclam}$  complexes. From comparison with  $^1\text{H}$  NMR data it is seen that  $^{13}\text{C}$  resonances of axial methyl groups in these compounds occur at  $\delta \sim 16$  while those of equatorial methyl groups are seen at  $\delta \sim 23$ . This is in good agreement with studies made on methyl-substituted cyclohexanes,<sup>21</sup> where differences in resonance position between axial and equatorial methyl groups are of the order of  $\delta$  5–10, the axial resonance being upfield relative to the equatorial. The  $^{13}\text{C}$  spectra support the assignment of two equatorial methyl substituents to the  $\alpha$ - $[\text{Ni}(\text{M}_m)]^{2+}$  isomer and two axial substituents to  $\beta$ - $[\text{Ni}(\text{M}_m)]^{2+}$ . Furthermore, data suggest that in the case of the substituents in the  $\delta$ - $[\text{Ni}(\text{M}_m)]^{2+}$  isomer, the groups are intermediate between axial and equatorial. This is also the case for one of the substituents in the  $[\text{Ni}(\text{M}_R)]^{2+}$  complex.

The fact that  $\alpha$ - $[\text{Ni}(\text{M}_m)]^{2+}$  is formed from all other  $[\text{Ni}(\text{M}_m)]^{2+}$  complexes under kinetically controlled conditions (in basic media) suggests that it is the thermodynamically preferred conformation with the least steric interactions, i.e. the *trans*-III conformation<sup>16</sup> with equatorial methyl groups. It is known that the  $\beta$ - $[\text{Ni}(\text{M}_m)]^{2+}$  isomer also has this ring conformation but differs in having axial substituents. In view of the similarity of their structures, the differences in their  $^{13}\text{C}$  NMR spectra (Figure 3a,c and Figure 4) seem unexpectedly great. However, when intramolecular interactions are considered, the positional changes seem rational. Changing from equatorial to axial substituents clearly alters the resonances of C15 and C16 as has already been shown. In turn, this will affect directly the resonance positions of C5 and C12, as is shown in Figure 4. In addition, models show changes in interaction between the methyl groups and C6, C13, C3, and C10 atoms in going from equatorial to axial substituents (chair conformations (*trans*-III structure) of the six-membered chelate rings). These differences in interaction are manifested in the spectra as an upfield shift in the resonances of these carbon atoms. Atoms C7, C14, C2, and C9 are spatially most remote from the substituents on the ring and show the least effect when equatorial groups are replaced by axial. Indeed C9 and C2 show practically no change in chemical shift on going from  $\alpha$ - $[\text{Ni}(\text{M}_m)]^{2+}$  to  $\beta$ - $[\text{Ni}(\text{M}_m)]^{2+}$ .

For the  $\alpha$ -,  $\beta$ -, and  $\delta$ - $[\text{Ni}(\text{M}_m)]^{2+}$  complexes, only six carbon resonances are observable, indicating at least a  $C_2$  axis of symmetry in these isomers. Figure 2 shows the thermodynamically favored ring conformations of macrocyclic ligands of this type. The *trans*-II structure is excluded as one feasible conformer of  $\delta$ - $[\text{Ni}(\text{M}_m)]^{2+}$  since it lacks the necessary symmetry properties, leaving the *trans*-I and *trans*-IV conformations as possible structures for this isomer. Another isomer,  $\gamma$ - $[\text{Ni}(\text{M}_m)]^{2+}$ , has already been described<sup>6,11</sup> as having the *trans*-I structure (the  $\gamma$  isomer was not isolated in this work), so that the *trans*-IV structure is likely for  $\delta$ - $[\text{Ni}(\text{M}_m)]^{2+}$ .

The *trans*-IV structure has the symmetry required by the  $^{13}\text{C}$  NMR results. Models also show that the methyl substituents in this conformation would lie between the axial and equatorial positions as is indicated by the resonance at  $\delta$  19.05 in the spectrum of the  $\delta$ - $[\text{Ni}(\text{M}_m)]^{2+}$  isomer. The  $^{13}\text{C}$  NMR spectrum of the  $[\text{Ni}(\text{M}_r)]^{2+}$  isomer shows 12 resonances, as would be expected for the 12 non-symmetry-related carbon atoms in the molecule. Furthermore, the spectrum approximates to the summation of the spectra for both the  $\alpha$ - and  $\beta$ - $[\text{Ni}(\text{M}_r)]^{2+}$  isomers, indicating the presence of the two types of six-membered chelate ring found in these two compounds, i.e. chair ring conformations, one with an axial substituent and one with an equatorial substituent. Again, models show that the equatorial substituent is slightly displaced from the equatorial plane, in agreement with the observed  $^{13}\text{C}$  and  $^1\text{H}$  NMR data.

From similarities with the  $\alpha$ - $[\text{Ni}(\text{M}_m)]^{2+}$  isomer in both redox and solution equilibrium studies, a *trans*-III structure with equatorial substituents was proposed for the  $[\text{Ni}(\text{E}_m)]^{2+}$  complex.

**Table II.** Description of Ring Conformations of (5,12-Dialkylcyclam)nickel(II) Complexes

compd	substituent <sup>a</sup>	ring conform <sup>b</sup>	confgn (1,4,8,11)
$\alpha$ - $[\text{Ni}(\text{M}_m)]^{2+}$	eq, eq	<i>trans</i> -III	S,S,R,R
$\beta$ - $[\text{Ni}(\text{M}_m)]^{2+}$	ax, ax	<i>trans</i> -III	S,S,R,R
$\delta$ - $[\text{Ni}(\text{M}_m)]^{2+}$	int, int	<i>trans</i> -IV	S,R,R,S
$[\text{Ni}(\text{M}_r)]^{2+}$	int, ax	<i>trans</i> -III	S,S,R,R
$[\text{Ni}(\text{E}_m)]^{2+}$	eq, eq	<i>trans</i> -III	S,S,R,R

<sup>a</sup>Abbreviations: eq, equatorial; ax, axial; int, intermediate. <sup>b</sup>See Figure 2.

**Table III.** Spectroscopic, Equilibrium, and Redox Properties of (5,12-Dialkylcyclam)nickel(II/III) Complexes

compd	$\lambda_{\text{max}}(\text{Ni(II)})$ ( $\epsilon$ ) <sup>a</sup>	$K_{\text{eq}}^b$	$\lambda_{\text{max}}(\text{Ni(III)})$ ( $\epsilon$ ) <sup>c</sup>	$E^\circ$ <sup>d</sup>
$\alpha$	460 (65)	0.4 ( $\pm 0.1$ )	637 (84)	995
$\beta$	455	<0.05	580	1155
$\delta$	451 (81)	<0.05	599 (84)	1145
<i>rac</i>	457 (70)	0.2 ( $\pm 0.1$ )	616 (140)	1115
$\text{Et}_2$	468 (47)	0.7 ( $\pm 0.1$ )	640 (72)	990

<sup>a</sup>In  $\text{CH}_3\text{NO}_2$ . Units:  $\lambda_{\text{max}}$ , nm;  $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ . <sup>b</sup>For square planar  $\rightleftharpoons$  octahedral in 0.5 M  $\text{HClO}_4$ . <sup>c</sup>In  $\text{CH}_3\text{CN}$ , with  $\text{NO}^+$  as oxidant. Units:  $\lambda_{\text{max}}$ , nm;  $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ . <sup>d</sup>In 0.5 M  $\text{HClO}_4$  vs.  $[\text{Ni}(\text{9}]\text{aneN}_3)_2]^{2+/3+}$  ( $E^\circ = 947$  mV). Units: mV.

The  $^{13}\text{C}$  NMR spectrum is reported in Table I, but no attempt has been made to assign the carbon resonances. Studies are under way to determine the crystal structure.

(b) **UV/Visible Spectra, Equilibrium Studies, and Electrochemistry.** Details of solution spectra for the square-planar nickel(II) species in  $\text{CH}_3\text{NO}_2$  are shown in Table III. All show the expected  $^1\text{B}_{1g} \leftarrow ^1\text{A}_{1g}$  transition expected for square-planar nickel(II) complexes at about  $22\,500\text{ cm}^{-1}$  ( $450\text{ nm}$ ) with extinction coefficients typically of about  $60\text{--}70\text{ M}^{-1}\text{cm}^{-1}$ . Dissolution in aqueous media demonstrates that a square-planar  $\rightleftharpoons$  octahedral equilibrium exists, presumably with solvent water ligating at the two axial sites in the octahedral coordination sphere. This is accompanied by a marked decrease in the absorbance at  $\sim 450\text{ nm}$ . An approximate determination of the square-planar  $\rightleftharpoons$  octahedral equilibrium constant ( $K_e$ ) for the various isomers studied in this work may be made by monitoring the change in extinction coefficient with temperature in 0.5 M  $\text{HClO}_4$ . The results obtained are given in Table III. Not surprisingly, the  $\alpha$ - $[\text{Ni}(\text{M}_m)]^{2+}$  isomer with unhindered axial sites is about 30% octahedral ( $K_e \sim 0.4$ ), in good agreement with the value of 0.39 obtained by Fabbrizzi and co-workers<sup>22</sup> for the parent compound  $[\text{Ni}(\text{cyclam})]^{2+}$ . Two more recent studies<sup>23,24</sup> on the same  $[\text{Ni}(\text{cyclam})]^{2+}$  system using magnetic and NMR techniques have verified the value obtained spectrophotometrically, a method that is sometimes subject to error owing to absorption band overlap. It should be noted that the  $[\text{Ni}(\text{E}_m)]^{2+}$  isomer shows a  $K_e$  of magnitude similar to that of the  $\alpha$ - $[\text{Ni}(\text{M}_m)]^{2+}$  compound, and it is on this evidence, along with the similarity of its Ni(III) and Ni(II) spectra and Ni(II/III) redox potential, that it has been assigned the same conformation as the  $\alpha$ - $[\text{Ni}(\text{M}_m)]^{2+}$  isomer. Only the  $\beta$  and  $\delta$  isomers of  $[\text{Ni}(\text{M}_m)]^{2+}$  show a substantial tendency to square-planar geometry in aqueous solution. In the case of the  $\beta$  isomer, steric hindrance to axial addition is anticipated. The origin of the effect in the  $\delta$  isomer is more obscure. The  $\delta$  and  $\alpha$  isomers have very similar geometry, the main difference being in nitrogen configuration (*SRRS* and *SSRR* respectively). Large kinetic effects have been noted for substitution reactions on cobalt(III) macrocycles differing only in nitrogen configuration.<sup>25</sup> It has been suggested<sup>26</sup> that, in the formation of reaction intermediates, the ability of the

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**Table IV.** Rate Constants for the Reaction of  $[\text{Ni}(\text{MAC})]^{3+}$  with  $[\text{Ni}(\text{[9]aneN}_3)_2]^{2+}$  and the Derived Values of Self-Exchange Rate Constants for  $[\text{Ni}(\text{MAC})]^{3+/2+}$ 

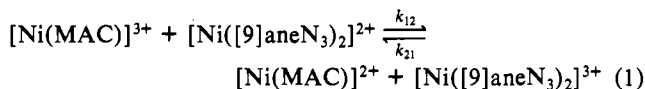
compd	$k_{12}$ (forward) <sup>a</sup>	$\Delta E$ , mV <sup>b</sup>	$k_{11}$ , M <sup>-1</sup> s <sup>-1</sup>
$\alpha$	$1.74 \times 10^4$	+48	$(8 \pm 1) \times 10^3$
$\beta$	$(8.9 \pm 1.5) \times 10^3$	+208	$6 \pm 2$
$\delta$	$1.55 \times 10^4$	+198	$26 \pm 5$
<i>rac</i>	$2.2 \times 10^4$	+168	$200 \pm 45$
Et <sub>2</sub>	$2.9 \times 10^4$ ( $(4.0 \pm 1.0) \times 10^3$ ) <sup>d</sup>	+43	$(2.5 \pm 0.1) \times 10^4$ $((1.4 \pm 0.8) \times 10^4)$ <sup>c</sup>

<sup>a</sup>Error on rate constant  $\pm 5\%$ . <sup>b</sup>Relative to  $[\text{Ni}(\text{[9]aneN}_3)_2]^{2+}$ .  
<sup>c</sup>Determined from the back-reaction (eq 1),  $k_{21}$ . <sup>d</sup> $k_{21}$  (eq 1).

macrocycle to fold is an important criterion in determining the reaction rate; such a process is affected by nitrogen configuration. Similar effects may well play a role during electron-transfer reactions of these nickel macrocycles.

The d-d spectra of the oxidation products of the isomers (obtained in  $\text{CH}_3\text{CN}$  via  $\text{NO}^+$  oxidation) show  $\lambda_{\text{max}}$  and extinction coefficients typical of those found for other nickel(III) complexes.<sup>1</sup> A significant variation is observed in redox potentials (see Table III) of the compounds, all of which show the quasi-reversible behavior typical of many nickel(II/III) macrocyclic couples. A relationship is noted between the energy of the d-d transition observed for compounds in this series and the magnitude of the redox couple. A plot of the energy of the d-d transition ( $10^3 \text{ cm}^{-1}$ ) against  $E^\circ$  (in  $\text{kJ mol}^{-1}$ ) yields a straight line of slope 0.076 (correlation 0.980). Similar correlations have been noted by Busch<sup>27</sup> for anionic macrocyclic nickel complexes.

**(c) Redox Kinetics and Electron-Self-Exchange Reactions.** The nickel(III) complexes were sufficiently stable with respect to redox decomposition that kinetic studies were undertaken to derive the electron-self-exchange rates for the nickel(II/III) couples. The nickel(III) macrocyclic complexes  $[\text{Ni}(\text{MAC})]^{3+}$  were reacted with bis(1,4,7-triazacyclononane)nickel(II) ( $[\text{Ni}(\text{[9]aneN}_3)_2]^{2+}$ ) according to the reaction in eq 1.



Redox reactions of the  $[\text{Ni}(\text{[9]aneN}_3)_2]^{2+}$  complex have recently been extensively studied.<sup>28-30</sup> These processes are exclusively outer sphere ( $E^\circ = 947 \text{ mV}$  (vs. NHE)), with self-exchange rate  $k_{22} = 6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . The nickel(III) macrocycles were generated in situ by oxidation using  $\text{Co}^{3+}(\text{aq})$ .<sup>10</sup> Redox reactions were monitored by following the absorbance decrease at 403 nm. In some cases, similarities in  $E^\circ$  rendered reaction 1 reversible, and reaction concentrations were chosen such that both nickel(II) complexes  $[\text{Ni}(\text{MAC})]^{2+}$  and  $[\text{Ni}(\text{[9]aneN}_3)_2]^{2+}$  were present in at least 10-fold excess to ensure pseudo-first-order conditions for the forward and reverse reactions. In the case of  $\beta$ - $[\text{Ni}(\text{M}_m)]^{3+}$  no back-reaction was observed. Excellent linearity of  $\ln(\text{OD}_t - \text{OD}_\infty)$  vs. time plots was exhibited to at least 4 half-lives. Rate constants for the forward reactions,  $k_{12}$ , are presented in Table IV.

## Discussion

Previous studies in these laboratories<sup>31</sup> and those by Endicott<sup>32</sup> have shown that, in nickel(II) complexes where there are negligible

axial interactions, similar intrinsic barriers to outer-sphere electron transfer are involved, with self-exchange rates  $\sim 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . The present work confirms these findings. From the cross-reactions, the Marcus theory<sup>33,34</sup> has been used to estimate self-exchange rates for the complexes. In a recent modification of the theory,<sup>34</sup>  $k_{12}$  is related to the individual self-exchange rates  $k_{11}$  and  $k_{22}$  and the equilibrium constant  $k_{12}$  by the expression

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \quad (2)$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (W_{12} - W_{21})/RT]^2}{4 \left[ \ln \left( \frac{k_{11}k_{22}}{A_{11}A_{22}} \right) + \frac{W_{11} + W_{22}}{RT} \right]} \quad (3)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \quad (4)$$

In these expressions,  $w_{ij}$  is the work required to bring ions  $i$  and  $j$  (charges  $Z_i$  and  $Z_j$ ) to a separation distance  $\sigma_{ij}$  (the sum of the ionic radii). A value of  $A/\sigma^2$  of  $3 \times 10^{10} \text{ M}^{-1} \text{ \AA}^{-2} \text{ s}^{-1}$  was used.

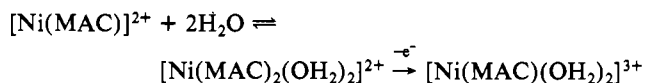
Under conditions of excess of the Ni(II) complexes (eq 1), the observed first-order rate constant may be expressed in the form

$$k_{\text{obsd}} = k_f[[\text{Ni}(\text{[9]aneN}_3)_2]^{2+}] + k_b[[\text{Ni}(\text{MAC})]^{2+}]$$

At constant  $[[\text{Ni}(\text{MAC})]^{2+}]$ , plots of  $k_{\text{obsd}}$  against  $[[\text{Ni}(\text{[9]aneN}_3)_2]^{2+}]$  should exhibit linear constant slopes, the intercepts being a linear function of  $[[\text{Ni}(\text{MAC})]^{2+}]$ . From such data both  $k_f$  and  $k_b$  may be derived. Good plots were obtained, and forward rate constants are presented in Table IV. For the  $\beta$ - $[\text{Ni}(\text{M}_m)]^{2+}$  and the *C-rac* isomers,  $k_b$  was zero within experimental error.

Although the rates for the cross-reactions are fairly similar, there is a remarkable spread in the calculated self-exchange rates. For the equatorially substituted dimethyl and diethyl complexes,  $k_{11}$  is similar to that derived for other Ni(III/II) couples.<sup>31,32,34</sup> In the case of the  $\delta$  isomer, however, the self-exchange rate is  $\sim 10^3$  lower.

Similarly for the racemic species, which again displays axial coordination, a relatively low exchange rate constant is obtained. Clearly either axial interactions or solvation effects (or both) are important in the electron-transfer process. In the case of  $[\text{Ni}(\text{[9]ane}_2)]^{3+/2+}$  ( $E^\circ = 947 \text{ mV}$ ,  $k_{11} = 6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ) and  $[\text{Ni}(\text{[10]ane}_2)]^{3+/2+}$  ( $E^\circ = 965 \text{ mV}$ ,  $k_{11} = 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>35</sup> both of which react unambiguously as outer-sphere systems, the electron-transfer-reaction parameters provide an indication of those that might be expected for other octahedral  $\rightarrow$  octahedral systems. For other complexes, the rates are influenced to a large extent by changes in the primary coordination sphere and solvation shells. Where the species involved exhibit similar geometrical arrangements and charges, the nature of the reorganizational energies could be expected to be of the same order of magnitude. Comparison of the data for these couples with those for  $[\text{Ni}(\text{cyclam})]^{3+/2+}$  ( $E^\circ = 1000 \text{ mV}$ ,  $k_{11} = 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>31</sup> and  $\alpha$ - $[\text{Ni}(\text{M}_m)]^{3+/2+}$  ( $E^\circ = 995 \text{ mV}$ ,  $k_{11} = 8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ) suggests that, for these complexes and the corresponding diethylcyclam species ( $E^\circ = 990 \text{ mV}$ ,  $k_{11} = 2.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ), the electron transfer occurs via an octahedral Ni(II) complex  $[\text{Ni}(\text{MAC})(\text{OH}_2)_2]^{2+}$ :



The low-spin  $d^7$  product is known to be octahedral.<sup>1,3</sup> Such reasoning is further substantiated by the fact that some acid-stable nickel(II) species (e.g.  $[\text{Ni}(\text{[8]aneN}_2)_2]^{2+}$ ,<sup>36,37</sup> and  $[\text{Ni}(\text{[N-Me]}_4\text{cyclam})]^{2+}$ )<sup>38</sup> do not readily undergo oxidation to Ni(III).

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**Table V.** Calculated Values of the Outer- and Inner-Shell Reorganizational Barriers

Ni(II) complex	approx radius, Å	$\lambda_0$ , kJ mol <sup>-1</sup>	$k_{22}$ , M <sup>-1</sup> s <sup>-1</sup>	$\lambda_i$ , kJ mol <sup>-1</sup>
Et <sub>2</sub> cyclam	4.0	94.5	$2.5 \times 10^4$	63.3
$\alpha$ - <i>meso</i> -Me <sub>2</sub> cyclam	3.8	97.0	$7.5 \times 10^3$	66.8
cyclam	3.6	100.0	$1.0 \times 10^3$	73.8
<i>rac</i> -Me <sub>2</sub> cyclam	3.8	97.0	155	86.8
tet <i>c</i>	3.8	97.0	31	94.0
$\delta$ - <i>meso</i> -Me <sub>2</sub> cyclam	3.8	97.0	26	94.8
$\beta$ - <i>meso</i> -Me <sub>2</sub> cyclam	3.8	97.0	6	102.0
tet <i>a</i>	3.8	97.0	2	107.6

In fact, the geometry of the former ion may have CH<sub>2</sub> groups of the eight-membered ring blocking the axial sites in the complex.

Assuming the requirement of an easily formed octahedral species in solution for facile outer-sphere electron transfer, some consideration must be given to the nickel(III) species. The X-ray crystal data available for hexacoordinate ions show that, upon electron transfer, there is a shortening of the axial metal-ligand bonds. The data for [Ni(cyclam)Cl<sub>2</sub>]<sup>+0</sup> show a decrease on oxidation of about 0.04 Å,<sup>39,40</sup> while the change is comparable to that observed in initial investigations of the [Ni([9]aneN<sub>3</sub>)<sub>2</sub>]<sup>2+/3+</sup> couple.<sup>41,42</sup> In view of the slightly shortened axial bond in the nickel(III) complexes, it might be expected that axial interactions might be more pronounced in nickel(III) species than in nickel(II) complexes. Changes in d-d spectra (and hence ligand field) are observed for the series of compounds, indicating that the differing geometries suggested in the nickel(II) species are retained in the nickel(III) ions.

In terms of the Marcus theory, such steric effects should contribute to the intrinsic reorganizational energy term  $\lambda$ , where

$$\lambda = \lambda_i + \lambda_0 = 2(\Delta G^*_{11} + \Delta G^*_{22}) \quad (5)$$

$\lambda_0$ , the solvent-shell reorganization energy, may be calculated from<sup>43</sup>

$$\lambda_0 = e^2(1/2r_1 + 1/2r_2 - 1/r_{12})(1/D_0 - 1/D) \quad (6)$$

where  $r_1$  and  $r_2$  are the solvated radii of the two reacting species,  $r_{12}$  is the separation distance (taken to be  $r_1 + r_2$ ),  $D_0$  is the optical dielectric constant (square of the refractive index), and  $D$  has its usual value of 78.5 for water. In aqueous solution the nickel(II) complexes all have a radius of 3.6–4 Å, yielding  $\lambda_0 = 95$ –100 kJ mol<sup>-1</sup>. This value should be fairly typical for the series of com-

pounds studied. The overall value of  $\lambda$  can be determined from eq 5. Estimates may be made of  $\lambda_i$ , the energy changes involved in reorganization of the primary coordination sphere. Calculation for the species [Ni([9]aneN<sub>3</sub>)<sub>2</sub>]<sup>2+/3+</sup>, [Ni([10]aneN<sub>3</sub>)<sub>2</sub>]<sup>2+/3+</sup>, [Ni(cyclam)]<sup>2+/3+</sup>,  $\alpha$ -[Ni(M<sub>m</sub>)]<sup>2+/3+</sup>, and [Ni(E<sub>m</sub>)]<sup>2+/3+</sup> show  $\lambda$  to be in the range 160–200 kJ mol<sup>-1</sup>, leading to  $\lambda_i \sim 63$ –102 kJ mol<sup>-1</sup> (Table V). This implies that similar energy changes are involved in the inner coordination sphere for this series where axial coordination is relatively unhindered. For compounds where axial substituent effects have been indicated such as  $\beta$ -[Ni(M<sub>m</sub>)],  $\delta$ -[Ni(M<sub>m</sub>)], and nickel isomers of hexamethylcyclam<sup>44</sup> (tet *a*, tet *b*, tet *c*, and tet *d*), all of which have self-exchange rate constants of  $50 (\pm 30) \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>32,45</sup> the values of  $\lambda_i$  are significantly greater. The requirements for reorganization of the bulkier methyl groups, which present a barrier for solvation, may contribute significantly in this regard. It is of interest that similar features are observed in the increased  $E^\circ$  values for these complexes.

The present results are consistent with two distinct trends that depend on both axial steric interactions and a facile square-planar–octahedral equilibration of the nickel(II) species<sup>24</sup> in solution. Compounds with little or no axial steric hindrance have similar intrinsic energy terms for reorganization in the primary coordination sphere and fairly large ( $\sim 10^3$ – $10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) electron-self-exchange rate constants. A second series has also been identified in which axial addition is hindered, with substantial reorganizational energy requirements in the primary coordination sphere upon electron transfer, leading to significantly lower electron-self-exchange rates.

Detailed kinetic investigations correlating structure with electron-exchange parameters for a wide variety of nickel complexes are currently under way in this laboratory. It appears steric effects and ring geometry play an important role in the electron-transfer reactions of nickel(II/III) couples.

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**Registry No.** E<sub>m</sub>, 96866-25-0; E<sub>r</sub>, 96947-06-7;  $\alpha$ -[Ni(M<sub>m</sub>)](ClO<sub>4</sub>)<sub>2</sub>, 96947-08-9;  $\alpha$ -[Ni(M<sub>m</sub>)]<sup>3+</sup>, 96947-11-4;  $\alpha$ -[Ni(M<sub>m</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, 96866-29-4;  $\beta$ -[Ni(M<sub>m</sub>)](ClO<sub>4</sub>)<sub>2</sub>, 26371-25-5;  $\beta$ -[Ni(M<sub>m</sub>)]<sup>3+</sup>, 96947-12-5;  $\beta$ -[Ni(M<sub>m</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, 96947-14-7;  $\delta$ -[Ni(M<sub>m</sub>)](ClO<sub>4</sub>)<sub>2</sub>, 96996-76-8;  $\delta$ -[Ni(M<sub>m</sub>)]<sup>3+</sup>, 96996-77-9;  $\delta$ -[Ni(M<sub>m</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, 96996-78-0; [Ni(M<sub>r</sub>)](ClO<sub>4</sub>)<sub>2</sub>, 96947-10-3; [Ni(M<sub>r</sub>)]<sup>3+</sup>, 96947-13-6; [Ni(M<sub>r</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, 96947-15-8; [Ni(E<sub>m</sub>)](ClO<sub>4</sub>)<sub>2</sub>, 96866-27-2; [Ni(E<sub>m</sub>)]<sup>3+</sup>, 96866-28-3; [Ni(E<sub>m</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, 96866-30-7; Ni<sup>II</sup>cyclam, 46365-93-9; Ni<sup>II</sup>tet *c*, 57427-10-8; Ni<sup>II</sup>tet *a*, 47105-35-1; [Ni([9]aneN<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>, 59034-11-6; 5,12-diethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate, 60920-26-5; 1,2-diaminoethane, 107-15-3; ethyl vinyl ketone, 1629-58-9.

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