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Studies on Nickel(II) Complexes of Cyclam Ligands Containing Functionalized Nitrogen Substituents: Synthesis, Isomerization, and N-Dealkylation[1]

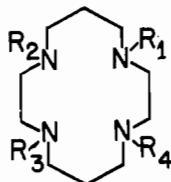GARY M. FREEMAN, E. KENT BAREFIELD,* and DONALD G. VAN DERVEER

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Two isomeric forms (α, β) of the nickel(II) complexes of the ligands 1,4,8,11-tetrakis(2-cyanoethyl)-1,4,8,11-tetraazacyclotetradecane (E) and 1,4,8,11-tetrakis(2-carbamoylethyl)-1,4,8,11-tetraazacyclotetradecane (F) have been isolated. In each case the kinetic product obtained by combination of nickel salt with the free ligand (α isomer) was converted to the second isomer (β form) by heating in the appropriate solvent (acetonitrile for [Ni(E)]$^{2+}$; water for [Ni(F)]$^{2+}$). A structure determination on α-trans-[Ni(E)(NCS)$_2$] ($P2_1/c$, $a = 10.526$ (2) Å, $b = 13.719$ (4) Å, $c = 20.625$ (3) Å, $\beta = 107.05$ (1)°, $\rho_{\text{calcd}} = 1.370$ g cm^{-3} for $Z = 4$ and $M_r = 587.46$, $R = 0.057$, $R_w = 0.055$) indicates that it has the trans-I stereochemistry. Structure determinations on β-trans-[Ni(E)(NCCH$_3$)$_2$](ClO$_4$)$_2$·H$_2$O ($P2_1/n$, $a = 12.726$ (7) Å, $b = 11.712$ (6) Å, $c = 11.182$ (6) Å, $\beta = 95.40$ (4)°, $\rho_{\text{calcd}} = 1.542$ g cm^{-3} for $Z = 2$ and $M_r = 770.32$, $R = 0.070$, $R_w = 0.074$) and β-[Ni(F)](ClO$_4$)$_2$·CH$_3$NO$_2$ ($P2_1/n$, $a = 16.798$ (2) Å, $b = 11.588$ (3) Å, $c = 17.882$ (4) Å, $\beta = 91.84$ (1)°, $\rho_{\text{calcd}} = 1.533$ g cm^{-3} for $Z = 4$ and $M_r = 803.30$, $R = 0.066$, $R_w = 0.066$) show that both complexes have the trans-III stereochemistry. Heating α- or β-[Ni(E)]$^{2+}$ in water for 18 h resulted in formation of a complex of 1,8-bis(2-carbamoylethyl)-4-(2-cyanoethyl)-1,4,8,11-tetraazacyclotetradecane (G) isolated in 35–50% yield. The X-ray structure of [Ni(G)](ClO$_4$)$_2$ (*Pna2*$_1$, $a = 16.454$ (9) Å, $b = 16.730$ (6) Å, $c = 10.338$ (4) Å, $\rho_{\text{calcd}} = 1.524$ g cm^{-3} for $Z = 4$ and $M_r = 653.16$, $R = 0.067$, $R_w = 0.073$) shows it to contain a six-coordinate nickel ion with the two amide oxygen atoms coordinated in cis positions as a result of folding of the macrocycle along the 1,8-direction. Other products resulting from hydrolysis and/or dealkylation (of cyanoethyl but not carbamoylethyl groups) were also isolated. The kinetic product obtained from complexation of Ni(II) by 1,4-bis(2-carbamoylethyl)-8,11-dimethyl-1,4,8,11-tetraazacyclotetradecane also isomerized upon heating in water.
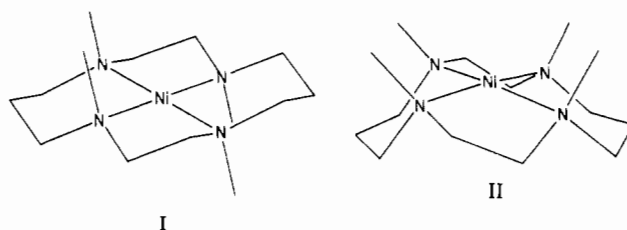
Introduction

Macrocyclic ligands that contain tertiary nitrogen donors represent a relatively unstudied class of metal complexing agent. On the basis of the limited information that is currently available, it appears that the conversion of secondary amines to tertiary amines in a macrocyclic ligand decreases its effective ligand field strength.[2] As a result, the redox and spectral properties of a metal complex can be "tuned" over a considerable range by varying the number of tertiary nitrogen donors. This has been demonstrated for a series of ligands derived from A.[2–4] In addition, the effective ligand field strengths of such

ligands, the kinetic stabilities of their complexes, and even the preferred coordination numbers of these complexes are dependent upon the relative stereochemistries of the tertiary donors.[2,8–11]

Of the five possible stereoisomers that can exist for a planar complex of a ligand such as A, the thermodynamically most stable form should have structure I (trans-III according to


I   II

Bosnich et al.[12]), in which the five-membered and six-membered rings adopt their most stable conformations.[13] All metal

A: R = H (cyclam)
B: R$_2$ = R$_3$ = CH$_3$, R$_1$ = R$_4$ = H
C: R$_1$ = R$_2$ = R$_3$ = CH$_3$, R$_4$ = H
D: R = CH$_3$ (tetramethylcyclam)
E: R = CH$_2$CH$_2$C≡N
F: R = CH$_2$CH$_2$C(O)NH$_2$
G: R$_1$ = R$_3$ = CH$_2$CH$_2$C(O)NH$_2$, R$_2$ = CH$_2$CH$_2$C≡N, R$_4$ = H
H: R$_1$ = R$_3$ = CH$_2$CH$_2$C(O)NH$_2$, R$_2$ = R$_4$ = H
I: R$_1$ = CH$_2$CH$_2$C(O)NH$_2$, R$_2$ = R$_3$ = CH$_2$CH$_2$C≡N, R$_4$ = H
J: R$_1$ = R$_2$ = R$_3$ = CH$_2$CH$_2$C≡N, R$_4$ = H
K: R$_2$ = R$_3$ = CH$_3$, R$_1$ = R$_4$ = CH$_2$CH$_2$C(O)NH$_2$

(1) Presented in part at the 34th Southeastern Regional Meeting of the American Chemical Society, Birmingham, AL, Nov 3–5, 1982, Abstract No. 258. A preliminary account of a portion of this work has appeared: Barefield, E. K.; Freeman, G. M.; Van Derveer, D. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1358.
(2) Wagner, F.; Barefield, E. K. *Inorg. Chem.* **1976**, *15*, 408.
(3) Barefield, E. K.; Wagner, F.; Hodges, K. D. *Inorg. Chem.* **1976**, *15*, 1370. More efficient syntheses of the partially alkylated complexes are given in this paper.
(4) Limited electrochemical data has been published. This includes reduction potentials for the nickel complex of A (III/II, 0.68 V; II/I, –1.70 V[5]) and the two isomers of the nickel complex of D (trans-III isomer: III/II, 1.23 V;[6] II/I, –1.35 V.[7] trans-I isomer: III/II, 1.22 V;[6] II/I, –1.18 V (Freeman, G. M. Ph.D. Thesis, Georgia Institute of Technology, 1983).). All data were obtained on 10^{-3} M acetonitrile solutions and are referenced to the 0.1 M Ag(I)/Ag electrode. A paper describing a complete electrochemical study of complexes of ligands A–D is in preparation.

(5) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.
(6) Deming, R. L.; Allred, A. L.; Dahl, A. R.; Herlinger, A. W. *J. Am. Chem. Soc.* **1976**, *98*, 4132.
(7) Becker, J. Y.; Kerr, J. B.; Pletcher, D.; Rosas, R. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *117*, 87.
(8) Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435.
(9) Buxtorf, R.; Steinmann, W.; Kaden, T. A. *Chimia* **1974**, *28*, 19. Buxtorf, R.; Kaden, T. A. *Helv. Chim. Acta* **1974**, *57*, 1035. Hertli, L.; Kaden, T. A. *Helv. Chim. Acta* **1974**, *57*, 1328.
(10) D'Aniello, M. J., Jr.; Mocella, M. T.; Wagner, F.; Barefield, E. K.; Paul, I. C. *J. Am. Chem. Soc.* **1975**, *97*, 192.
(11) Wagner, F.; Mocella, M. T.; D'Aniello, M. J., Jr.; Wang, A. H.-J.; Barefield, E. K. *J. Am. Chem. Soc.* **1974**, *96*, 2625.
(12) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.
(13) The five sets of nitrogen configurations for the planar array of nitrogen donors
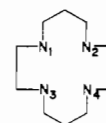
are as follows: (a) N$_{1,2}$$^+$, N$_{3,4}$$^-$; (b) N$_{1-4}$$^+$; (c) N$_{1,4}$$^-$, N$_{2,3}$$^+$; (d) N$_{1,3}$$^+$, N$_{2,4}$$^-$; (e) N$_{1-3}$$^+$, N$_4$$^-$. (a) and (b) correspond to structures I and II, respectively. Detailed analyses of stereochemical aspects of such systems are given by: Warner, L. G.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 4092. "Coordination Chemistry: Papers Presented in Honor of J. C. Bailar, Jr."; Plenum Press: New York, 1969. DeHayes, L. Ph.D. Thesis, The Ohio State University, 1972.

complexes of A in which the metal and nitrogen atoms are coplanar probably assume this structure upon equilibration in basic medium although there is no evidence that suggests that the four nitrogen donors have the same relative stereochemistry throughout the sequence of reactions that leads to complex formation. In fact, it is likely that nitrogen inversions take place via the conjugate base during metal complex formation.[14] However, when two or more tertiary nitrogen donors are present in A, their relative stereochemistry is fixed so long as they remain coordinated to the metal since the conjugate base pathway for inversion is no longer available.[15] Consequently, the stereochemistry of the tertiary donors in the complex will be determined, at least initially, by their relative configurations at the time that the metal–nitrogen bonds are formed. The relative configurations of the tertiary nitrogens can be expected to depend on the conformation of the macrocyclic ligand and on the way that it changes as each metal–nitrogen bond is formed.

On the basis of the above considerations, it might be expected that the stereochemistry of a complex might be influenced by the number of tertiary donors present. Evidence that this is the case is shown by the fact that ligands B and C yield mixtures of two nickel complexes that have stereochemistries I and II[3] whereas D yields a single stereoisomer with stereochemistry II.[8,9] All other known metal complexes of D appear to also have this stereochemistry[16] (trans-I according to Bosnich et al.[12]). A complex of D with structure I can be prepared from [Ni(A)]$^{2+}$ by a sequence of deprotonation-methylation reactions.[2,11]

Since relatively few examples of ligands that contain tertiary nitrogen donors have been prepared, little information is available concerning the effect of the nature of the nitrogen substituents on the stereochemistry of metal complexes prepared from them. Because of this we were very interested in Wainwright's report of the nickel complexes of E and F.[20] Although no structural information was obtained, the chemical properties of [Ni(E)]$^{2+}$ suggested that it might have structure II, whereas the information reported for the complex of F did not seem to be consistent with such a structure even though the complex was prepared by hydrolysis of [Ni(E)]$^{2+}$. We decided to undertake structural investigations on these complexes to determine their stereochemistry. During the course of our attempts to obtain crystals of [Ni(E)](ClO$_4$)$_2$ we found that a second isomer could be obtained whose stereochemistry is that shown by structure I. This was a very surprising result since the two forms of the complex of D were believed at the time to be noninterconvertible. However, after the studies described in this paper were completed, Moore and co-workers reported that the two forms of the nickel(II) complex of D could be equilibrated under certain conditions.[21] Their results

are complementary to those described here and will be considered further in the Discussion. We have also found that the complex reported to be [Ni(F)](ClO$_4$)$_2$ is actually [Ni(G)](ClO$_4$)$_2$, which results from partial hydrolysis and dealkylation of [Ni(E)]$^{2+}$, but that authentic material can be obtained from the reaction of preformed F with nickel salts. In fact, two isomeric complexes of F were ultimately prepared from reactions of preformed F, and one of these was shown to have structure I by an X-ray structure determination. Finally, the preparation of the nickel complex of K was undertaken to determine whether a difunctionalized ligand was also capable of forming more than one stereoisomer in analogy with ligands E and F.

Experimental Section

All chemicals obtained from commercial sources were reagent grade and were used without further purification. Cyclam (ligand A) and 1,4-dimethylcyclam (ligand B) were prepared by the literature procedures.[3,22] Analytical, infrared, and electronic spectral and ^{1}H NMR data for ligands and complexes are given in Tables I, II, and III, respectively, which are available as supplementary material. Details of acquisition of these data are also given as supplementary material.

1,4,8,11-Tetrakis(2-cyanoethyl)-1,4,8,11-tetraazacyclotetradecane (E). Ligand E was prepared according to Wainwright's procedure[20] except that the product was recrystallized from acetonitrile. One recrystallization from the minimum amount of hot acetonitrile resulted in somewhat lower yields (78% as compared to 94%) but gave cleaner product as indicated by the elemental analysis; mp 131–132 °C. Mass spectrum: m/e for parent ion 412 (calcd 412). TLC on silica gel using a water/pyridine/methanol/acetic acid solvent mixture (15:15:15:1 by volume, respectively) gave a single spot with R_f 0.74.

α-[Ni(E)](ClO$_4$)$_2$·H$_2$O. An acetonitrile solution of Ni(ClO$_4$)$_2$·6H$_2$O (1.77 g, 4.84 mmol in 10 mL) was added over 2–3 min to a continuously stirred acetonitrile solution of ligand E (2.0 g, 4.85 mmol in 50 mL). After the mixture was stirred overnight at room temperature, the deep green solution was gravity filtered and the volume reduced to ca. 20 mL by directing a flow of air over the surface. The green complex was precipitated by adding 100 mL of anhydrous ether to the continuously stirred solution over ca. 1 h. The finely divided, green product was collected, washed with fresh portions of anhydrous ether, and dried overnight in vacuo (0.01 torr, 100 °C); yield 3.3 g or 99%.

α-[Ni(E)Cl]Cl. A methanol solution of NiCl$_2$·6H$_2$O (0.5, g, 2.4 mmol in 10 mL) was added over 3–4 min to a continuously stirred acetonitrile solution of ligand E (1 g, 2.43 mmol in 25 mL). The solution was stirred for an additional 2 h whereupon the yellow-green product began to crystallize. Further crystallization was induced by evaporating the solution to near-dryness by directing a flow of air over the surface. The yellow-green product was collected, washed with absolute ethanol, and dried overnight in vacuo (0.01 torr, 100 °C); yield 1.1 g or 84%.

α-trans-[Ni(E)(NCS)$_2$]. α-[Ni(E)Cl]Cl (0.30 g, 0.55 mmol) was suspended in 50 mL of acetonitrile, and an acetonitrile solution of NaSCN (0.3 g, 3.7 mmol in 5 mL) was added over 1–2 min with continuous stirring. The mixture was stirred for 1 h and the resulting NaCl removed by gravity filtration. The blue filtrate was reduced to ca. 10 mL by directing a flow of air over the surface. After the mixture sat overnight, the blue crystalline product was collected, washed with portions of absolute ethanol, and dried at room temperature in vacuo (0.01 torr); yield 0.30 g or 92%. The same complex was also prepared by a similar procedure from α-[Ni(E)](ClO$_4$)$_2$·H$_2$O. Crystallographic quality crystals of this complex were grown by slow evaporation of an acetonitrile solution.

β-[Ni(E)](ClO$_4$)$_2$·2H$_2$O. A suspension of α-[Ni(E)](ClO$_4$)$_2$·H$_2$O (1.00 g, 1.45 mmol) in 80 mL of acetonitrile was heated at reflux for ca. 14 h. After it was cooled to room temperature, the resulting bluish green solution was gravity filtered. The filtrate was reduced to ca. 25 mL by directing a flow of air across its surface whereupon anhydrous ether was added with continuous stirring until a tacky oil formed. After the supernatant was decanted off, the product was triturated with several portions of anhydrous ether to yield a finely divided, green solid. This solid was collected, washed with additional

(14) This has been demonstrated for the formation of the Cu(II) complex of *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, a carbon-substituted form of A: Bauer, R. A.; Robinson, W. F.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1973**, 289.

(15) It has recently been demonstrated that there are also acid-catalyzed isomerization pathways for nitrogen inversion; i.e., the conversion of *cis*-[Ni(A)(OH$_2$)$_2$]$^{2+}$ to planar [Ni(A)]$^{2+}$ (trans-III stereochemistry) is acid catalyzed: Billo, E. J. *Inorg. Chem.* **1981**, *20*, 4019. Such a pathway is not expected to apply to N-alkylated examples.

(16) X-ray structures have been reported for [Zn(D)Cl]ClO$_4$,[17] [Fe(D)NO](BF$_4$)$_2$,[18] and *trans*-[Fe(D)(NO)(OH)]ClO$_4$·CH$_3$CN.[18]

(17) Alcock, N. W.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1978**, 1282.

(18) Hodges, K. D.; Wollman, R. G.; Kessel, S. L.; Hendrickson, D. N.; Van Derveer, D. G.; Barefield, E. K. *J. Am. Chem. Soc.* **1979**, *101*, 906.

(19) The structure of [N$_3$Ni(D)(μ-N$_3$)Ni(D)N$_3$]I is reported in ref 11. Structures of [Ni(D)](CF$_3$SO$_3$)$_2$ and *trans*-[Ni(D)(OH$_2$)$_2$]Cl$_2$·2H$_2$O, which both have the trans-III structure, have been determined and will be described in a later paper.

(20) Wainwright, K. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2117.

(21) Moore, P.; Sachinidis, J.; Willey, G. R. *J. Chem. Soc., Chem. Commun.* **1983**, 522.

(22) Barefield, E. K.; Wagner, F.; Herlinger, A. W.; Dahl, A. R. *Inorg. Synth.* **1976**, *16*, 220.

fresh ether, and dried overnight in vacuo (0.01 torr, 100 °C); yield 0.82 g or 80%.

β-*trans*-[Ni(E)(NCCH₃)₂](ClO₄)₂·H₂O. The preparation of this complex was analogous to that for β-[Ni(E)](ClO₄)₂·2H₂O except that the bluish green filtrate was reduced to ca. 10 mL under the air stream and the solution allowed to stand undisturbed overnight to allow for crystallization. Further crystallization of the violet product was induced by periodically adding small portions of acetone. The product was collected, washed with portions of absolute ethanol, and allowed to air-dry; yield 0.30 g or 27%. Crystallographic quality crystals were grown by dissolving β-[Ni(E)](ClO₄)₂·2H₂O in a minimal amount of acetonitrile and periodically adding small portions of acetone to the solution, which was kept in a stoppered flask.

β-*trans*-[Ni(E)(NCS)₂]·H₂O. β-[Ni(E)](ClO₄)₂·2H₂O (0.50 g, 0.71 mmol) was dissolved in 50 mL of acetonitrile and treated with an acetonitrile solution of NaSCN (0.4 g, 5 mmol in 5 mL) over 1–2 min. The mixture was stirred for 2 h and then gravity filtered. The product was obtained by reducing the filtrate volume to 10–15 mL with a stream of air and subsequently allowing the solution to stand undisturbed overnight. The light violet product was collected, washed with portions of methanol, and dried at room temperature in vacuo (0.01 torr); yield 0.25 g or 58%. The same complex was prepared from β-*trans*-[Ni(E)(NCCH₃)₂](ClO₄)₂·H₂O by a similar procedure.

1,4,8,11-Tetrakis(2-carbamoylethyl)-1,4,8,11-tetraazacyclotetradecane (F). Acrylamide (2.5 g, 35 mmol) was dissolved in 75 mL of methanol and the solution gravity filtered. Cyclam (1.00 g, 5 mmol) was added, and the solution was heated at reflux for 48 h. After this time a white, crystalline material had formed. The mixture was allowed to cool to room temperature and sit for several hours. The white crystals were then collected, washed with portions of absolute ethanol, and dried overnight in vacuo (0.01 torr, 100 °C): yield 2.2 g or 91%; mp 200–202 °C. Carbon-13 NMR (D₂O δ vs. Me₄Si): 177.7, 50.7, 49.8, 47.1, 32.5, and 20.3. TLC on silica gel using a water/pyridine/methanol/acetic acid solvent mixture (15:15:15:1 by volume, respectively) gave a single spot with R_f 0.55.

α-[Ni(F)](ClO₄)₂. Ligand F (1.60 g, 3.30 mmol) was dissolved in 50 mL of water at reflux and treated with an aqueous solution of Ni(ClO₄)₂·6H₂O (1.2 g, 3.3 mmol in 5 mL of water) over ca. 1 min. The mixture was heated at reflux for 2 min and then rapidly cooled to room temperature with use of an ice bath. The green solution was then gravity filtered and the filtrate evaporated to dryness under a stream of air. The resulting oily, green residue was redissolved in 25–30 mL of dry acetonitrile and gravity filtered. Anhydrous ether was then added with continuous stirring until a tacky oil formed. After the supernatant was decanted off, the product was triturated with several portions of anhydrous ether to yield a finely divided, blue-green solid. This solid was collected, washed with additional fresh ether, and dried overnight in vacuo (0.01 torr, 100 °C); yield 1.90 g or 78%.

α-[Ni(F)(NCS)₂]·⁵/₂H₂O. An aqueous solution of α-[Ni(F)](ClO₄)₂ (0.30 g, 0.40 mmol in 10 mL) was treated with NaSCN (0.5 g, 6 mmol). This mixture was stirred at room temperature for ca. 5 min and gravity filtered. The blue filtrate was then reduced to ca. 5 mL under a stream of air. The flask was stoppered and allowed to stand undisturbed overnight in a refrigerator. The light blue crystals that formed were collected, washed with portions of 2-propanol, and dried at room temperature in vacuo (0.01 torr); yield 0.15 g or 53%. Recrystallization of the product from an aqueous solution of NaSCN (0.4 g, 5 mmol in ca. 5 mL) was necessary to obtain satisfactory analyses. The light blue crystals were treated as described above: recovery 70%.

β-[Ni(F)](ClO₄)₂·CH₃NO₂. Ligand F (1.00 g, 2.06 mmol) was dissolved in 30 mL of hot water and treated with an aqueous solution of Ni(ClO₄)₂·6H₂O (0.75 g, 2.05 mmol in 5 mL) over 2–3 min. The mixture was heated at reflux for 1.5–2 h whereupon the solution color changed from deep green to blue. After this time, the solution was evaporated nearly to dryness on a rotary evaporator. The residue was dissolved in ca. 20 mL of methanol and gravity filtered. The filtrate was continuously stirred while portions of anhydrous ether were added until a tacky oil formed. The supernatant was decanted off and the product triturated with several portions of anhydrous ether to yield a finely divided, light blue solid. This solid was collected, washed with fresh portions of ether, and dried in vacuo (0.01 torr, 100 °C); yield of crude β-[Ni(F)](ClO₄)₂ 1.4 g or 92%. The product could be obtained as an analytically pure nitromethane solvate by recrystallization from hot nitromethane. Crystallographic quality crystals of the nitromethane solvate were obtained by slow evaporation of a

nitromethane solution at room temperature.

β-[Ni(F)(NCS)₂]·H₂O. An aqueous solution of β-[Ni(F)](ClO₄)₂ (0.50 g, 0.67 mmol in 15 mL) was treated with NaSCN (0.8 g, 10 mmol). The mixture was stirred at room temperature for 2–3 min and then gravity filtered. The filtrate was allowed to stand undisturbed for ca. 2 days, during which a violet solid formed. This solid was collected, washed with portions of 2-propanol, and dried at room temperature in vacuo (0.01 torr); yield 0.30 g or 66%.

[Ni(G)](ClO₄)₂. Ligand E (0.50 g, 1.2 mmol) and Ni(ClO₄)₂·6H₂O (0.44 g, 1.2 mmol) were added to 30 mL of water, and the mixture was heated at reflux for 18–20 h. The resulting mauve solution was cooled to room temperature, treated with 1.0 g (8.2 mmol) of NaClO₄, and extracted with 2 × 25 mL portions of nitromethane. The nitromethane extracts were combined and evaporated to dryness on a rotary evaporator. The solid residue was recrystallized from a hot, aqueous solution of NaClO₄ (0.5 g, 4 mmol in 15 mL). The purple-violet product was collected, washed with absolute ethanol, and dried at room temperature in vacuo (0.01 torr); yield 0.40 g or 51%. The same complex was prepared by Wainwright's procedure (38–46%),[20] and by heating of α-[Ni(E)](ClO₄)₂·H₂O (34%) or β-[Ni(E)](ClO₄)₂·2H₂O (36%) in water. This complex was recovered in 92% yield after heating an aqueous solution for 60 h at reflux. Crystallographic quality crystals of the complex were obtained by slow evaporation of an aqueous solution.

Generation of [Ni(G)]²⁺ from Free G. The ligand was isolated as an HCl salt by the following procedure. To a mixture of 1 g (1.53 mmol) of [Ni(G)](ClO₄)₂ in 20 mL of water was added with stirring 0.38 g (7.8 mmol) of sodium cyanide. After the mixture changed to a homogeneous orange solution, stirring was ceased and the solution allowed to stand for 0.5 h. Then 2 mL of concentrated hydrochloric acid was added over 3 min (*Caution!*). The opaque mixture that developed was stirred for 5 min and gravity filtered to remove a small amount of bluish solid. The water and excess HCl was then evaporated to leave a yellow oil. This oil was triturated in 50 mL of absolute ethanol for 2 h, which resulted in the formation of a white solid. This material was collected by filtration and dried (room temperature, 25 torr for 2 h); yield 0.65 g or 78% assuming that it is the tetrahydrochloride of G. [Ni(G)](ClO₄)₂ was regenerated from this material as follows. A solution of 0.2 g (0.38 mmol) of the above HCl salt in 5 mL of water was brought to pH 6 (pH paper) by the addition of 25% w/w aqueous sodium hydroxide. A solution of 0.14 g (0.38 mmol) of Ni(ClO₄)₂·6H₂O in 2 mL of water was added dropwise with stirring. The pH of the solution was then raised to 8 by the addition of 0.1 M sodium hydroxide. The small amount of nickel hydroxide that formed was removed by gravity filtration. To the lavender filtrate was added 0.5 g of sodium perchlorate, and the mixture was extracted with 2 × 20 mL portions of nitromethane. The combined extracts were dried with sodium sulfate and evaporated to dryness, at room temperature, on a rotary evaporator; yield of crude product 0.18 g or 74%. This material was recrystallized from water by addition of concentrated sodium perchlorate. The material had visible and IR spectra identical with those of a sample obtained from the hydrolysis of [Ni(E)](ClO₄)₂.

Hydrolysis of Ligand E in the Presence of Nickel Ion. Formation of [Ni(H)](ClO₄)₂. A mixture of E (0.9 g, 2.2 mmol), Ni(ClO₄)₂·6H₂O (0.8 g, 2.2 mmol) and 50 mL of water was heated at reflux for 18–20 h. After it was cooled to room temperature, the mauve solution was gravity filtered and chromatographed on a Sephadex C-25 column (40 cm × 2 cm) with use of 0.2 M sodium perchlorate as eluent. Two bands developed on the column and were collected as separate fractions; band 1 was violet, and band 2 was orange. Evaporation of band 1 to ca. 20 mL resulted in the crystallization of a purple-violet complex, which was collected, washed with absolute ethanol, and dried in vacuo (0.01 torr) at room temperature; yield 0.6 g or 42% of [Ni(G)](ClO₄)₂. Careful evaporation of band 2 yielded a red-violet material as the first fraction and an orange material as the second. Both materials were collected, washed with absolute ethanol, and dried in vacuo (0.01 torr) at room temperature. The orange material (0.05 g, 5% yield) was identified as [Ni(cyclam)](ClO₄)₂ by comparison of its infrared spectrum with an authentic sample. The red-violet complex (0.2 g, 15% yield) was [Ni(H)](ClO₄)₂.

Formation of [Ni(I)](ClO₄)₂. A solution of 0.9 g of F and 0.8 g of nickel perchlorate was heated at reflux for only 25 min prior to chromatography. Elution of the column resulted in the formation of five distinct bands: band 1, deep blue; band 2, orange; band 3, violet; band 4, orange; band 5, light blue. Only the material in band

Table IV. Crystal Data for α-*trans*-[Ni(E)(NCS)₂] (1), β-*trans*-[Ni(E)(NCCH₃)₂](ClO₄)₂·H₂O (2), β-[Ni(F)](ClO₄)₂·CH₃NO₂ (3), and [Ni(G)](ClO₄)₂ (4)

	1	2	3	4
mol wt	587.46	770.32	803.30	653.16
dimens, mm	0.37 × 0.33 × 0.26	0.44 × 0.26 × 0.22	0.44 × 0.33 × 0.22	0.74 × 0.48 × 0.37
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$Pna2_1$
cell constants				
a, Å	10.526 (2)	12.726 (7)	16.798 (2)	16.454 (9)
b, Å	13.719 (4)	11.712 (6)	11.588 (3)	16.730 (6)
c, Å	20.625 (3)	11.182 (6)	17.882 (4)	10.338 (4)
β, deg	107.05 (1)	95.40 (4)	91.84 (1)	
no. of reflcns used to determine cell constants	15	15	15	15
2θ limits, deg	$15.4 < 2\theta < 22.6$	$10.3 < 2\theta < 18.3$	$15.8 < 2\theta < 23.2$	$12.9 < 2\theta < 24.6$
Z	4	2	4	4
ρ_{calcd}, g cm⁻³	1.370	1.542	1.533	1.524
ρ_{exptl},ᵃ g cm⁻³	1.37	1.51	1.53	1.51

ᵃ By flotation in carbon tetrachloride/*n*-hexane.

1 was characterized. It was isolated by extracting the fraction with portions of nitromethane, which were evaporated to dryness to yield a blue solid. The solid was dissolved in 20 mL of water and treated with 1 g of sodium perchlorate dissolved in 5 mL of water. After gravity filtration the solution was slowly concentrated under a stream of air to induce crystallization of deep blue [Ni(I)](ClO₄)₂. The product was collected, washed with portions of 2-propanol, and dried at room temperature in vacuo (0.01 torr); yield 0.35 g or 25%. This complex was converted to [Ni(G)](ClO₄)₂ (97% isolated yield) upon heating an aqueous solution at reflux for 18 h.

Hydrolysis Reactions of Ligand E in the Absence of Nickel Ion. Experiment 1. A suspension of E (0.50 g, 1.2 mmol) in 50 mL of water was heated at reflux for 48 h. The solution obtained was evaporated to give a viscous, colorless oil; yield 0.5 g. The infrared spectrum of this material exhibited absorptions for N—H, C=O, and C≡N. Carbon-13 NMR (D₂O, δ vs. Me₄Si): carbonyl region, a single peak at 183.7 and 13 major peaks between 181 and 176; nitrile region, a single peak at 120. Thin-layer chromatography on silica gel using water/pyridine/methanol/acetic acid (15:15:15:1 by volume, respectively) as eluent indicated that there were at least 6 components with R_f's of 0.59, 0.52, 0.38, 0.32, 0.24, and 0.14.

Experiment 2. A vigorously stirred suspension of α-[Ni(E)](ClO₄)₂·H₂O (0.8 g, 1.2 mmol) in 30 mL of water was treated over a 1–2-min period with 0.3 g (6.1 mmol) of NaCN dissolved in 5 mL of water. A blue precipitate formed and then redissolved to yield a light yellow solution. This solution was then maintained at reflux for 10 min. When it was cooled to room temperature, the solution was adjusted to pH 13 with 25% w/w NaOH and evaporated to dryness on a rotary evaporator. The solid residue was extracted with 3 × 50 mL portions of chloroform; the combined extracts were dried with anhydrous sodium sulfate and evaporated to give a viscous, yellow oil. The infrared spectrum of this material contained absorptions for N—H, C=O, and C≡N functions.

Ni(I)(NCS)₂. [Ni(I)](ClO₄)₂ (0.10 g, 0.16 mmol) and NaSCN (0.2 g, 2.5 mmol) were added to 15 mL of room-temperature water, and the mixture was vigorously stirred for 4 h. During this time the complex dissolved and was replaced by a finely divided, light blue solid. The light blue product was collected, washed with absolute ethanol, and dried at room temperature in vacuo (0.01 torr); yield 0.08 g or 92%.

Ni(J)(NCS)₂·H₂O. An acetonitrile solution of Wainwright's complex "Ni(E)(ClO₄)₂" (0.75 g, ca. 1.1 mmol in 40 mL) was treated with NaSCN (0.5 g, 6 mmol) and stirred at room temperature for 30 min. After gravity filtration, the solution volume was reduced to ca. 10 mL by directing an air stream across the surface whereupon a reddish violet product began to precipitate. After standing overnight, the product was collected, washed with portions of methanol, and dried at room temperature in vacuo (0.01 torr); yield 0.2 g or 20%.

α-[Ni(K)](ClO₄)₂. Ligand B (1.50 g, 6.6 mmol) and acrylamide (2.4 g, 34 mmol) were added to 25 mL of methanol, and the mixture was heated at reflux for ca. 18 h. After it was cooled to room temperature, the solution was gravity filtered and the filtrate treated with a methanol solution of Ni(ClO₄)₂·6H₂O (2.40 g, 6.6 mmol in 5 mL) over 2–3 min. The mixture was stirred at room temperature for 30 min and gravity filtered. The green filtrate was reduced to ca. 10 mL under a stream of air and allowed to stand overnight. The green crystals were collected, washed with absolute ethanol, and dried in vacuo (0.01 torr, 100 °C) overnight; yield 1.90 g or 46%. Satisfactory elemental analyses were obtained upon one recrystallization from acetonitrile by addition of ether; recovery 93%. This complex could also be obtained as a monohydrate by recrystallization from aqueous sodium perchlorate solution.

β-[Ni(K)](ClO₄)₂·2H₂O. α-[Ni(K)](ClO₄)₂ (0.50 g, 2.4 mmol) was dissolved in 60 mL of hot water and the green solution heated at reflux for 72 h. After this time the blue solution was cooled to room temperature and gravity filtered. Half the filtrate (ca. 30 mL) was chromatographed on a Sephadex C-25 column (40 cm × 2 cm) using 0.25 M sodium perchlorate as eluent. Three bands developed on the column and were collected as separate fractions; band 1 was light blue, band 2 was green, and band 3 was blue-violet. The chromatography procedure was repeated for the second 30-mL portion, and the analogous fractions were combined. Band 1 was quite small and was not characterized. Band 2 was evaporated to ca. 20 mL on a rotary evaporator, and a crop of green crystals formed upon standing overnight. The green product (0.06 g, 4% yield) was identified as α-[Ni(K)](ClO₄)₂·H₂O by its infrared spectrum. Band 3 was evaporated to ca. 25 mL on a rotary evaporator and upon standing produced a crop of violet crystals. These crystals were collected, washed with absolute ethanol, and dried at room temperature in vacuo (0.01 torr); yield 0.76 g or 48% of a complex that analyzed as [Ni(K)](ClO₄)₂·2H₂O.

Crystallographic Studies on α-*trans*-[Ni(E)(NCS)₂] (1), β-*trans*-[Ni(E)(NCCH₃)₂](ClO₄)₂·H₂O (2), β-[Ni(F)](ClO₄)₂·CH₃NO₂ (3), and [Ni(G)](ClO₄)₂ (4). The unit cell parameters and other relevant crystal data are listed in Table IV. Certain details of data collection and refinement are given in Table V. Scattering factors were taken from the usual source;[23] those for all atoms except hydrogen were corrected for real and imaginary anomalous dispersion components with use of the dispersion factors given by Cromer.[24] Additional information concerning data collection, structure solution, and refinement are given as supplementary material.

Final positional parameters for non-hydrogen atoms in structures 1–4 are given in Tables VI–IX, respectively. Available as supplementary material are tables of thermal parameters for non-hydrogen atoms in 1–4 (Tables VIa–IXa, respectively), tables of positional and thermal parameters for hydrogen atoms in 1–4 (Tables VIb–IXb, respectively), and structure factor tables for 1–4.

Results

Syntheses and Properties of Nickel Complexes of Ligand E. At the onset of this investigation we attempted to prepare [Ni(E)](ClO₄)₂ by refluxing nickel perchlorate and E in ethanol according to Wainwright's procedure.[20] Although the product obtained by this procedure had the physical properties described by Wainwright, the infrared spectrum of the material contained absorptions for N—H and C=O functions, in ad-

(23) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(24) Cromer, D. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table V. Data Collection and Refinement Details for α-trans-[Ni(E)(NCS)$_2$] (1), β-trans-[Ni(G)(NCCH$_3$)$_2$](ClO$_4$)$_2$·H$_2$O (2), β-[Ni(F)](ClO$_4$)$_2$·CH$_3$NO$_2$ (3), and [Ni(G)](ClO$_4$)$_2$ (4)

	1	2	3	4
h,k,l limits	$-h,0,0 \rightarrow +h,+k,+l$	$-h,0,0 \rightarrow +h,+k,+l$	$-h,0,0 \rightarrow +h,+k,+l$	$0,0,0 \rightarrow +h,+k,+l$
no. of data	5050	2933	6146	2686
no. of data used in final refinement ($F > 3\sigma_F$)	3774	2149	4652	2254
no. of data/no. of variables	11.0	9.8	10.1	8.7
μ, cm^{-1}	8.03	7.42	7.26	8.67
$R = [\Sigma ||F_o| - |F_c||]/[\Sigma |F_o|]$	0.057	0.070	0.066	0.067
$R_w = [\Sigma (|F_o| - |F_c|)w^{1/2}]/[\Sigma (|F_o|)w^{1/2}]^a$	0.055	0.074	0.066	0.073

^{a} $w = n/(\sigma_F^2 + mF^2)$. In the final cycle values of n and m for each refinement were as follows: (1) $n = 1.55$, $m = 9.4 \times 10^{-4}$; (2) $n = 1.27$, $m = 4.1 \times 10^{-3}$; (3) $n = 2.06$, $m = 7.2 \times 10^{-4}$; (4) $n = 1.47$, $m = 2.8 \times 10^{-3}$.

Table VI. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of α-trans-[Ni(E)(NCS)$_2$]

atom	x	y	z
Ni	0.32217 (5)	0.23591 (4)	0.06735 (3)
S1	0.2028 (1)	−0.08060 (9)	−0.02574 (7)
S2	0.2689 (2)	0.56799 (9)	0.12812 (8)
N1	0.2133 (4)	0.2088 (3)	0.1405 (2)
N2	0.1424 (3)	0.2743 (3)	−0.0176 (2)
N3	0.4311 (3)	0.2939 (3)	0.0024 (2)
N4	0.4977 (3)	0.1919 (3)	0.1478 (2)
N5	0.2662 (8)	0.0149 (5)	0.3040 (3)
N6	−0.0586 (5)	0.2685 (4)	−0.2218 (3)
N7	0.5941 (5)	0.1149 (4)	−0.1630 (2)
N8	0.7671 (5)	−0.1019 (4)	0.1719 (2)
N9	0.3055 (3)	0.0973 (2)	0.0309 (2)
N10	0.3362 (4)	0.3782 (3)	0.1051 (2)
C1	0.1036 (5)	0.2831 (4)	0.1338 (3)
C2	0.0110 (5)	0.2983 (4)	0.0627 (3)
C3	0.0631 (5)	0.3423 (4)	0.0084 (3)
C4	0.2005 (5)	0.3244 (4)	−0.0696 (3)
C5	0.3372 (5)	0.3668 (4)	−0.0393 (3)
C6	0.5539 (5)	0.3478 (4)	0.0422 (3)
C7	0.6452 (5)	0.2945 (4)	0.1019 (3)
C8	0.5932 (5)	0.2741 (4)	0.1615 (3)
C9	0.4451 (5)	0.1743 (4)	0.2093 (2)
C10	0.3192 (5)	0.2283 (4)	0.2056 (2)
C11	0.1614 (5)	0.1083 (3)	0.1371 (2)
C12	0.0981 (6)	0.0748 (4)	0.1925 (3)
C13	0.1939 (7)	0.0408 (4)	0.2552 (3)
C14	0.0637 (4)	0.1884 (3)	−0.0518 (2)
C15	−0.0710 (4)	0.2078 (4)	−0.1054 (2)
C16	−0.0626 (5)	0.2431 (4)	−0.1706 (3)
C17	0.4644 (5)	0.2160 (3)	−0.0407 (2)
C18	0.5161 (7)	0.2524 (4)	−0.0977 (3)
C19	0.5598 (5)	0.1742 (5)	−0.1338 (3)
C20	0.5597 (4)	0.0994 (3)	0.1339 (2)
C21	0.6900 (5)	0.0722 (4)	0.1888 (2)
C22	0.7325 (5)	−0.0261 (4)	0.1787 (2)
C23	0.2653 (4)	0.0229 (3)	0.0081 (2)
C24	0.3127 (4)	0.4576 (3)	0.1154 (2)

Table VII. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of β-trans-[Ni(E)(NCCH$_3$)$_2$](ClO$_4$)$_2$·H$_2$O

atom	x	y	z
Ni	0.00000	0.00000	0.00000
N1	−0.0106 (3)	−0.1502 (4)	0.1122 (4)
N2	−0.0518 (3)	−0.0916 (4)	−0.1645 (4)
N3	0.1568 (4)	−0.0436 (4)	−0.0272 (4)
N4	0.0916 (5)	−0.3310 (6)	0.4157 (7)
N5	−0.1313 (7)	−0.4088 (7)	−0.3008 (7)
C1	−0.1143 (5)	−0.2089 (5)	0.0803 (6)
C2	−0.1308 (5)	−0.2498 (5)	−0.0468 (6)
C3	−0.1480 (4)	−0.1568 (5)	−0.1440 (6)
C4	−0.0784 (5)	0.0057 (5)	−0.2484 (5)
C5	0.0077 (5)	0.0959 (5)	−0.2342 (5)
C6	0.2358 (5)	−0.0647 (5)	−0.0565 (5)
C7	0.3385 (5)	−0.0889 (7)	−0.0986 (6)
C8	0.0778 (5)	−0.2338 (5)	0.1114 (5)
C9	0.0715 (5)	−0.3464 (5)	0.1822 (5)
C10	0.0821 (5)	−0.3373 (6)	0.3127 (7)
C11	0.0278 (5)	−0.1660 (5)	−0.2165 (5)
C12	−0.0075 (6)	−0.2321 (6)	−0.3306 (6)
C13	−0.0727 (8)	−0.3314 (7)	−0.3133 (7)
Cl	−0.7681 (1)	−0.4309 (2)	−0.0956 (2)
O1	−0.7682 (6)	−0.3632 (6)	−0.2016 (6)
O2	−0.8730 (5)	−0.4597 (6)	−0.0792 (6)
O3	−0.7083 (7)	−0.5283 (6)	−0.1132 (8)
O4	−0.7261 (5)	−0.3653 (6)	0.0020 (6)

dition to the reported nitrile absorptions. Further investigations left little doubt that, in our hands, Wainwright's procedure yielded a complex product mixture that contained amide groups, arising from hydrolysis of nitrile, and secondary amine functions, arising from dealkylation reactions. As evidence of the latter, addition of sodium thiocyanate to an acetonitrile solution of the material prepared by Wainwright's procedure resulted in the crystallization (in ca. 20% yield) of a complex whose infrared spectrum contained absorptions for O—H, N—H, and C≡N. On the basis of elemental analyses we believe that this complex is [Ni(J)(NCS)$_2$]·H$_2$O. No evidence is available concerning the stereochemistry of the metal ion in this complex.

Products that were analyzed as [Ni(E)](ClO$_4$)$_2$·H$_2$O and [Ni(E)Cl]Cl (designated hereafter as α forms) and whose infrared spectra contained no inconsistent absorptions were ultimately obtained from the reaction of the respective nickel salts with E in acetonitrile at room temperature. Both of these

complexes have electronic spectra (Table II) that are consistent with their formulations as high-spin, five-coordinate species. This is not unexpected since we have shown that these complexes have the trans-I stereochemistry, vide infra, and, by analogy with complexes of D, should be prone to penta-coordination. It is not clear, however, what the fifth ligand is in the former complex. Its stability to loss of water when it is heated in vacuo at 100 °C might be taken as evidence for coordination of the water to the metal ion; however, the presence of an absorption at 2315 cm^{-1} in the infrared spectrum of the complex is also consistent with the presence of end-bonded coordinated nitrile. Therefore, we, like Wainwright, favor a polymeric structure with intermolecular coordination of nitrile functions. Although models suggest that intramolecular π bonding of a nitrile group should be possible, such interactions are characterized by low-frequency C≡N stretching absorptions,[25] which are not observed for this complex. Both α-[Ni(E)](ClO$_4$)$_2$·H$_2$O and α-[Ni(E)(Cl)]Cl display the same high reactivity of the complexes of ligand D toward ligand dissociation. In fact, because of the very high insolubility of E in water, aqueous solutions of either complex decompose on standing overnight to give crystalline E and Ni(H$_2$O)$_6$$^{2+}$.

α-trans-[Ni(E)(NCS)$_2$] was prepared by metathesis from α-[Ni(E)]$^{2+}$ or α-[Ni(E)(Cl)]$^+$. This complex exhibits two thiocyanate C≡N stretching absorptions at 2120 and 2102

(25) Farona, M. F.; Bremer, N. J. *J. Am. Chem. Soc.* **1966**, *88*, 3735.

Table VIII. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of β-[Ni(F)](ClO₄)₂·CH₃NO₂

atom	x	y	z
Ni	0.21559 (3)	0.22502 (5)	0.04573 (3)
O1	0.0998 (2)	0.2796 (3)	0.0295 (2)
O2	0.1716 (3)	0.6284 (4)	-0.1160 (2)
O3	0.3731 (3)	-0.0759 (4)	-0.1370 (3)
O4	0.3332 (2)	0.1708 (3)	0.0612 (2)
N1	0.2029 (2)	0.2633 (3)	0.1619 (2)
N2	0.2578 (2)	0.3964 (3)	0.0191 (2)
N3	0.2214 (2)	0.1917 (3)	-0.0728 (2)
N4	0.1791 (2)	0.0526 (3)	0.0704 (2)
N5	-0.0241 (3)	0.3399 (6)	0.0396 (3)
N6	0.2855 (4)	0.7290 (5)	-0.0837 (5)
N7	0.3889 (3)	-0.0086 (5)	-0.2544 (3)
N8	0.4437 (2)	0.0662 (4)	0.0754 (3)
C1	0.2780 (3)	0.3175 (5)	0.1910 (3)
C2	0.3027 (3)	0.4294 (5)	0.1529 (3)
C3	0.3263 (3)	0.4218 (4)	0.0726 (3)
C4	0.2869 (3)	0.3795 (5)	-0.0588 (3)
C5	0.2283 (3)	0.3091 (5)	-0.1044 (3)
C6	0.1444 (3)	0.1362 (5)	-0.0990 (3)
C7	0.1298 (3)	0.0184 (5)	-0.0648 (3)
C8	0.1121 (3)	0.0163 (5)	0.0175 (3)
C9	0.1482 (3)	0.0618 (4)	0.1471 (3)
C10	0.1936 (3)	0.1480 (5)	0.1969 (3)
C11	0.1359 (3)	0.3398 (5)	0.1886 (3)
C12	0.0522 (3)	0.3075 (5)	0.1544 (3)
C13	0.0451 (3)	0.3086 (4)	0.0707 (3)
C14	0.1963 (3)	0.4901 (4)	0.0201 (3)
C15	0.2252 (3)	0.6133 (5)	0.0086 (4)
C16	0.2254 (4)	0.6559 (5)	-0.0708 (4)
C17	0.2917 (3)	0.1205 (5)	-0.0937 (3)
C18	0.2978 (4)	0.0905 (6)	-0.1770 (3)
C19	0.3557 (3)	-0.0056 (5)	-0.1865 (3)
C20	0.2397 (3)	-0.0421 (5)	0.0696 (3)
C21	0.3194 (3)	-0.0203 (5)	0.1107 (3)
C22	0.3660 (3)	0.0782 (4)	0.0802 (3)
O5	0.9930 (5)	0.0229 (8)	0.2479 (4)
O6	0.8712 (5)	0.020 (1)	0.2771 (5)
N9	0.9409 (5)	-0.017 (1)	0.2858 (5)
C23	0.9635 (7)	-0.106 (1)	0.3452 (7)
Cl1	0.03432 (8)	0.2265 (1)	0.4185 (1)
Cl2	0.43573 (8)	0.1775 (1)	0.32733 (7)
O7	0.1023 (3)	0.1963 (4)	0.3795 (3)
O8	0.0629 (4)	0.2719 (6)	0.4881 (4)
O9	-0.0139 (3)	0.1322 (5)	0.4265 (5)
O10	-0.0051 (3)	0.3188 (5)	0.3842 (4)
O11	0.4794 (3)	0.1002 (4)	0.3743 (2)
O12	0.3669 (5)	0.1329 (7)	0.3085 (6)
O13	0.4216 (5)	0.2737 (6)	0.3642 (5)
O14	0.4757 (6)	0.1994 (8)	0.2664 (4)

Table IX. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of [Ni(G)](ClO₄)₂

atom	x	y	z
Ni	-0.22026 (6)	-0.08624 (6)	0.00000
O1	-0.1526 (5)	-0.0699 (4)	-0.1678 (8)
O2	-0.2928 (4)	-0.1646 (4)	-0.1053 (7)
N1	-0.1416 (5)	-0.1810 (5)	0.0535 (9)
N2	-0.3059 (5)	-0.1030 (4)	0.1577 (8)
N3	-0.2977 (5)	0.0086 (4)	-0.061 (1)
N4	-0.1378 (5)	-0.0118 (5)	0.099 (1)
N5	-0.1225 (8)	-0.1148 (8)	-0.363 (1)
N6	-0.4295 (8)	0.056 (1)	0.423 (2)
N7	-0.3773 (7)	-0.2205 (6)	-0.247 (1)
C1	-0.1855 (7)	-0.2503 (7)	0.072 (3)
C2	-0.2450 (7)	-0.2356 (7)	0.208 (2)
C3	-0.3225 (7)	-0.1865 (6)	0.177 (1)
C4	-0.3792 (7)	-0.0614 (7)	0.106 (1)
C5	-0.3646 (7)	0.0168 (7)	0.035 (1)
C6	-0.2577 (8)	0.0863 (7)	-0.080 (1)
C7	-0.2012 (7)	0.1125 (7)	0.026 (1)
C8	-0.1201 (8)	0.0665 (7)	0.041 (1)
C9	-0.0627 (7)	-0.0597 (7)	0.118 (1)
C10	-0.0855 (7)	-0.1453 (7)	0.151 (1)
C11	-0.0868 (8)	-0.2104 (8)	-0.054 (1)
C12	-0.1237 (8)	-0.2102 (7)	-0.182 (1)
C13	-0.1348 (7)	-0.1262 (7)	-0.238 (1)
C14	-0.2803 (7)	-0.0646 (7)	0.280 (1)
C15	-0.339 (1)	-0.0699 (9)	0.395 (2)
C16	-0.392 (1)	-0.001 (1)	0.413 (2)
C17	-0.3334 (8)	-0.0054 (8)	-0.194 (1)
C18	-0.3851 (9)	-0.0786 (7)	-0.220 (2)
C19	-0.3435 (6)	-0.1562 (6)	-0.189 (1)
Cl1	-0.0211 (1)	-0.2815 (2)	-0.5544 (3)
Cl2	-0.3450 (2)	-0.4123 (1)	-0.0458 (3)
O3	-0.0257 (6)	-0.3342 (6)	-0.660 (1)
O4	0.0365 (9)	-0.2251 (9)	-0.575 (2)
O5	-0.0052 (8)	-0.3257 (8)	-0.443 (1)
O6	-0.0994 (7)	-0.2463 (8)	-0.543 (1)
O7	-0.2949 (7)	-0.3812 (6)	-0.144 (1)
O8	-0.3859 (6)	-0.3552 (7)	0.018 (2)
O9	-0.3911 (7)	-0.4753 (8)	-0.089 (2)
O10	-0.294 (1)	-0.446 (1)	0.045 (2)

cm⁻¹. A single-crystal X-ray structure (to be described in a later section) shows it to have the trans-I set of nitrogen configurations.

When an acetonitrile solution of α-[Ni(E)](ClO₄)₂·H₂O was heated at reflux for ca. 14 h, the complex that was obtained by evaporation of solvent had an infrared spectrum that was very similar to that of the starting material except that it contained only two C≡N stretching absorptions. The visible spectra of the two complexes were essentially identical with respect to absorption maxima (see Table II for spectral data); however, the extinction coefficient for the complex obtained after heating was only about half that for α-[Ni(E)]-(ClO₄)₂·H₂O. The existence of a new form of [Ni(E)]²⁺ with the trans-III structure was confirmed by a single-crystal X-ray structure determination on β-*trans*-[Ni(E)(NCCH₃)₂]-(ClO₄)₂·H₂O, which was obtained by slow addition of acetone to the acetonitrile solution. A bis(thiocyanate) complex obtained by metathesis was light violet and had physical properties and an infrared spectrum different from those of the pale blue α-*trans*-[Ni(E)(NCS)₂].

Synthesis and Properties of [Ni(G)](ClO₄)₂. Once the preparation and properties of the complexes of ligand E were

established, we turned to the question of the stereochemistry of the complex characterized by Wainwright as [Ni(F)](ClO₄)₂.[20] A sample of this complex was readily prepared, but a single-crystal X-ray structure (described in a subsequent section) showed that it was actually [Ni(G)](ClO₄)₂, a product derived from partial hydrolysis and mono-dealkylation of [Ni(E)](ClO₄)₂. The cation [Ni(G)]²⁺ is six-coordinate as a result of coordination of the two carbamoyl group oxygen atoms. As the ORTEP drawing in Figure 4 shows, inversion of configuration has occurred at two of the nitrogen donors, which are in 1,8-positions, relative to α-[Ni(E)]²⁺.

Subsequent experiments showed that both α- and β-[Ni(E)]²⁺ produced [Ni(G)]²⁺ in 34–36% yield when they were heated for 18–20 h in aqueous solution. A slightly higher yield (up to 51%) of the complex of G could be obtained by heating an aqueous mixture of nickel perchlorate and E at reflux for an equal period of time. Longer reaction times did not increase the yield of this hydrolysis product in any case. When ligand G was combined with nickel perchlorate in water, the complex obtained was identical (infrared and visible spectra) with that obtained from hydrolysis of α-[Ni(E)]²⁺.

In an effort to determine what other products were produced in the hydrolysis of [Ni(E)]²⁺, chromatographic separations of reaction mixtures were undertaken. After equimolar amounts of nickel perchlorate and E were heated in water for 18–20 h, the mixture was separated on an ion-exchange column. [Ni(G)](ClO₄)₂ was isolated in 42% yield from the first of two bands that developed. The second band yielded [Ni-(cyclam)](ClO₄)₂ (5%) and a complex that we believe to be [Ni(H)](ClO₄)₂ (15%). The infrared spectrum of the latter compound clearly indicated the presence of an amide function

but no evidence for a nitrile. The presence of only two nitrogen substituents was indicated by the elemental analysis. Assignment of the structure as the 1,8-isomer, rather than the
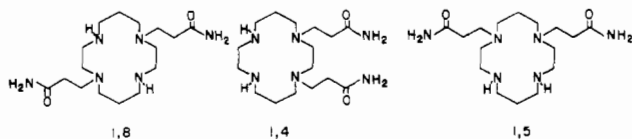

1,4- or 1,5-isomer, was based on the ^{1}H NMR spectrum of the free ligand. The 1,4-isomer could be eliminated since the singlets expected for the ethylene linkages in a such a species were absent. Irradiation of the high-field methylene resonance at 1.48 ppm, which is due to the center methylene groups of the six-membered chelate rings, allowed the assignment of a triplet at 2.48 ppm to an adjacent methylene group. Comparison of this chemical shift value with chemical shift values for methylene groups in A and F suggests that this methylene group is α to a secondary amine. Irradiation of this 2.48 ppm methylene resonance resulted in the collapse of the 1.48 ppm multiplet to a simple triplet. This result is only consistent with a structure in which the two trimethylene chains are equivalent. Since the 1,4-isomer has already been eliminated, the 1,8-isomer is the only remaining possibility.

The electronic spectrum (solid and solution) of [Ni(H)]$^{2+}$ is consistent with it being a six-coordinate complex. Six-coordination could probably be achieved with H in a complex having either structure I or II. In the latter case six-coordination would be achieved by folding of the ligand with cis coordination of the two amide functions. However, no evidence concerning the metal–nitrogen stereochemistry is available.

It is clear that [Ni(H)]$^{2+}$ is not formed from [Ni(G)]$^{2+}$ since this complex could be recovered in greater than 90% yield after heating an aqueous solution at reflux for 60 h. This observation suggests that there are two divergent pathways for hydrolysis/dealkylation of E. It is not possible to say for sure that the pathway leading to H involves the nickel ion. We do know, however, that the production of cyclam must involve the nickel ion since this was not among the products produced in the nickel-free hydrolysis reaction.

Some additional information concerning the sequence of events leading to the production of [Ni(G)]$^{2+}$ was obtained by examination of reaction mixtures that were heated for only 25 min before ion-exchange chromatographic separation. The major product was a deep blue species contained in the first band. This complex (25% isolated yield) exhibited a single carbonyl absorption at 1660 cm^{-1} and two nitrile absorptions at 2272 and 2258 cm^{-1}. Coupled with the elemental analyses this complex appeared to contain one amide and two nitrile groups. When this complex was heated in water, it was quantitatively converted to [Ni(G)]$^{2+}$. The complex has been characterized as [Ni(I)](ClO$_4$)$_2$ although we do not have evidence to allow a choice between the two possible structural isomers for I
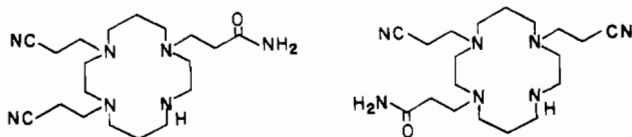
It should be noted that the above species could arise from hydrolysis of either the 1- or 8-substituent in [Ni(J)]$^{2+}$. The question of the metal–nitrogen stereochemistry in [Ni(I)]$^{2+}$ also cannot be satisfactorily answered with the data currently available.

Hydrolysis Reactions of Ligand E in the Absence of Nickel Ion. Wainwright's identification of the hydrolysis product of [Ni(E)](ClO$_4$)$_2$ as a complex of F was based in part on the

^{13}C NMR and mass spectra of the organic materials obtained by chloroform extraction of the hydrolysis reaction mixture after addition of NaCN and heating at reflux. We have not been able to satisfactorily duplicate this result. It is very unlikely that F could be derived from [Ni(G)]$^{2+}$, but since this complex accounts for only about $^1/_3$ of the starting material, F might somehow have been derived from the E that is unaccounted for. We did find that nitrile hydrolysis occurred readily in the presence of cyanide. For example, when α-[Ni(E)]$^{2+}$ was decomposed by treatment with 5–6 equiv of NaCN (at room temperature) and the mixture heated at reflux for 10 min, the ligand obtained by extraction with chloroform exhibited strong absorptions for both N—H and C=O functions. In other cases nitrile hydrolysis was observed at room temperature in cyanide-containing medium. In fact, this facile hydrolysis precluded the acquisition of ^{13}C data on cyanide decomposition reactions in cases where long data collection times were required.

Hydrolysis of E also occurs in the absence of additives. After 48-h reflux, the material obtained after evaporation of water exhibited absorptions for both nitrile and amide. Thin-layer chromatography showed that there were at least six components. Neither unreacted E nor cyclam (A) was among the reaction products (based on their known R_f's), but it was not possible to unambiguously determine if either F or G was present. The complexity of the ^{13}C NMR spectrum obtained on the mixture suggested that there could easily be more than six components present.

Synthesis and Properties of Nickel Complexes of F. In view of the unanticipated reactivity patterns of complexes of E it became especially interesting to undertake the synthesis of F and its metal complexes. An independent synthesis of F had been mentioned by Wainwright,[26] but without experimental details. We found that F could be prepared in greater than 90% yield by the alkylation of cyalam with acrylamide and that two forms of the nickel(II) complex could be prepared in water by proper choice of conditions. When a 1:1 mixture of nickel perchlorate and F dissolved in water was heated at reflux for only 2–3 min, a green complex was obtained, which was analyzed as [Ni(F)](ClO$_4$)$_2$ (designated hereafter as the α form). If, on the other hand, the solution of nickel perchlorate and F was heated for 1.5–2 h, it became bright blue in color. After suitable workup and recrystallization of the product from nitromethane a second complex of F, β-[Ni(F)](ClO$_4$)$_2$·CH$_3$NO$_2$, was obtained. That these two complexes are, in fact, stereoisomers was demonstrated by metathesis to their bis(thiocyanates), α-[Ni(F)(NCS)$_2$]·$^5/_2$H$_2$O and β-[Ni(F)(NCS)$_2$]·H$_2$O, which exhibited distinctly different physical and spectral properties.

The electronic spectrum of α-[Ni(F)]$^{2+}$ (Table II) suggested that it was probably a high-spin, five-coordinate species. Presumably pentacoordination is achieved by binding of one of the carbamoyl group oxygen atoms. However, the spectrum of the β form was characteristic of a six-coordinate species. This form was determined to have the trans-III stereochemistry by a single-crystal X-ray structure determination (vide infra) with six-coordination resulting from complexation of 1,4-carbamoyl functions. We assume that the α form has the same stereochemistry as the α form of E (i.e., the trans-I structure), but we have no direct evidence. An attempt was made to monitor the conversion of the α to the β form by spectrophotometry to determine whether intermediates could be detected. Unfortunately, the rather large differences in extinction coefficients for the two stereoisomers made detection of an isosbestic point impossible and no useful information could be obtained.

(26) Bennur, S. C.; Wainwright, K. P. *Proc. Int. Conf. Coord. Chem.* **1980**, *21*, 254.
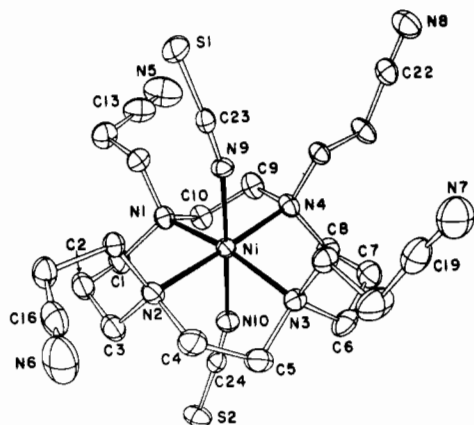
Figure 1. ORTEP drawing of α-trans-[Ni(E)(NCS)$_2$] (1). Thermal ellipsoids are at the 30% level; hydrogen atoms are not shown.

Table X. Selected Interatomic Distances (A) and Angles (deg) in α-trans-[Ni(E)(NCS)$_2$] (1)

Distances

Ni–N1	2.177 (4)	N1–C11	1.478 (6)
Ni–N2	2.232 (4)	C11–C12	1.552 (6)
Ni–N3	2.154 (4)	C12–C13	1.463 (9)
Ni–N4	2.175 (4)	C13–C15	1.127 (8)
Ni–N9	2.034 (3)	N2–C14	1.493 (6)
Ni–N10	2.091 (4)	C14–C15	1.545 (6)
N1–C1	1.516 (6)	C15–C16	1.456 (7)
C1–C2	1.520 (7)	C16–N6	1.124 (6)
C2–C3	1.509 (8)	N3–C17	1.496 (6)
C3–N2	1.456 (6)	C17–C18	1.518 (7)
N2–C4	1.543 (6)	C18–C19	1.456 (8)
C4–C5	1.507 (7)	C19–N7	1.132 (7)
C5–N3	1.489 (6)	N4–C20	1.492 (5)
N3–C6	1.506 (6)	C20–C21	1.546 (6)
C6–C7	1.511 (7)	C21–C22	1.455 (7)
C7–C8	1.511 (7)	C22–N8	1.124 (6)
C8–N4	1.481 (6)	S1–C23	1.633 (4)
N4–C9	1.545 (6)	C23–N9	1.151 (5)
C9–C10	1.501 (7)	S2–C24	1.626 (5)
C10–N1	1.497 (6)	C24–N10	1.151 (6)

Angles

N1–Ni–N2	95.0 (1)	Ni–N2–C3	108.0 (3)
N1–Ni–N3	167.9 (1)	Ni–N2–C4	103.5 (3)
N1–Ni–N4	85.8 (1)	Ni–N2–C14	114.2 (3)
N1–Ni–N9	95.2 (1)	Ni–N3–C6	111.8 (3)
N1–Ni–N10	84.0 (1)	Ni–N3–C5	102.9 (3)
N2–Ni–N3	84.7 (1)	Ni–N3–C17	111.4 (3)
N2–Ni–N4	177.3 (1)	Ni–N4–C8	108.2 (3)
N2–Ni–N9	88.2 (1)	Ni–N4–C9	103.9 (3)
N2–Ni–N10	91.3 (1)	Ni–N4–C20	114.3 (2)
N3–Ni–N4	95.1 (1)	N1–C1–C2	115.8 (4)
N3–Ni–N9	96.9 (1)	C1–C2–C3	120.1 (4)
N3–Ni–N10	83.9 (1)	C2–C3–N2	112.8 (4)
N4–Ni–N9	89.1 (1)	C3–N2–C4	110.9 (4)
N4–Ni–N10	91.4 (1)	N2–C4–C5	114.1 (4)
N9–Ni–N10	179.0 (1)	C4–C5–N3	111.8 (4)
Ni–N9–C23	164.1 (3)	C5–N3–C6	107.7 (4)
Ni–N10–C24	163.2 (4)	N3–C6–C7	116.4 (4)
Ni–N1–C1	111.4.(3)	C6–C7–C8	117.2 (4)
Ni–N1–C10	100.8 (3)	C7–C8–N4	111.9 (4)
Ni–N1–C11	112.9 (3)	C8–N4–C9	110.4 (4)
		N4–C9–C10	113.9 (4)
		C9–C10–N1	111.8 (4)
		C10–N1–C1	107.9 (4)

Synthesis and Properties of Nickel(II) Complexes of K. The isomerization processes observed for the complexes of E and F raise numerous questions about the properties required of a ligand in order that such an isomerization can occur. In order to begin to acquire such information, ligand K was synthesized, by the Michael addition reaction of acrylamide with B, and its nickel complex investigated.

Although K proved difficult to obtain in pure form, a green nickel complex was readily prepared by addition of nickel perchlorate to the crude material. This complex, α-[Ni(K)]$^{2+}$, could be obtained as the perchlorate salt in anhydrous or monohydrated form depending upon the method of recrystallization. The solid-state electronic spectra of these complexes were slightly different (Table II), but both are consistent with the presence of high-spin, five-coordinate nickel. The anhydrous material most likely has one of the carbamoyl groups coordinated. However, the monohydrate could not be dehydrated by heating at 100 °C in vacuo so that there is a possibility that it may contain coordinated water. It seems reasonable to assume that these complexes have the trans-I, metal–nitrogen stereochemistry.

When an aqueous solution of α-[Ni(K)]$^{2+}$ was heated at reflux for 72 h, the color slowly changed from green to blue. A complex that was analyzed as [Ni(K)](ClO$_4$)$_2$·2H$_2$O (48% isolated yield) but whose infrared and electronic spectra were very different from those of the α isomer was obtained after ion-exchange chromatography. The electronic spectral data suggest six-coordination for the nickel ion, but no additional information concerning its structure is available. The material from the first band on the column, which was light blue in color, was not characterized.

Description of the Structure of α-*trans*-[Ni(E)(NCS)$_2$] (1). The crystal structure consists of monomeric, neutral species of composition [Ni(E)(NCS)$_2$]. The nickel atom is six-coordinate with bonds to the four tertiary amine nitrogen atoms of the macrocyclic ligand and to the nitrogen atoms of the thiocyanate anions, which are coordinated in a trans arrangement. A perspective drawing of 1 is shown in Figure 1. A listing of selected interatomic distances and angles is given in Table X.

The four *N*-(2-cyanoethyl) groups of the macrocyclic ligand in 1 are on the same side of the nickel–nitrogen plane such that the stereochemistry of the complex is that shown by structure II. This is the same metal–ligand stereochemistry determined previously for four complexes of ligand D, which were prepared by combination of metal salt with preformed ligand.[10,16-18] However, of these four complexes only [Fe-(D)(NO)(OH)]$^{2+}$ was six-coordinate.[18] In contrast to this iron complex, where the iron–nitrogen distances were all quite similar and the four nitrogen donors form a nearly exact plane,

the nickel donor arrangement in 1 is less regular. The nickel–tertiary amine nitrogen atom distances vary from 2.154 (4) to 2.232 (4) Å with an average distance of 2.186 Å. The longest and shortest Ni–N distances are cis to each other in one of the five-membered chelate rings (Ni–N2, Ni–N3). In addition to the variation in Ni–N distances, the ring nitrogen atoms are nonplanar. This distortion from planarity is of a tetrahedral nature as reflected by the deviations of the nitrogen atoms from their least-squares plane. The nickel atom is almost 0.1 Å above this least-squares plane toward N9. To some extent this analysis is deceptive since the N2–Ni–N4 arrangement is nearly linear (177.3°), whereas the N1–Ni–N3 angle is only 167.9°. The Ni–N9(thiocyanate) distance of 2.034 Å is 0.057 Å shorter than the Ni–N10(thiocyanate) distance. As noted earlier, this nonequivalence was also indicated by the observation of two thiocyanate C≡N stretching absorptions.

It might be noted that the average Ni–N(macrocycle) distance in 1 is 0.08 Å longer than the average Ni–N(macrocycle) distance in [Ni(D)N$_3$]$^+$,[10] where the nickel ion is 0.33 Å above the plane of the four tertiary amine nitrogen donors (toward the azide ion). The longer Ni–N distance in 1 can be attributed to the greater antibonding character of the nickel $d_{x^2-y^2}$ and d_{z^2} orbitals that results from the more nearly planar
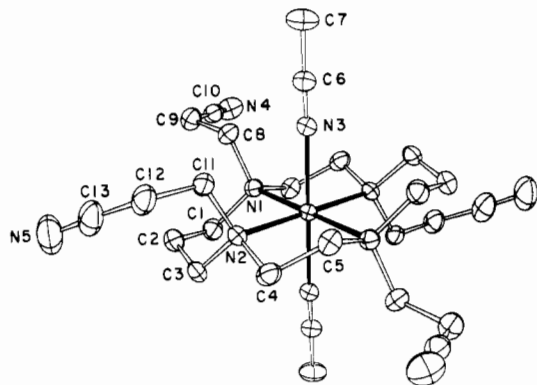
Figure 2. ORTEP drawing of the cation β-*trans*-[Ni(E)(NCCH$_3$)$_2$]$^{2+}$ (2^{2+}). Thermal ellipsoids are at the 30% level; hydrogen atoms are not shown.

Table XI. Selected Interatomic Distances (A) and Angles (deg) in β-*trans*-[Ni(E)(NCCH$_3$)$_2$](ClO$_4$)$_2$·H$_2$O (2)

Distances			
Ni–N1	2.172 (5)	N1–C8	1.493 (7)
Ni–N2	2.177 (4)	C8–C9	1.544 (8)
Ni–N3	2.109 (5)	C9–C10	1.457 (9)
N1–C1	1.501 (7)	C10–N4	1.149 (8)
C1–C2	1.495 (9)	N2–C11	1.494 (7)
C2–C3	1.540 (9)	C11–C12	1.524 (8)
C3–N2	1.479 (7)	C12–C13	1.452 (12)
N2–C4	1.495 (7)	C13–N5	1.191 (11)
C4–C5	1.520 (9)	N3–C6	1.114 (7)
C5–N1′	1.502 (7)	C6–C7	1.459 (8)

Angles			
N1–Ni–N2	93.3 (2)	N1–C1–C2	114.5 (5)
N1–Ni–N3	89.9 (2)	C1–C2–C3	116.2 (5)
N2–Ni–N3	88.5 (2)	C2–C3–N2	114.1 (5)
Ni–N1–C1	109.6 (3)	C3–N2–C4	110.3 (4)
Ni–N1–C5′	100.6 (3)	N2–C4–C5	110.2 (4)
Ni–N1–C8	116.1 (3)	C4–C5–N1′	110.2 (4)
Ni–N2–C3	108.2 (3)	C5–N1′–C1′	110.8 (4)
Ni–N2–C4	100.8 (3)	C8–N1–C1	110.1 (4)
Ni–N2–C11	117.0 (3)	C8–N1–C5′	109.2 (4)
Ni–N3–C6	171.2 (5)	C11–N2–C3	111.2 (4)
		C11–N2–C4	108.8 (4)

arrangement of the nickel–tertiary amine nitrogen atoms and the presence of the second axial donor.

As is usually the case in complexes of cyclam-like ligands, the N–Ni–N angles in **1** are larger in the six-membered chelate rings (95°) than in the five-membered rings (ca. 85°). However, the long Ni–N(macrocycle) distances in **1** result in very large C1–C2–C3 and C6–C7–C8 angles (120.1 and 117.2°, respectively). These are extraordinarily large angles for aliphatic carbon and must surely be accompanied by a substantial amount of strain energy. There are other indications that there may be a good deal of strain in the ring. In particular, the N2–C4 and N4–C9 distances (1.543 (6) and 1.545 (6) Å, respectively) are longer than other N–C distances in this molecule and in other complexes of cyclam type ligands.

The only other reported six-coordinate nickel(II) complex of a peralkylated macrocyclic ligand believed to have stereochemistry I is the bis(thiocyanate) complex of D (prepared from preformed ligand). This complex exhibits two C≡N stretching absorptions in its infrared spectrum. The structure of this complex is unknown although it was suggested earlier that it was most likely cis.[8] Most of the reasons for that conclusion are no longer valid, and the fact that a *trans*-bis-(thiocyanate) complex has been observed for E makes it fairly likely that [Ni(D)(NCS)$_2$] also has a trans, six-coordinate structure.
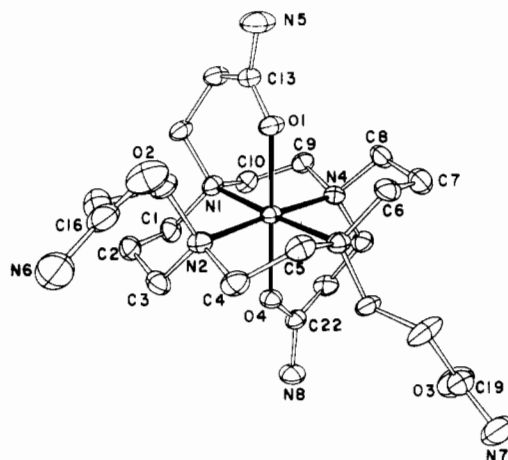
Description of the Structure of β-*trans*-[Ni(E)-(NCCH$_3$)$_2$](ClO$_4$)$_2$·H$_2$O (2). The crystal structure consists of monomeric cations of the indicated formula and noninteracting perchlorate anions. Although the infrared spectrum and elemental analyses for **2** are consistent with the presence of a molecule of water, it could not be located in any difference Fourier map. The cation has a crystallographically imposed center of symmetry. A perspective drawing of the cation is shown in Figure 2. A partial listing of interatomic distances and angles is given in Table XI.

The nickel atom in the cation is six-coordinate with bonds to the four tertiary amine nitrogen atoms and to the nitrogen atoms of the two acetonitrile molecules. The nickel–nitrogen stereochemistry is the same as in structure I (trans-III). The Ni–N(macrocycle) distances are the same at 2.172 (5) and 2.177 (5) Å. The Ni–acetonitrile distance is somewhat shorter at 2.109 (5) Å. The trans-acetonitrile molecules are end bonded to the nickel ion, and the Ni–acetonitrile attachment is slightly bent (Ni–N–C angle 171.1 (5)°).

There are no anomalously long bond distances in the macrocyclic ring in **2**, as described above for **1**, and the C1–C2–C3 angle is only 116.2 (5)°. This leads to the conclusion that there is less strain in the ligand in this complex than in **1**. In this connection it is interesting to compare the structural parameters of the macrocyclic ring in **2** with the parameters for ligand A (cyclam) in *trans*-[Tc(A)O$_2$]$^+$,[27] which has the

Figure 3. ORTEP drawing of the cation β-[Ni(F)]$^{2+}$ (3^{2+}). Thermal ellipsoids are at the 30% level; hydrogen atoms are not shown.

longest metal–nitrogen distances of any cyclam complex that has been structurally characterized (2.125 Å). The most obvious differences in the two structures are the smaller angles around the donor nitrogen atoms in **2**, which appear to be a direct result of the steric requirements of the nitrogen substituent. For example, in **2** the Ni–N2–C3, Ni–N2–C4, and C3–N2–C4 angles are decreased by 5.2, 5.8, and 3.4°, respectively, over those in the technetium–cyclam structure. Similarly decreased angles are found at N1. These changes result in large differences in torsion angles associated with the five-membered rings. In particular, the C3–N2–C4–C5 and C4–C5–N1′–C1′ angles (159 and 161°, respectively) are 9 and 5°, respectively, smaller than in the cyclam structure. These changes result in a very highly puckered five-membered ring where the N2–C4–C5–N1′ angle (66.5°) is 9° larger than in the cyclam structure. This extremely large torsion angle may be one reason that the N2–Ni–N3 angle is 86.7° whereas it is about 84° in the technetium–cyclam structure.

Description of the Structure of β-[Ni(F)](ClO$_4$)$_2$·CH$_3$NO$_2$ (3). The crystal structure consists of monomeric cations, noninteracting perchlorate anions, and a nitromethane molecule of crystallization. A perspective drawing of the cation

(27) Zuckman, S. A.; Freeman, G. M.; Troutner, D. E.; Volkert, W. A.; Holmes, R. A.; Van Derveer, D. G.; Barefield, E. K. *Inorg. Chem.* **1981**, *20*, 2386.

Table XII. Selected Interatomic Distances (A) and Angles (deg) in β-[Ni(F)](ClO$_4$)$_2$·CH$_3$NO$_2$ (3)

Distances			
Ni-N1	2.142 (4)	N1-C1	1.488 (6)
Ni-N2	2.166 (4)	C1-C2	1.528 (8)
Ni-N3	2.159 (4)	C2-C3	1.504 (8)
Ni-N4	2.140 (4)	C3-N2	1.502 (6)
Ni-O1	2.058 (3)	N2-C4	1.505 (6)
Ni-O4	2.084 (3)	C4-C5	1.500 (7)
		C5-N3	1.479 (7)
N1-C11	1.494 (7)	N3-C6	1.505 (6)
N2-C14	1.499 (6)	C6-C7	1.519 (9)
N3-C17	1.499 (6)	C7-C8	1.511 (8)
N4-C20	1.497 (7)	C8-N4	1.507 (6)
		N4-C9	1.486 (6)
O1-C13	1.242 (6)	C9-C10	1.527 (7)
O2-C16	1.236 (8)	C10-N1	1.486 (7)
O3-C19	1.232 (8)		
O4-C22	1.248 (6)		

Angles			
N1-Ni-N2	93.8 (2)	N1-C1-C2	116.3 (4)
N1-Ni-N3	176.4 (1)	C1-C2-C3	117.4 (5)
N1-Ni-N4	87.4 (2)	C2-C3-N2	113.5 (4)
N2-Ni-N3	85.6 (1)	C3-N2-C4	110.5 (4)
N2-Ni-N4	177.3 (1)	N2-C4-C5	110.3 (4)
N3-Ni-N4	93.3 (1)	C4-C5-N3	110.5 (4)
O1-Ni-O4	179.4 (1)	C5-N3-C6	110.6 (4)
		N3-C6-C7	114.0 (4)
Ni-N1-C1	108.5 (3)	C6-C7-C8	116.5 (5)
Ni-N1-C10	103.8 (3)	C7-C8-N4	116.2 (4)
Ni-N1-C11	118.3 (3)	C8-N4-C9	108.8 (4)
Ni-N2-C3	106.8 (3)	N4-C9-C10	113.7 (4)
Ni-N2-C4	101.7 (3)	C9-C10-N1	113.5 (4)
Ni-N2-C14	115.6 (3)	C10-N1-C1	109.4 (4)
Ni-N3-C6	108.4 (3)		
Ni-N3-C5	102.6 (3)	Ni-O1-C13	135.5 (3)
Ni-N3-C17	113.8 (3)	Ni-O4-C22	134.7 (3)
Ni-N4-C8	110.1 (3)		
Ni-N4-C9	103.5 (3)		
Ni-N4-C20	118.9 (3)		

Figure 4. ORTEP drawing of the cation [Ni(G)]$^{2+}$ (4^{2+}). Thermal ellipsoids are at the 30% level; hydrogen atoms are not shown.

Table XIII. Selected Interatomic Distances (A) and Angles (deg) in [Ni(G)](ClO$_4$)$_2$ (4)

Distances			
Ni-O1	2.079 (8)	N1-C11	1.515 (16)
Ni-O2	2.081 (7)	C11-C12	1.457 (18)
Ni-N1	2.121 (8)	C12-C13	1.529 (16)
Ni-N2	2.174 (8)	C13-O1	1.223 (14)
Ni-N3	2.130 (8)	C13-N5	1.320 (17)
Ni-N4	2.106 (8)		
		N2-C14	1.476 (16)
N1-C1	1.456 (14)	C14-C15	1.540 (21)
C1-C2	1.486 (17)	C15-C16	1.465 (22)
C2-C3	1.550 (16)	C16-N6	1.139 (21)
C3-N2	1.437 (13)		
N2-C4	1.491 (14)	N3-C17	1.513 (17)
C4-C5	1.591 (16)	C17-C18	1.514 (17)
C5-N3	1.487 (15)	C18-C19	1.502 (15)
N3-C6	1.470 (14)	C19-O2	1.212 (12)
C6-C7	1.505 (19)	C19-N7	1.352 (14)
C7-C8	1.548 (17)		
C8-N4	1.469 (15)		
N4-C9	1.485 (14)		
C9-C10	1.520 (16)		
C10-N1	1.493 (15)		

Angles			
N1-Ni-N2	95.9 (3)	Ni-N2-C3	110.7 (7)
N1-Ni-N3	177.9 (4)	Ni-N2-C4	101.2 (6)
N1-Ni-N4	85.6 (3)	Ni-N2-C14	113.5 (6)
N1-Ni-O1	89.4 (3)	Ni-N3-C6	115.5 (7)
N1-Ni-O2	90.9 (3)	Ni-N3-C5	108.3 (7)
N2-Ni-N3	86.0 (3)	Ni-N3-C17	112.6 (7)
N2-Ni-N4	97.5 (3)	Ni-N4-C8	117.3 (8)
N2-Ni-O1	171.9 (3)	Ni-N4-C9	106.3 (7)
N2-Ni-O2	86.5 (3)	N1-C1-C2	116.8 (1.0)
N3-Ni-N4	95.0 (3)	C1-C2-C3	118.6 (1.1)
N3-Ni-O1	88.6 (3)	C2-C3-N2	112.8 (9)
N3-Ni-O2	88.4 (3)	C3-N2-C4	110.5 (8)
N4-Ni-O1	88.9 (3)	N2-C4-C5	116.6 (9)
N4-Ni-O2	174.9 (3)	C4-C5-N3	111.1 (9)
O1-Ni-O2	87.3 (3)	C5-N3-C6	109.9 (9)
Ni-O1-C13	121.3 (7)	N3-C6-C7	115.8 (1.1)
Ni-O2-C19	134.1 (7)	C6-C7-C8	117.4 (1.1)
Ni-N1-C1	112.5 (6)	C7-C8-N4	108.2 (1.0)
Ni-N1-C10	104.7 (7)	C8-N4-C9	111.7 (9)
Ni-N1-C11	114.4 (7)	N4-C9-C10	109.5 (9)
		C9-C10-N1	112.1 (9)
		C10-N1-C1	113.0 (9)

is given in Figure 3. A listing of selected interatomic distances and angles is given in Table XII.

The nickel atom is trans six-coordinate as a result of bonding of the four tertiary amine nitrogen atoms and two of the carbamoyl group oxygen atoms. The four *N*-(2-carbamoyl-ethyl) substituents are arranged such that the nickel–nitrogen stereochemistry is the same as shown by structure I (trans-III). With this arrangement, the carbamoyl groups in either the 1,4- or the 1,8-substituents could coordinate in the trans positions. It is the carbamoyl groups in the 1,4-substituents that are coordinated in the solid state even though this results in a complex of much lower symmetry than could have resulted from the other combination. The possibility that there might be an equilibrium between the two forms in solution was considered, but no experimental evidence for the existence of a second isomer was obtained.

The Ni–N distances in this complex vary by only a small amount (minimum 2.140 (4) Å; maximum 2.166 (4) Å), and the average of the four distances is slightly less than the average distance in **2** (2.152 vs. 2.174 Å). The trans-Ni–O distances differ by only a small amount (0.026 Å). There is a slight tetrahedral distortion of the tertiary amine nitrogen atoms about the nickel ion as reflected by the distances of the atoms from their least-squares plane. This distortion may be a result of the chelation of the N1 and N4 substituents as these atoms are above and below, respectively, the least-squares plane. In spite of the chelation of two of the tertiary nitrogen substituents, most of the structural parameters associated with the macrocyclic ring are remarkably similar to those observed for the ring in **2**.

Description of the Structure of [Ni(G)](ClO₄)₂ (4). The crystal structure of the complex consists of monomeric cations and noninteracting anions. A perspective drawing of the [Ni(G)]$^{2+}$ cation is shown in Figure 4. A listing of selected

bond distances and angles is given in Table XIII.

The nickel atom in [Ni(G)]$^+$ is six-coordinate with bonds to the four nitrogen atoms in the macrocycle and the carbonyl oxygen atoms of the appended carbamoyl groups. As shown by the drawing in Figure 4, this is achieved by folding of the macrocycle along the N1–Ni–N3 diagonal, which allows both of the carbamoyl oxygen atoms to coordinate in a cis arrangement. In a planar arrangement of the nickel and macrocycle nitrogen atoms, the N1 and N3 substituents would be on one side of the coordination plane with the N2 and N4

substituents on the opposite side. Folding of a ligand with this set of nitrogen configurations allows the six-membered rings to adopt chair conformations, whereas they would have the skew boat conformation if the nitrogen atoms were coplanar.[13] Isomerization of two nitrogen donors, in 1,8-positions relative to α-[Ni(E)]$^{2+}$ or in 1,4-positions relative to β-[Ni(E)]$^{2+}$, is required to generate the observed structure. If dealkylation occurred prior to inversion of N4, then stereochemical changes at this nitrogen could readily occur via the conjugate base. However, as in the α-[Ni(E)]$^{2+}$ to β-[Ni(E)]$^{2+}$ or α-[Ni(F)]$^{2+}$ to β-[Ni(F)]$^{2+}$ conversions, a change in the stereochemistry of N2 requires dissociation of N2 followed by inversion and rotation about the ring N2–C bonds.

The Ni–N2(tertiary) distance in **4** is 0.068 Å longer than the Ni–N4(secondary) distance. This is about the difference that is observed between the Ni–N distance in *trans*-[Ni(cyclam)Cl$_2$][28] and the average of the distances in **1–3** and *trans*-[Ni(D)(OH$_2$)$_2$]$^{2+}$ [19] (which has trans-III stereochemistry) and is apparently characteristic of secondary amine– vs. tertiary amine–nickel(II) distances. The Ni–N1 and Ni–N3 distances are surprisingly short in comparison to these tertiary amine–nickel distances and probably are the result of some constrictions by the carbamoylethyl chelate rings.

Discussion

The results reported here indicated that the coordination chemistry of peralkylated cyclam ligands is much more complex than was previously suspected. Two particularly significant features are the demonstration that the kinetic products of metal–ligand complexation reactions, which have the trans-I structure, can isomerize and that retro Michael reactions can occur for cyanoethyl-substituted ligands. Both of these points deserve further consideration.

The isomerizations of the trans-I forms of [Ni(E)]$^{2+}$ and [Ni(F)]$^{2+}$ to the trans-III forms were unexpected. Even more surprising was Moore's report of a similar, *reversible*, interconversion of the two isomers of [Ni(D)]$^{2+}$.[21] Although the two isomers of [Ni(D)]$^{2+}$ are configurationally stable in solvents such as water, acetonitrile, and nitromethane, they isomerize in donor solvents (rate order: *n*-PrNH$_2$ >> DMF > Me$_2$SO). These isomerizations require changes in configuration of 1,5-donor atoms, which can only occur via dissociation of the tertiary amine from the nickel atom followed by inversion of the nitrogen atom and rotation about the nitrogen–carbon bonds. The role of the pendant groups in [Ni(E)]$^{2+}$ and [Ni(F)]$^{2+}$ and the donor solvent for [Ni(D)]$^{2+}$ is undoubtedly to displace the tertiary amine donor and/or occupy the coordination site vacated by the amine while these changes are occurring.

It is only reasonable that the trans-I to trans-III conversion is a stepwise process in which one donor atom inversion occurs, followed by the second. We were unable to obtain evidence for an intermediate in our isomerization reactions. However, Moore detected a third species by NMR and obtained kinetic evidence for the presence of an intermediate. His NMR data are consistent with a structure having the set of nitrogen configurations shown as (e) in ref 13.

Moore determined that an equilibrium was established between the trans-I and trans-III isomers of [Ni(D)]$^{2+}$, which favored the trans-I form in some cases. We have not obtained any evidence for reversibility of the isomerizations of [Ni(E)]$^{2+}$ or [Ni(F)]$^{2+}$, but it is clear that if an equilibrium exists it greatly favors the trans-III form in both cases since this form of [Ni(E)]$^{2+}$ was isolable in greater than 80% yield and [Ni(F)]$^{2+}$ in nearly quantitative yield. In fact, the 80% yield of β-[Ni(E)]$^{2+}$ probably does not reflect the relative stabilities

of the two isomers. Although some of the trans-I form can also be recovered after a 14-h reaction time, longer reaction times result in dealkylation and formation of [Ni(J)]$^{2+}$ at the expense of isomerized product. It is interesting to note that the rate of isomerization of [Ni(F)]$^{2+}$ is much greater than that of [Ni(E)]$^{2+}$. This is probably due to the much higher donor strength of the amide oxygen atoms compared to that of the nitrile group. This is the same donor strength effect noted by Moore for isomerization of [Ni(D)]$^{2+}$. Isomerization of [Ni(D)]$^{2+}$ was not effected by acetonitrile, or it was extremely slow. Thus, in spite of the seemingly unfavorable orientation of the nitrile functions for intramolecular chelation in [Ni(E)]$^{2+}$, their proximity is enough to induce isomerization. Wainwright has also prepared *N,N′,N″,N‴*-tetrakis(3-aminopropyl)cyclam and its nickel complex.[29] Although only the trans-I isomer was apparently characterized, if the same trends observed for isomerization of [Ni(D)]$^{2+}$ by Moore are followed, this complex should readily isomerize to the trans-III form.

[Ni(K)]$^{2+}$ also underwent isomerization, presumably from the trans-I to the trans-III isomer, albeit at a much lower rate than [Ni(F)]$^{2+}$. At this point the relative effects of number of donors and their location about the ring cannot be estimated. In work related to what is reported here, we have synthesized a number of (β-substituted alkyl)trimethylcyclam ligands and their metal complexes. Isomerization reactions of these complexes have not been observed. Although too little information is yet available to completely map out the most favorable substituent pattern for isomerization, it does appear that at least two substituents that contain donor groups are required. Another point that has not been investigated concerns the effect of the length of the aliphatic chain by which the pendant group is attached. In addition there is the very interesting question of whether isomerization reactions can be performed with other metal ions.[30] The isomerization reactions of α-[Ni(E)]$^{2+}$ and α-[Ni(F)]$^{2+}$ are very important synthetically since there is probably no alternative synthesis for the trans-III isomers. Attempts to alkylate deprotonated [Ni(cyclam)]$^{2+}$ with acrylonitrile were unsuccessful, and the use of alkylating agents that contain β-hydrogens resulted in protonation of the complex and formation of olefin (E$_2$ elimination).[31]

Metal-promoted or -catalyzed hydrolysis reactions of nitriles are well-known[32] so that hydrolysis of the pendant nitrile groups in [Ni(E)]$^{2+}$ is not so surprising. The ease with which decyanoethylation occurred was unexpected at the time, but in retrospect, it is quite reasonable since retro Michael reactions of cyanoethylated amines are well-known[33] and complexation of the amine should make it a better leaving group. Dealkylation reactions of [Ni(F)]$^{2+}$ have not been observed; therefore, we believe that the production of G, H, and I resulted from decyanoethylation processes. Qualitatively, the relative rate of dealkylation varied with solvent, with reaction being faster in ethanol and water than in acetonitrile. This suggests the participation of an external acid or base in the reaction, but this point has not yet been explored in any detail. Although loss of acrylamide was not confirmed for any of the complexes described in this report, we have observed dealkylation of complexes of (2-carbamoylethyl)- and (2-carbomethoxyethyl)trimethylcyclam when they were heated in acetonitrile in the presence of sodium methoxide.[34] Certainly

(28) Bosnich, B.; Mason, R.; Pauling, P. J.; Robertson, G. B.; Tobe, M. L. *J. Chem. Soc., Chem. Commun.* **1965**, 97.

(29) Wainwright, K. P. *J. Chem. Soc., Dalton Trans.* **1983**, 1149.
(30) The copper(II) complex of ligand G has been prepared although only one isomer was characterized: Hay, R. W.; Bembi, R. *Inorg. Chim. Acta* **1982**, *65*, L227.
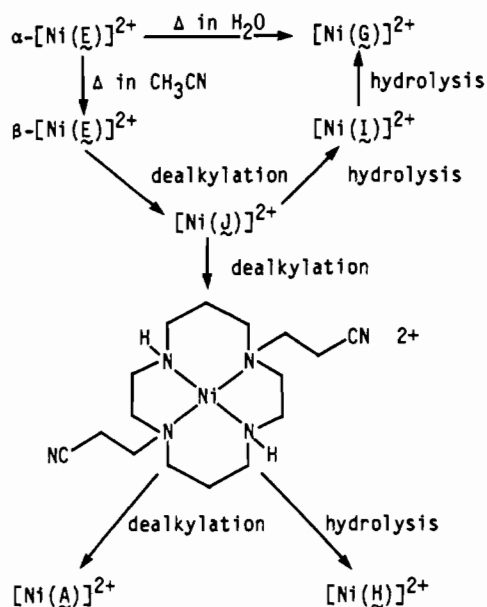(31) Wagner, F.; Barefield, E. K., unpublished results.
(32) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 809–810.
(33) Butskus, P. F. *Russ. Chem. Rev. (Engl. Transl.)* **1961**, *30*, 583.
(34) Freeman, G. M. Ph.D. Thesis, Georgia Institute of Technology, 1983.

Scheme I

the possibility of dealkylation must be considered for any ligand for which a retro Michael reaction can occur.

The apparent ease of formation and high stability of [Ni-(G)]$^{2+}$ and the probable sequence of reactions that lead to its formation and to the formation of other products from [Ni-(E)]$^{2+}$ merit discussion. Scheme I summarizes the results described earlier concerning the hydrolysis and dealkylation reactions of ligand E as we currently perceive them. With the exception of the 1,8-bis(cyanoethyl)cyclam complex all of the complexes shown in Scheme I were isolated. Since [Ni(I)]$^{2+}$ is converted only to [Ni(G)]$^{2+}$ upon heating in water, and this complex is extremely resistant to further reaction, [Ni(H)]$^{2+}$ and [Ni(cyclam)]$^{2+}$ must arise via an independent pathway. The apparent stability of the carbamoylethyl complexes to dealkylation suggests that [Ni(cyclam)]$^{2+}$, at least, must arise exclusively from decyanoethylation as shown. Obviously, a variety of other species must also have been formed to account for the products shown, but no efforts were made to isolate and characterize them.

The stability of [Ni(G)]$^{2+}$ to further hydrolysis is undoubtedly because the cyanoethyl group can no longer effectively interact with the nickel ion because of its orientation

(see Figure 4). The fact that this complex also does not decyanoethylate is somewhat surprising and suggests that interaction of the cyano group with the nickel ion may also be important for dealkylation. It was anticipated that these and other points concerning the formation of this novel product might be tested by isolating the free ligand and then regenerating the nickel complex. However, the expected trans-I kinetic product was not detected. Instead, [Ni(G)]$^{2+}$ that was identical with that obtained from the hydrolysis reaction was formed. It is noteworthy that both α- and β-[Ni(E)]$^{2+}$ produced [Ni(G)]$^{2+}$ in about the same yield upon heating for equal periods in aqueous solution. In both cases other products were also formed, since [Ni(G)]$^{2+}$ accounted for only about one-third of the starting material. To produce this product directly, inversion of 1,8-donors must occur in the reaction of the α isomer, whereas the β isomer requires inversion of 1,4-donors. If decyanoethylation occurs first, as we previously suggested, then inversion of the secondary amine could readily occur via the conjugate base mechanism. No intermediates or other products have been isolated in the reaction of β-[Ni(E)]$^{2+}$ so it is not possible to compare the two reactions further. However, it is certainly possible that [Ni(G)]$^{2+}$ is formed from α- and β-[Ni(E)]$^{2+}$ via a common intermediate. The possibility that [Ni(G)]$^{2+}$ arises from a combination of free ligand with nickel ion cannot be ruled out.