

potential of the He, Ne, and Ar is commensurate with F but much higher than that of N and B, and thus only with F is it possible to have the large energy level splitting associated with strong bonding. The appropriate comparison is the sequence of the  $1\Sigma \pi^4$  fluorides,  $1\Sigma \pi^2$  nitrides, and  $1\Sigma \pi^4$  borides because they have respectively eight, six, and four  $\pi$  (and  $\pi^*$ ) electrons. (The alternate sequence using the  $1\Sigma \pi^4$  nitrides would be out of place, since there are also eight electrons in this case.)

Although  $\text{HeB}^+$  is isoelectronic to HB and HeBe,  $\text{NeB}^+$  to FB and NeBe, and  $\text{ArB}^+$  to ClB and ArBe, the binding energies within each group are quite different. This is easily rationalized by the following considerations. For a crude estimate the binding energies of HeBe, NeBe, and ArBe may be taken as comparable to that of  $\text{Be}_2$  (16 kcal/mol<sup>12</sup>). On the other hand, HB, FB, and ClB have dissociation energies of 58, 181, and 118 kcal/mol,<sup>12</sup> respectively. The wave functions for these species may be schematically written in a valence-

$$\psi(\text{NeB}^+) = a_1\varphi(\text{NeB}^+) + a_2\varphi(\text{Ne}^+\text{B}) + a_3\varphi(\text{Ne}^2+\text{B}^-)$$

$$\psi(\text{NeBe}) = b_1\varphi(\text{NeBe}) + b_2\varphi(\text{Ne}^+\text{Be}^-) + b_3\varphi(\text{Ne}^2+\text{Be}^-)$$

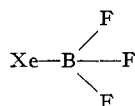
$$\psi(\text{FB}) = c_1\varphi(\text{F}^-\text{B}^+) + c_2\varphi(\text{FB}) + c_3\varphi(\text{F}^+\text{B}^-)$$

bond form. From simple electronegativity arguments,  $a_1 \gg a_2 \gg a_3$ ,  $b_1 \gg b_2 \gg b_3$ , and  $c_2 > c_1 > c_3$ . Therefore, the noble gas-boron compounds are *not* analogous to the highly stable boron monohalides but rather to the unbound noble gas beryllium diatomics.<sup>13</sup> The stability of xenon and krypton trifluoroborate has been also rationalized by isoelectronic analogy to  $\text{ICF}_3$  and  $\text{BrCF}_3$ .<sup>14</sup> Again this analogy is invalid since

$$\psi(\text{XeBF}_3) = d_1\varphi(\text{XeBF}_3) + d_2\varphi(\text{Xe}^+\text{BF}_3^-) + d_3\varphi(\text{Xe}^2+\text{BF}_3^{2-})$$

$$\psi(\text{ICF}_3) = e_1\varphi(\text{I}^-\text{CF}_3^+) + e_2\varphi(\text{ICF}_3) + e_3\varphi(\text{I}^+\text{CF}_3^-)$$

and from ionization potentials  $d_1 > d_2 \gg d_3$ . But for  $\text{ICF}_3$  its known reactions<sup>15</sup> show that  $e_2 > e_3 > e_1$ . This suggests that xenon trifluoroborate does not have the structural formula<sup>16</sup>



In addition, the charge transfer from the noble gas atom to  $\text{B}^+$  in  $\text{ArB}^+$  (0.4 at  $R = 1.6 \text{ \AA}$ ) is sufficient to suggest the potential occurrence of a large inelastic resonant scattering contribution from Ar, Kr, or Xe with  $\text{B}^+$  in a crossed-beams experiment. Based on

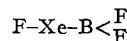
(12) See A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed, Chapman and Hall, London, 1968, for all of the experimental data.

(13) J. F. Liebman, *J. Chem. Educ.*, **48**, 188 (1971).

(14) B.-M. Fung, *J. Phys. Chem.*, **69**, 896 (1965).

(15) This order is rationalized by the alkaline hydrolysis of  $\text{CF}_3\text{I}$ :  $\text{CF}_3\text{I} + \text{KOH} \rightarrow \text{CF}_3\text{H} + \text{KOI}$  (an  $\text{S}_\text{N}2$  reaction on I). This indicates the bond polarity is  $\text{C}^-\text{I}^+$ . See H. J. Emeléus, "The Chemistry of Fluorine and Its Compounds," Academic Press, New York, N. Y., 1969, pp 4, 46.

(16) (a) The analysis in this paper was carried out before it was known to us that the correct structure is



The grossly different electronic charge distribution between  $\text{ICF}_3$  and xenon trifluoroborate indicated by the breakdown of isoelectronic analogy leads to the possibility that the atoms may be connected in a different way. However, we make no claim to have anticipated the structure found by Goetschel.<sup>16</sup> The large number of electrons in this system renders a geometry search economically out of reach at present. (b) A referee has suggested to us that both isomers  $\text{XeBF}_3$  and  $\text{FXeBF}_3$  may exist (with different stabilities), require different syntheses, and be unlikely to rearrange.

the rough qualitative idea that chemical bonding is associated with charge transfer, one might anticipate  $\text{XeB}^+$  to be bound by 10–20 kcal. In spite of this, however, the B–F bond strength is sufficiently high to discourage  $\text{XeB}^+$  salt formation, even using the highly stable fluorinated anions  $\text{SbF}_6^-$ ,  $\text{Sb}_2\text{F}_{11}^-$ , or  $\text{PtF}_6^-$ .<sup>17</sup>

Finally, the possibility of ionic salts and other isolable noble gas boron compounds, in addition to the diatomic cations discussed above, is also of interest. We suggest that Xe–B compounds may be synthesized and observed by decomposition of iodoboranes analogous to the synthetic work of Perlow<sup>4</sup> on  $\text{XeCl}_4$ ,  $\text{XeCl}_2$ , and  $\text{XeBr}_2$ . Considering the stability of the  $\text{B}_{10}$  and  $\text{B}_{12}$  polyhedral cages to oxidative cleavage, a study of  $\text{IB}_{10}\text{H}_9^{2-}$  and  $\text{IB}_{12}\text{H}_{11}^{2-}$  to form the zwitterionic  $^+\text{XeB}_{10}\text{H}_9^{2-}$  and  $^+\text{XeB}_{12}\text{H}_{11}$  (analogous to  $^+\text{N}_2\text{B}_{10}\text{H}_8^{2-}\text{N}_2^+$ ,  $^+\text{OCB}_{10}\text{H}_8^{2-}\text{CO}^+$ ) seems desirable. More direct synthesis such as treating various lower boranes with noble gases at low temperatures and/or in a mass spectrometer is another approach.

(17) For example,  $\text{XeB}^+\text{Sb}_2\text{F}_{11}^- \rightarrow \text{Xe} + \text{BF}_3 + \text{SbF}_6^- + \text{SbF}_5$ . However, in  $\text{XeB}^+\text{SbF}_6^- \rightarrow \text{Xe} + \text{BF}_3 + \text{SbF}_5$ , the total loss of crystal stability might allow the salt to be metastable.

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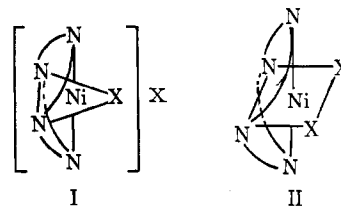
## Strained Five- and Six-Coordinated Macrocylic Nickel(II) Complexes<sup>1</sup>

BY GEORGE A. KALIGEROS AND ELLIOTT L. BLINN\*

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Most of the research on macrocyclic complexes has utilized cyclic tetraamine ligands with at least 13 atoms composing the ring.<sup>2–4</sup> In general, the donor atoms in such complexes are coplanar, and the geometry of the complex is either square planar or trans octahedral. Although little work has been done on the complexes of saturated cyclic tetraamine ligands, it is already known that the 14-membered macrocycle 1,4,8,11-tetraazacyclotetradecane, cyclam, forms a trans octahedral complex with the nickel(II) ion.<sup>5</sup>

Models of 12-membered saturated cyclic tetraamines suggest that the small ring size does not permit coplanar coordination of the four nitrogen atoms in the macrocycle, but such a ligand can be coordinated around the face of either a trigonal-bipyramidal structure (I) or an octahedral structure (II). Two studies of the 12-



(1) Paper presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

(2) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

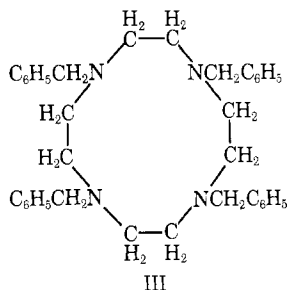
(3) D. H. Busch, *Rec. Chem. Progr.*, **25**, 107 (1964).

(4) D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius, Alfred Werner*, 174 (1967).

(5) B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

member cyclic tetradentate ring system have been reported. First Collman and Schneider<sup>6</sup> conducted a study of the cobalt(III) complexes of 1,4,7,10-tetraazacyclododecane, "cyclen," and found that the resulting complexes exist exclusively in a cis octahedral configuration. This research was not extended to other metal ions such as nickel(II) because of the difficulties in synthesizing the ligand. Rosen and Busch<sup>7</sup> prepared the nickel(II) complex of the sulfur analog of cyclen, 1,4,7,10-tetrathiacyclododecane, which also contained the macrocyclic ligand folded around the face of an octahedron.

The present study deals with nickel(II) complexes of 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane (TACD) (III). This derivative of cyclen was chosen



because it can be prepared much easier than cyclen and the steric crowding due to the *N*-benzyl groups might force the resulting nickel(II) complex to a reduced coordination number. Finally, the Ni<sup>II</sup>-TACD complexes should be highly strained, and because of this strain, these complexes might simulate some attributes of metalloenzyme systems.

#### Experimental Section

**Synthesis of 1,4,7,10-Tetrabenzyl-1,4,7,10-tetraazacyclododecane.**—The 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane was prepared by the method of Hansen and Burg.<sup>8</sup> The total yield was 50%; mp 142–143°. The nmr spectrum in deuterated chloroform showed a singlet (area 16) at 2.66 ppm, a singlet (area 8) at 3.40 ppm, and a multiplet (area 20) at 7.15 ppm. The molecular weight was determined by isothermal distillation in carbon tetrachloride: calcd, 532; found, 560. *Anal.* Calcd for C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>: N, 10.51. Found: N, 10.44.

**Synthesis of Chloro(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)nickel(II) Chloride Hemihydrate.**—A solution of 1.0 g of NiCl<sub>2</sub>·6H<sub>2</sub>O in 60 ml of absolute ethanol was heated to boiling and 1.0 g of TACD was added to it with stirring. After boiling the solution for 15–20 min and cooling, the yellow-green crystals were centrifuged, washed with ether and alcohol, and dried on a steam bath; yield 0.85 g (68%). *Anal.* Calcd for Ni(C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>)Cl<sub>2</sub>·0.5H<sub>2</sub>O: C, 64.1; H, 6.71; N, 8.33; Cl, 10.5. Found: C, 64.04; H, 6.97; N, 8.12; Cl, 10.35.

**Synthesis of Chloro(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)nickel(II) Perchlorate Monohydrate.**—To a solution of 0.135 g of Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O in 20 ml of 95% ethanol, 4.0 ml of 0.1 M NaClO<sub>4</sub> was added and the mixture was allowed to stand for 15 min. The pale green precipitate formed was centrifuged, washed with alcohol and water, and dried over a steam bath; yield 0.105 g (71%). *Anal.* Calcd for Ni(C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>)ClO<sub>4</sub>·H<sub>2</sub>O: C, 58.1; H, 6.33; N, 7.54; Cl, 4.77. Found: C, 57.87; H, 6.08; N, 7.54; Cl, 4.70.

**Synthesis of Nitrate(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)nickel(II) Nitrate Hemihydrate.**—To a boiling solution of 1.00 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 100 ml of ethanol, 1.00 g of TACD was added. The mixture was boiled for 20 min and was allowed to cool. The blue crystalline product was filtered, washed with ethanol, and then dried over a steam bath; yield 1.10 g (74%).

- (6) J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5**, 1380 (1966).  
 (7) W. Rosen and D. H. Busch, *ibid.*, **9**, 262 (1970).  
 (8) G. R. Hansen and T. E. Burg, *J. Heterocycl. Chem.*, **5**, 305 (1968).

*Anal.* Calcd for Ni(C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O: C, 59.7; H, 6.08; N, 11.6. Found: C, 59.7; H, 6.20; N, 11.75.

**Apparatus.**—All electronic spectra were recorded employing a Beckman DK-2 ratio recording spectrophotometer. The spectra of the solids were measured in a Nujol mull using the diffuse-transmittance technique.<sup>9</sup> Infrared spectra were taken on a Perkin-Elmer 337 instrument. The magnetic moments of all complexes except Ni(TACD)ClO<sub>4</sub>·H<sub>2</sub>O were measured using the Gouy method. The magnetic moment of Ni(TACD)ClO<sub>4</sub>·H<sub>2</sub>O was measured using the Faraday method. (The magnetic susceptibility of this complex was measured by Dr. Susan Cummings of Wright State University.) Susceptibilities of the ligand and anions were calculated from Pascal's constants.<sup>10</sup> Conductivity measurements were taken using an Industrial Instruments conductivity bridge. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nitrogen analysis was performed on a Coleman Model 29 nitrogen analyzer and the chloride analysis was performed by a modified Volhard method.<sup>11</sup>

#### Results and Discussion

The Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O and Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O were prepared by direct combination of TACD and NiCl<sub>2</sub>·6H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, respectively, in absolute ethanol. Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O is green while Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O is blue. The green Ni(TACD)ClO<sub>4</sub>·H<sub>2</sub>O was prepared from the reaction of Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O and NaClO<sub>4</sub> in 95% ethanol. The fact that the perchlorate anion replaced only one chloride in the complex Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O suggests that the two chlorides are not equivalent, and one chloride is coordinated to the nickel(II) ion while the other chloride acts as a counteranion. Two absorption bands found in the infrared spectrum of Ni(TACD)ClO<sub>4</sub>·H<sub>2</sub>O at 1090 and 630 cm<sup>-1</sup> were assigned to the uncoordinated perchlorate. There was no indication in the spectrum that the perchlorate had coordinated to the nickel(II). The equivalent conductivities of Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O in nitromethane,<sup>12</sup> acetonitrile,<sup>13</sup> and methanol<sup>14</sup> exhibit typical 1:1 electrolyte behavior (Table I). Also, Ni(TACD)ClO<sub>4</sub>·H<sub>2</sub>O appears to

TABLE I  
CONDUCTIVITY DATA FOR Ni<sup>II</sup>-TACD COMPLEXES<sup>a</sup>

Complex	Λ <sub>e</sub> , ohm <sup>-1</sup> cm <sup>2</sup> equiv <sup>-1</sup>			
	H <sub>2</sub> O	CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> CN	CH <sub>3</sub> OH
Ni(TACD)Cl <sub>2</sub> ·0.5H <sub>2</sub> O	195 <sup>b</sup>	65 <sup>b</sup>	150	59
Ni(TACD)ClO <sub>4</sub> ·H <sub>2</sub> O	...	61	...	...
Ni(TACD)(NO <sub>3</sub> ) <sub>2</sub> ·0.5H <sub>2</sub> O	168 <sup>b</sup>	62 <sup>b</sup>	...	59

<sup>a</sup> All measurements were made on ~10<sup>-3</sup> M solutions at 25°. <sup>b</sup> A plot of the equivalent conductances against the square root of the concentrations of the nickel(II) complex resulted in a curve.

be a 1:1 electrolyte in nitromethane. These data are consistent with the formulation that Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O and Ni(TACD)ClO<sub>4</sub>·H<sub>2</sub>O are complexes with a coordination number of 5, provided that all four nitrogens in TACD are coordinated to the nickel(II). Based on models, a trigonal bipyramid is the most likely five-coordinate structure, in which the four nitrogen atoms in the macrocyclic ligand occupy two equa-

- (9) R. H. Lee, E. Griswald, and J. Kleinberg, *Inorg. Chem.*, **3**, 1279 (1964).  
 (10) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., p 403.  
 (11) R. F. Milton and W. A. Waters, "Methods of Quantitative Micro-Analysis," Edward Arnold, London, 1949, p 180.  
 (12) V. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).  
 (13) T. J. Hutterman, Jr., B. M. Foxman, C. R. Sperate, and J. G. Verhode, *Inorg. Chem.*, **4**, 950 (1965).  
 (14) C. A. Root, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1965.

torial positions and two axial positions while one of the chlorides occupies the remaining equatorial position (I).

The conductivity data of  $\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$  were further expanded by plotting the equivalent conductances in nitromethane against the square root of the equivalent concentrations. A curve resulted. Such a deviation from linearity suggests that the coordinated chloride is partially displaced by the solvent.<sup>15</sup> (The small deviations ( $<10\%$ ) from Beer's law can also be rationalized on the basis of a partial solvolysis.) Unfortunately, the Onsager slopes<sup>16</sup> cannot be employed to determine whether  $\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$  exists as a polynuclear complex because  $[\text{Ni}(\text{TACD})\text{Cl}]^+$  acts as a weak electrolyte.

The magnetic moments of  $\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$  and  $\text{Ni}(\text{TACD})\text{ClO}_4 \cdot \text{H}_2\text{O}$  are 3.7 and 3.6 BM, respectively. These moments are too large for nickel(II) to exist in an octahedral configuration, but such values are consistent with the magnetic moments expected for either tetrahedral<sup>17</sup> or trigonal-bipyramidal nickel(II).<sup>18,19</sup> A fully coordinated macrocyclic complex in a tetrahedral configuration should be a 2:1 electrolyte but this configuration is not consistent with the conductivity data. Also, models cannot be constructed using fully coordinated saturated 12-membered tetradentate macrocyclic ligands positioned around nickel(II) in a tetrahedral configuration. Goedken, Quagliano, and Vallarino<sup>18</sup> observed magnetic moments of the same order of magnitude for trigonal-bipyramidal nickel(II) complexes containing the ligand *N*-methyl-1,4-diazabicyclo[2.2.2]octanium cation (3.69 BM) while Ciampolini and Nardi<sup>19</sup> found a magnetic moment of 3.42 BM for the trigonal-bipyramidal complex chloro[tris(2-aminoethyl)amino]nickel(II) chloride. Therefore, the magnetic data are also consistent with the nickel complex having a trigonal-bipyramidal configuration.

The visible spectra of  $\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$  and  $\text{Ni}(\text{TACD})\text{ClO}_4 \cdot \text{H}_2\text{O}$  in a variety of solvents and the spectra of the solids are given in Table II. The solid and solution spectra are very similar suggesting similar structures in the solid state and in solution. Because of the low solubility of these complexes in most solvents and the low extinction coefficients in the near-infrared region, it was difficult to obtain data in that region. Nevertheless, the spectra of both complexes do not resemble the spectra normally found for nickel(II) in a tetrahedral configuration.<sup>20</sup> Only in methanol is there sufficient solubility of  $\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$  to observe any bands in the near-infrared region, and in this solvent the spectrum resembles the spectrum of the trigonal-bipyramidal high-spin complex bromotris(2-dimethylaminoethyl)methylaminenickel(II) bromide.<sup>19</sup> However, there is a 20-fold difference in the extinction coefficients at wavelengths higher than 710 nm compared to bands at lower wavelengths. This was not observed in other high-spin nickel(II) trigonal-bipyramidal complexes. We have no adequate explanation

TABLE II  
ELECTRONIC SPECTRA OF  $\text{Ni}^{\text{II}}$ -TACD COMPLEXES<sup>a</sup>

Complex	Medium	$\lambda$ , nm ( $\epsilon$ )
$\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	Solid	440, 710
	$\text{CH}_3\text{NO}_2$	435 (365), 710 (150)
	$\text{CH}_3\text{CN}$	440 (345), 710 (164)
	$\text{CH}_3\text{OH}$	440 (245), 715 (100), 1090 (10), 1460 (5), 1560 sh (2.5)
	$\text{C}_2\text{H}_5\text{OH}$	440 (315), 710 (295)
$\text{Ni}(\text{TACD})\text{ClO}_4 \cdot \text{H}_2\text{O}$	Acetone- $\text{H}_2\text{O}$ (80:20)	435 (258), 725 (90)
	$\text{H}_2\text{O}$	400 sh (120), 480 (320), 650 (150)
$\text{Ni}(\text{TACD})(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$	Solid	440, 710
	$\text{CH}_3\text{NO}_2$	435 (260), 715 (95)
	Solid	380, 600, 1025
	$\text{CH}_3\text{NO}_2$	380 (55), 610 (35), 1000 (38)
	$\text{CH}_3\text{OH}$	384 (70), 610 (30), 850 sh (5), 1025 (25)
$\text{Ni}(\text{TACD})(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$	$\text{H}_2\text{O}$	400 sh (53), 480 (215), 650 (24)
	Acetone- $\text{H}_2\text{O}$ (80:20)	390 (46), 600 (30), 1000 (45)

<sup>a</sup> All measurements, except in ethanol and methanol, were made on solutions within the range of  $(0.82\text{--}2.5) \times 10^{-3} M$ . Electronic spectrum using ethanol were made on a  $1.5 \times 10^{-4} M$  solution, and spectra taken in methanol used solutions within the range of  $(5.6\text{--}14.2) \times 10^{-3} M$ .

for this, but the answer may lie in the nature of the highly strained nickel(II)-to-nitrogen bonds.

Although the solid spectra and the solution spectra in all solvents except water have similar wavelengths, the extinction coefficients at those wavelengths vary considerably from solvent to solvent. Also, the extinction coefficients for  $\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$  and  $\text{Ni}(\text{TACD})\text{ClO}_4 \cdot \text{H}_2\text{O}$  in nitromethane differ. These variations in the extinction coefficients may be caused in part by the partial solvolysis of the coordinated chloride. It is also possible that both chlorides in  $\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$  are coordinated, one chloride strongly bonded and within the coordination sphere of the nickel(II) and the other chloride weakly bonded and positioned somewhat outside the coordination sphere. The resulting structure could be considered either a highly distorted octahedron or an intermediate structure between a trigonal bipyramid and an octahedron. The fact that the electronic spectrum has features of both octahedral and trigonal-bipyramidal nickel(II) spectra lends support for this contention. The degree of coordination of both chlorides should be highly solvent dependent for such an intermediate structure, and this dependence may be reflected in differences in the extinction coefficients. Also, since the perchlorate ion is a weaker ligand than the chloride, it should not be able to coordinate as strongly to the nickel(II). Therefore,  $\text{Ni}(\text{TACD})\text{ClO}_4 \cdot \text{H}_2\text{O}$  may be either closer in structure to a trigonal bipyramid than  $\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$  or the water may be weakly bonded to the nickel(II). The differences in the spectra of  $\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$  and  $\text{Ni}(\text{TACD})\text{ClO}_4 \cdot \text{H}_2\text{O}$  in nitromethane may be due to the small differences in their respective structures. However, such an intermediate structure is speculative and would require an X-ray crystallographic study for more definite proof.

The  $\text{Ni}(\text{TACD})(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$  exhibits different physical properties than either  $\text{Ni}(\text{TACD})\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$  or  $\text{Ni}(\text{TACD})\text{ClO}_4 \cdot \text{H}_2\text{O}$ .  $\text{Ni}(\text{TACD})(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$  is blue while the other complexes are green. Also, the magnetic moment of  $\text{Ni}(\text{TACD})(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ ,

(15) F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.*, **6**, 929 (1967).

(16) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

(17) L. Sacconi, *Transition Metal Chem.*, **4**, 247 (1968).

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3.2 BM, is considerably smaller than those of the other two complexes, and it is within the range expected for octahedral nickel(II) complexes.<sup>21</sup> The visible spectrum of this complex is what is expected for a six-coordinated nickel(II) complex in nonaqueous solvents.<sup>21</sup> Accordingly, the assignment of the three bands in methanol are  $\nu_1$ ,  ${}^3T_{2g} \leftarrow {}^3A_{2g}$  (1025 nm),  $\nu_2$ ,  ${}^3T_{1g} \leftarrow {}^3A_{2g}$  (610 nm), and  $\nu_3$ ,  ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$  (384 nm). The shoulder at 850 nm can be assigned to the spin-forbidden transition  ${}^1E_g \leftarrow {}^3A_{2g}$ .

The extinction coefficients for all these bands are unusually high, but similar high extinction coefficients were observed by Collman and Schneider<sup>6</sup> for Co(cyclen) $X_2^+$  complexes. These high extinction coefficients were attributed to the strain in the nitrogen-to-metal bond. Based on models, such strain should also exist in all the metal complexes of TACD.

Since the Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O appears to be a 1:1 electrolyte in nonaqueous solvents and since this complex is six-coordinate, it is likely that one of the nitrate groups is acting as a bidentate. This hypothesis is difficult to confirm by infrared spectral analysis because the ligand bands overlap in all the regions that are diagnostic of bidentate nitrate. Nevertheless, based on spectral, conductivity, and magnetic data, Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O appears to have a distorted octahedral configuration.

The  $Dq$  for Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O, 975 cm<sup>-1</sup>, is much lower than the values found for other linear tetraamines. For example, *cis*-Ni(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> (en = ethylenediamine) has a  $Dq$  of 1050 cm<sup>-1</sup>, while Ni(tren)(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> (tren = tris(2-aminoethylamine)) has a  $Dq$  of 1085 cm<sup>-1</sup>.<sup>22</sup> The  $Dq$  value for Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O is between those of ammonia and water. It is therefore not surprising that NH<sub>3</sub>, CN<sup>-</sup>, and NO<sub>2</sub><sup>-</sup> can displace the TACD from the nickel ion. The addition of 1 drop of 0.1 M NaNO<sub>2</sub> or 0.1 M KCN to an approximately 1 × 10<sup>-3</sup> M solution of the nickel(II) complex in a water or alcohol solution resulted in a rapid decomposition of the complex. A white solid was isolated, and its infrared spectrum was identical with that of TACD. However, a large excess of anhydrous ammonia was required to decompose an absolute ethanol solution of the metal complex. Nevertheless, despite the fact that these complexes appear to be thermodynamically unstable relative to other linear tetraamines, they are stable in water at pH 1. This fact makes these complexes unique since there is no known macrocyclic nickel(II) complex which contains as weak a polydentate ligand as the nickel(II) complexes of TACD and yet is stable in an acid solution.<sup>2-4</sup>

Busch<sup>23</sup> has stated that the tertiary structure of an enzyme might represent "multiple juxtapositional fixedness" (MJF) to the metal ion at the active site; and since macrocyclic ligands coordinated to a metal ion cannot undergo stepwise dissociation, all macrocyclic complexes simulate this attribute of metalloenzymes. Also, it was suggested the donor atom-to-metal bonds in the metalloenzymes should be strained so as to ensure a high positive charge on the metal ion. Since most macrocyclic ligands appear to be strong-field ligands, they may contribute a large amount of electron

density to the metal ion; and, hence, they do not simulate metalloenzymes in this regard. In contrast, all the nickel(II) complexes of TACD have highly strained nickel-to-nitrogen bonds; and, hence, these simple complexes exhibit many of the attributes of a metalloenzyme.

In water the equivalent conductances of Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O and Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O are 195 and 168 cm<sup>2</sup> ohm<sup>-1</sup> equiv<sup>-1</sup>, respectively. In water, the equivalent conductance expected for a 2:1 electrolyte is within the range 220–250 cm<sup>2</sup> ohm<sup>-1</sup> equiv<sup>-1</sup>, while for a 1:1 electrolyte, the equivalent conductance expected is within the range 85–100 cm<sup>2</sup> ohm<sup>-1</sup> equiv<sup>-1</sup>.<sup>24</sup> (Ni(TACD)ClO<sub>4</sub>·H<sub>2</sub>O is insoluble in water.) The conductivity data suggest that water partially displaces the coordinated chloride or nitrate groups. Also, the wavelengths in the visible spectra in water of both complexes are identical suggesting that the same species may exist in solution. Nevertheless, the wide variation of the extinction coefficients for these bands of Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O and Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O indicates that the displacement of the coordinated chloride and the coordinated nitrate by the water molecule does not proceed to completion. The low equivalent conductances also support this observation as well as the nonlinear Onsager plots in water (Table I). The small deviations from Beer's law (~15%) for Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O and Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O can be attributed to the partial displacement of the coordinated nitrate and chloride, respectively. Although it was not possible to dissolve a sufficient amount of the complex in water to observe any bands in the near-infrared region, the visible spectrum obtained nearly matches the visible spectrum of other trigonal-bipyramidal complexes. Therefore, it appears that Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O and Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O are partially converted to the five-coordinated Ni(TACD)H<sub>2</sub>O<sup>2+</sup> in an aqueous solution.

In conclusion, the structures of Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O and Ni(TACD)ClO<sub>4</sub>·H<sub>2</sub>O more closely approximate that of a trigonal bipyramid, while the structure of Ni(TACD)(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O more closely approximates that of an octahedron. (Ni(TACD)Cl<sub>2</sub>·0.5H<sub>2</sub>O and Ni(TACD)ClO<sub>4</sub>·H<sub>2</sub>O are the first nickel(II) complexes containing a tetradentate macrocyclic ligand to have a trigonal-bipyramidal structure.) The large benzyl groups on the nitrogen prevent the nickel(II) ion from attaining a coordination number of 6, except in the case of a small planar bidentate nitrate ion. These complexes are also unique because of their stability with respect to dissociation in acid solution; yet the  $Dq$  values and the ease of displacement of TACD by such ligands as ammonia suggest that TACD is weakly coordinated.

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