PDTA)$^-$ ions, but it is doubtful if this increased splitting is great enough to account for the observed increase in net rotational strength. For Co(EDTP)$^-$, the splitting of the T_{1g} (O_h) level appears to be less than that for Co(EDTA)$^-$. The fact that this compound also shows a marked increase in net rotational strength when compared with that of Co(EDTA)$^-$ supports the contention that the net rotational strengths of the d–d transitions of the model complexes are higher than those for the corresponding transitions of Co(EDTA)$^-$.

It is interesting to note that the results of this study, *i.e.*, that an increase in the rotational strength of the d–d transitions accompanies a decrease in strain in systems such as Co(EDTA)$^-$, are compatible with the results for two other compounds studied earlier by Douglas and Haines.[8] The species Co(en)(ox)$_2^-$ and Co(en)(mal)$_2^-$ also have larger net rotational strengths for the d–d transitions than does Co(EDTA)$^-$. Co(en)(mal)$_2^-$, for which the distortion of the coordinating atoms from octahedral positions might be expected to be the least, has the largest net rotational strength for these transitions. There are also three closely spaced CD peaks of alternating signs in the first-band region, a situation ideally suited for reduced intensities from maximum cancelation. This correlation between the results for the model compounds studied previously and those studied in the present work may be strictly fortuitous, however, since the previously studied model compounds differ from Co(EDTA)$^-$ not only in the strain of the ligand system, but also in arrangement of chelate rings and the nature of coordinated atoms. Either of these latter two changes could be responsible for the observed differences in rotational strengths for these compounds and Co(EDTA)$^-$.

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Nickel(II) Complexes of the New Macrocyclic Ligands *meso*- and *rac*-2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene

BY JACK LEE KARN AND DARYLE H. BUSCH

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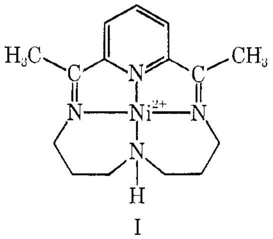
Hydrogenation under mild conditions of the macrocyclic complex 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaenenickel(II), abbreviated Ni(CR)$^{2+}$, yields two new isomeric complexes. The process hydrogenates the two azomethine linkages and produces two asymmetric carbon centers. The observed isomerism is due to the resulting *meso* and racemic ligand forms. Stereochemical considerations and derivatives have permitted identification of the more abundant (~10:1) red isomer as the *meso* structure. The *meso* form folds to admit the donors of bidentate ligands onto pairs of adjacent coordination sites, *e.g.*, oxalate or ethylenediamine. A variety of derivatives Ni(CRH)$X_2 \cdot x H_2O$ [X = Cl, Br, I, ClO_4, BF_4, NO_2, NCS, N_3, or $0.5C_2O_4$] have been prepared and characterized.

Introduction

The condensation of 2,6-diacetylpyridine with 3,3′-diaminodipropylamine in the presence of nickel(II) produces the macrocyclic complex cation 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaenenickel(II), hereafter referred to as Ni(CR)$^{2+}$, structure I.



I

This complex was first prepared as the perchlorate salt by Curry during an investigation of the reaction of linear polyamines with diacetylpyridine in the presence of metal ions.[1,2] The preparations of Ni(CR)(ZnCl$_4$) and Cu(CR)(ZnCl$_4$) were also reported by Rich and Stucky.[3]

Ni(CR)$^{2+}$ is a diamagnetic, planar complex with unhindered axial sites, and derivatives with coordinating anions comprise a series of paramagnetic, tetragonal complexes. The characterization and spectral and magnetic properties of a number of these complexes have been reported earlier.[4] The present communication concerns the reduction of the azomethine linkages of Ni(CR)$^{2+}$ and the characterization of the ligands produced by this reduction and their nickel(II) complexes.

Experimental Section

Materials.—2,6-Diacetylpyridine was obtained from Aldrich Chemical Co., and 3,3′-diaminodipropylamine was obtained from Matheson Coleman and Bell Chemical Co. and used without further purification. Platinum oxide catalyst was obtained from Matheson Coleman and Bell Chemical Co. All other chemicals were the usual reagent grade materials.

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[1] J. D. Curry, Ph.D. Thesis, The Ohio State University, 1964.

[2] J. D. Curry and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 592 (1964).

[3] R. L. Rich and G. L. Stucky, *Inorg. Nucl. Chem. Letters*, **1**, 85 (1965).

[4] J. L. Karn and D. H. Busch, *Nature*, **211**, 160 (1966).

2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaenenickel(II) Perchlorate, Ni(CR)(ClO$_4$)$_2$.—2,6-Diacetylpyridine (13 g, 0.08 mol) was dissolved in 160 ml of ethanol, and nickel(II) chloride hexahydrate (19 g, 0.08 mol) dissolved in 240 ml of water was added. The solution was heated to 65° and 10.5 g (0.08 mol) of 3,3′-diaminodipropylamine was added. The solution became slightly cloudy on addition of the amine. Five milliliters of acetic acid was added, clarifying the solution. The reaction mixture was held at 65° for 6 hr, after which the ethanol was removed in a rotary evaporator by reducing the volume of the solution to about 150 ml. After filtering the remaining solution, 50 ml of concentrated aqueous sodium perchlorate was added, precipitating the crude product. The product was collected by filtration, washed with ethanol, and recrystallized from 300–400 ml of warm (65°) water. After filtering the warm solution, 30 ml of 70% perchloric acid was added and the flask containing the acidified filtrate was allowed to cool slowly. Gray-brown needles of the hydrated product were formed. The product was collected by filtration, washed successively with ethanol and ether, and dried *in vacuo* over P_4O_{10}; yield of brick red anhydrous product, 58%. *Anal.* Calcd for $NiC_{15}H_{22}N_4(ClO_4)_2$: C, 34.91; H, 4.26; N, 10.86; Cl, 13.74. Found: C, 35.36; H, 4.41; N, 10.89; Cl, 14.06.

2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-trienenickel(II) Perchlorate, β Isomer, β-Ni(CRH)(ClO$_4$)$_2$.—Platinum oxide catalyst (0.01 g) was added to a solution of Ni(CR)(ClO$_4$)$_2$ (5.16 g, 0.01 mol) in 300 ml of water. The solution was allowed to shake on a Parr hydrogenation autoclave (about 50 psi of H_2, initially) for 24 hr or until no further pressure drop was observed. The solution was filtered to remove the catalyst, and the volume of the filtrate was reduced until saturated at 100°. On cooling, red crystals of the crude β isomer separated from solution. The slurry was filtered to collect the crude product, and the filtrate was saved for the isolation of the α isomer. The crystals of β-Ni(CRH)(ClO$_4$)$_2$ were washed with ethanol and recrystallized twice from water; yield, 50%. *Anal.* Calcd for $NiC_{15}H_{26}N_4(ClO_4)_2$: C, 34.61; H, 5.00; N, 10.77; Cl, 13.65. Found: C, 34.49; H, 5.21; N, 10.73; Cl, 13.48.

α-Ni(CRH)(ClO$_4$)$_2$.—The filtrate from which the bulk of the β isomer had been removed was heated to 100°, and a solution of sodium oxalate (2.0 g, 0.015 mol) in 30 ml of hot water was added. After stirring for 10 min, the solution was cooled to 10°, and the violet crystals of [β-Ni(CRH)]$_2$ox(ClO$_4$)$_2$ were removed by filtration. The filtrate was heated to 100° and Filter-aid was added. A slight excess of calcium chloride dihydrate was added to precipitate the excess oxalate ion. The resulting slurry was cooled slowly to room temperature, and the calcium oxalate was removed by filtering through extremely fine filter paper. The volume of the filtrate was reduced to about 30 ml by evaporation at 100° and 5 g of sodium perchlorate was added to the hot solution. On cooling slowly, yellow needles of crude α-Ni(CRH)(ClO$_4$)$_2$ formed. The crude product was dissolved in hot acetone and filtered, and ether was added slowly to induce nucleation of crystals of α-Ni(CRH)(ClO$_4$)$_2$; yield, 1–5%. *Anal.* Calcd for $NiC_{15}H_{26}N_4(ClO_4)_2$: C, 34.61; H, 5.00; N, 10.77. Found: C, 34.41; H, 5.10; N, 10.78.

[β-Ni(CRH)]$_2$ox(ClO$_4$)$_2$.—A solution of sodium oxalate (4.0 g, 0.03 mol) in 50 ml of boiling water was added to an aqueous solution of β-Ni(CRH)(ClO$_4$)$_2$ (5.2 g, 0.01 mol), saturated at 100°. The resulting solution was stirred for 10 min at 100° and allowed to cool slowly, whereupon violet crystals of the product separated from solution. The infrared spectrum of the product isolated at this point showed a splitting of the infrared absorption at 3500 cm^{-1} (H_2O, O–H stretch). This band disappeared upon recrystallization from acetonitrile containing about 5% dimethoxypropane; yield, 70%. *Anal.* Calcd for $(NiC_{15}H_{26}N_4)_2C_2O_4(ClO_4)_2$: C, 41.4; H, 5.61; N, 12.07; Cl, 7.65. Found: C, 41.20; H, 5.81; N, 12.08; Cl, 7.74.

2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene, α or β Isomer.—A solution of α- or β-Ni(CRH)(ClO$_4$)$_2$ (2.6 g, 0.005 mol) in 100 ml of water was heated to 80°, and sodium cyanide (1.5 g, 0.03 mol) was added. The solution changes color immediately, proceeding from red-brown, through violet, to the yellow of $Ni(CN)_4^{2-}$. After stirring for 20 min at 80°, the solution was made strongly basic with sodium hydroxide. The solution was allowed to cool, and the product was extracted with twenty 20-ml portions of ether. The ethereal extract was evaporated to dryness and the crude product was redissolved in about 100 ml of ether and filtered. The filtrate was allowed to evaporate slowly, forming white crystals of the product; yield, 60%. *Anal.* Calcd for α-$C_{15}H_{26}N_4\cdot 0.5H_2O$: C, 66.3; H, 9.96; N, 20.65. Found: C, 66.42; H, 10.02; N, 20.67. Calcd for β-$C_{15}H_{26}N_4\cdot H_2O$: C, 64.19; H, 9.99; N, 20.0. Found: C, 64.37; H, 9.95; N, 20.08.

β-Ni(CRH)Cl$_2$, β-Ni(CRH)Br$_2$, β-Ni(CRH)I$_2$, and β-Ni(CRH)(HCOO)$_2$.—Five grams of the potassium salt of the desired anion was dissolved in a minimum amount of water and added to a solution of β-Ni(CRH)(ClO$_4$)$_2$ (5.2 g, 0.01 mol) saturated in water at 100°. The volume of the solution was reduced to about 50 ml, and after cooling, the solution was filtered to remove the precipitated potassium perchlorate. The filtrate was taken to dryness in a rotary evaporator and the solid residue was recrystallized from chloroform, using ether to induce crystallization. The products were moisture sensitive and had to be collected under dried air (drybox); yield, 80%. *Anal.* Calcd for $NiC_{15}H_{26}N_4Cl_2$: C, 45.96; H, 6.68; N, 14.29. Found: C, 45.53; H, 6.80; N, 14.03. Calcd for $NiC_{15}H_{26}N_4Br_2$: C, 37.51; H, 5.46; N, 11.66. Found: C, 37.35; H, 5.58; N, 11.84. Calcd for $NiC_{15}H_{26}N_4I_2$: C, 31.39; H, 4.57; N, 9.74; I, 44.23. Found: C, 31.16; H, 4.77; N, 9.84; I, 44.18. Calcd for $NiC_{15}H_{26}N_4(HCOO)_2$: C, 49.64; H, 6.81; N, 13.63. Found: C, 49.43; H, 6.89; N, 13.65.

β-Ni(CRH)(NCS)$_2$.—A solution of sodium thiocyanate (4.0 g, 0.05 mol) in the minimum amount of acetone was added to an acetone solution of β-Ni(CRH)(ClO$_4$)$_2$ (2.6 g, 0.005 mol), saturated at the boiling point. The crude product precipitated on cooling. The product was recrystallized from chloroform, using ether to induce crystallization; yield, 60%. *Anal.* Calcd for $NiC_{15}H_{26}N_4(NCS)_2$: C, 46.70; H, 5.99; N, 19.22; S, 14.64. Found: C, 46.78; H, 5.98; N, 18.95; S, 15.03.

β-Ni(CRH)(NO$_2$)$_2$·H$_2$O.—A solution of sodium nitrite (14 g, 0.2 mol) dissolved in the minimum amount of hot water, was added to an aqueous solution of β-Ni(CRH)(ClO$_4$)$_2$ (5.2 g, 0.01 mol) saturated at 100°. On cooling, olive-colored crystals of product precipitated from solution. The product was recrystallized from water; yield, 60%. *Anal.* Calcd for $NiC_{15}H_{26}N_4(NO_2)_2H_2O$: C, 41.80; H, 6.49; N, 19.50. Found: C, 42.56; H, 6.43; N, 19.68.

β-Ni(CRH)N$_3$(H$_2$O)ClO$_4$.—A solution of sodium azide (6.0 g, 0.1 mol), dissolved in the minimum amount of water, was added to a solution of β-Ni(CRH)(ClO$_4$)$_2$ (5.2 g, 0.01 mol), saturated in water at 70°. Crystals of gray-green product precipitated from solution on cooling. The product was recrystallized from water; yield, 50%. *Anal.* Calcd for $NiC_{15}H_{26}N_4(ClO_4)N_3(H_2O)$: C, 37.50; H, 5.80; N, 20.40; Cl, 7.40. Found: C, 39.10; H, 5.67; N, 20.65; Cl, 7.27.

β-Ni(CRH)en(ClO$_4$)$_2$ and β-Ni(CRH)(NH$_3$)$_2$(ClO$_4$)$_2$.—Ten milliliters of concentrated ammonium hydroxide solution or 5 ml of ethylenediamine was added to a solution of β-Ni(CRH)(ClO$_4$)$_2$ (2.6 g, 0.005 mol), saturated in water at 60°. Violet crystals of the product formed on cooling. The product was not recrystallized; yield, 60%. *Anal.* Calcd for $NiC_{15}H_{26}N_4(en)(ClO_4)_2$: C, 35.17; H, 5.86; N, 14.49. Found: C, 35.23; H, 6.23; N, 14.41. Calcd for $NiC_{15}H_{26}N_4(NH_3)_2(ClO_4)_2$: C, 32.49; H, 5.78; N, 15.16; Cl, 12.80. Found: C, 32.64; H, 5.82; N, 14.86; Cl, 13.17.

Physical Measurements.—Visible and near-infrared absorption spectra were obtained on a Cary Model 14 recording spectrophotometer. Most of the spectra were run on solid samples as Nujol mulls impregnated on filter paper. Infrared spectra were obtained on a Perkin-Elmer Model 337 recording spectrophotometer, using both Nujol mulls and potassium bromide pellets.

Molecular weight determinations were performed on a Mechrolab Model 301A osmometer.

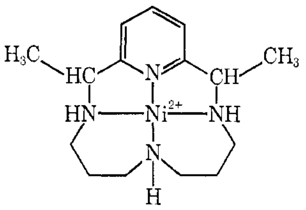
The conductances of the complexes were obtained using an Industrial Instruments Model RC 16B2 conductivity bridge and a conductance cell with a constant of 2.116. Conductances were determined at 25° at 1000 cps on samples $\sim 10^{-3}$ *M* in concentration.

The magnetic susceptibilities of solid samples were determined by the Gouy method. A Consolidated Engineering Corp. electromagnet and power supply operating at 8 A were used to produce the field, and the force developed on the sample was measured using a Sauter Monopan Model 200/.01 balance. The glass Gouy tubes were calibrated with HgCo(NCS)$_4$.

The Gouy balance used to determine solution moments employed a Pacific Electric Motor Co. power supply and Model 12A-HI electromagnet. The force developed on the sample was measured with an Ainsworth semimicro keyboard balance. The magnet was operated at a current of 1.5 A producing a field of 19 kG. The glass sample tube was calibrated with freshly boiled water. Elemental analyses were performed by the Galbraith Analytical Laboratory. Most of the nitrogen analyses were run in this department on a Coleman Model 29 nitrogen analyzer.

Results and Discussion

The catalytic hydrogenation of Ni(CR)(ClO$_4$)$_2$ yields two products, a yellow minor product and a predominate red form, temporarily designated as α- and β-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-trienenickel(II) perchlorate, respectively, structure II. These complexes will be abbreviated hereafter as α- and β-Ni(CRH)(ClO$_4$)$_2$. Both products have the elemental composition NiC$_{15}$H$_{26}$N$_4$(ClO$_4$)$_2$ but show dissimilar infrared spectra in the regions associated with >CH modes. As compared to starting material, the infrared spectra of both products show enhancement of the >NH band at 3180 cm^{-1} and the diminution of a band at 1570 cm^{-1} which presumably contains the C═N– band of the starting material. The complete disappearance of this band is not observed because it coincides with an absorption arising from the pyridine moiety. The volume of hydrogen consumed is consistent with that required for the reduction of both azomethine linkages.

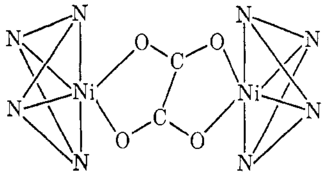


II

The macrocyclic ligands can be displaced from each isomer of the reduced complex by cyanide ion. The product isolated from α-Ni(CRH)(ClO$_4$)$_2$ has an elemental composition corresponding to the formulation C$_{15}$H$_{26}$N$_4\cdot$0.5H$_2$O and a melting point range of 131–134°, while the product isolated from β-Ni(CRH)(ClO$_4$)$_2$ has the composition C$_{15}$H$_{26}$N$_4\cdot$H$_2$O and the melting point range 83–85°C. The infrared spectra of both products show no bands assignable to –NH$_2$ or >C═O modes, indicating that both >C═N– linkages are reduced and not hydrolyzed in each isomer. In the event of incomplete hydrogenation, hydrolysis of the unreduced linkage would probably occur under the strongly basic conditions required to displace the macrocyclic ligands from the nickel ion.

Both α- and β-Ni(CRH)(ClO$_4$)$_2$ are diamagnetic and have visible absorption spectra typical of planar nickel(II) complexes. Peaks are observed at 22,400 and 21,000 cm^{-1} for α- and β-Ni(CRH)(ClO$_4$)$_2$, respectively. The two products are concluded to be stereoisomers derived from the presence of two asymmetric carbon atoms in the structure. The two methyl groups extend on either the same or opposite sides of the plane of the complex (*meso* or racemic, respectively). Assuming, for simplicity, *cis* hydrogenation of the >C═N– linkage, the structures should have the conformations indicated in Figure 1. The detailed stereochemistry of this ligand in its chelate will be the subject of a report to follow.

The ratio of the yields of the two isomeric products is greater than 10:1 favoring the red β isomer. The predominating red isomer forms a violet adduct with oxalate ion having the composition Ni$_2$(CRH)$_2$ox(ClO$_4$)$_2$. This product is paramagnetic, with a moment of 2.99 BM per nickel(II) ion. This oxalate adduct is similar to one reported by Curtis for one of the isomers of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) perchlorate[5,6] and presumably requires the folding of the macrocyclic ligand. The structure of [β-Ni(CRH)]$_2$ox(ClO$_4$)$_2$ is almost certainly similar to that observed for [Ni(en)$_2$]$_2$ox(ClO$_4$)$_2$ (structure III).[7]



III

The nonplanar configuration of the nitrogen donors in [β-Ni(CRH)]$_2$ox(ClO$_4$)$_2$ is indicated by a comparison of the visible absorption spectra of [β-Ni(CRH)]$_2$ox(ClO$_4$)$_2$ and β-Ni(CRH)(HCOO)$_2$, Figure 2. A better averaging of the ligand field is achieved in an adduct of structure III, where the two weakest donors are not *trans* to each other; and the spectrum is typical of pseudooctahedral nickel(II) complexes, having three spin-allowed transitions and a shoulder, usually assigned to the first spin-forbidden transition.[8] Although formate ion occupies about the same place in the spectrochemical series as oxalate ion,[9] situating both substituents on the same axis produces a more pronounced lower symmetry splitting of the O$_h$ term states. As a result, the visible spectrum of β-Ni(CRH)(HCOO)$_2$ is quite typical of those observed by the authors for similar pseudotetragonal nickel(II) complexes.[4,10]

(5) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

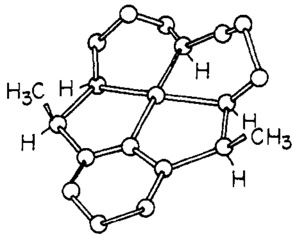
(6) N. F. Curtis, *ibid.*, 4109 (1963).

(7) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 33 (1968).

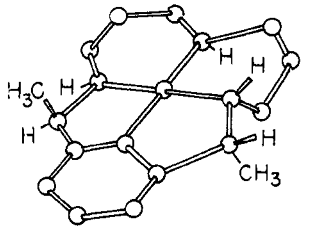
(8) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Inc., New York, N. Y., 1962.

(9) J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960.

(10) J. L. Karn and D. H. Busch, "Electronic Spectra of Tetragonal Nickel(II) Complexes," presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; J. L. Karn, Thesis, The Ohio State University, 1966.



Meso



Racemic

Figure 1.—Stereoisomers of $Ni(CRH)^{2+}$.

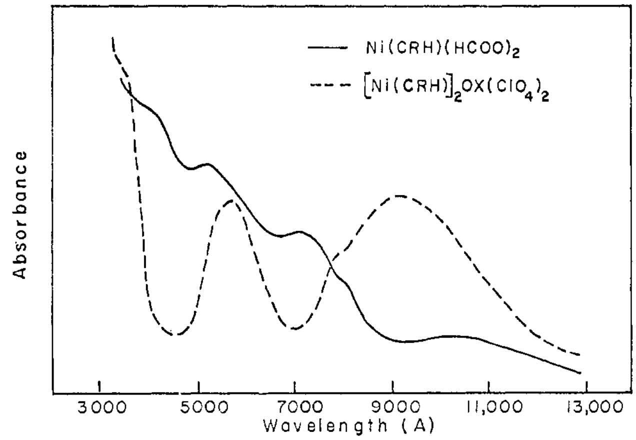


Figure 2.—Visible absorption spectra of solid $[Ni(CRH)]_2ox(ClO_4)_2$ and $Ni(CRH)(HCOO)_2$.

The bridging nature of the oxalate anion in $[\beta\text{-}Ni(CRH)]_2ox(ClO_4)_2$ is indicated by the infrared spectrum. Symmetrically bridged $C_2O_4^{2-}$ should exhibit an infrared spectrum similar to that of the planar $C_2O_4^{2-}$ anion in sodium oxalate. The infrared spectrum of sodium oxalate shows an antisymmetric C–O stretching band at 1640 cm^{-1} and symmetric C–O bands at 1335 and 1316 cm^{-1}.[6] If the symmetry of the oxalate ion is reduced, either by monodentate coordination or bidentate chelation, the antisymmetric band should shift to higher frequencies, and the symmetric, to lower, and the Raman-active bands at 1485 and 1450 cm^{-1} should become infrared active. In the infrared spectrum of $[\beta\text{-}Ni(CRH)]_2ox(ClO_4)_2$, C–H bands in the 1400–1500-cm^{-1} region make it impossible to tell whether the Raman bands of the oxalate ion are infrared active; however, the antisymmetric C–O band is at 1645 cm^{-1}, and the symmetric C–O bands are at 1312 and 1354 cm^{-1}, indicating that the oxalate ion is undistorted. On the basis of earlier work,[5-7] and the supposition that the five-membered ring is favored, structure III has been assumed for $[\beta\text{-}Ni(CRH)]_2ox(ClO_4)_2$.

The visible spectrum of $[\beta\text{-}Ni(CRH)]_2ox(ClO_4)_2$ in acetonitrile is similar to that of the solid complex. The formula weight in this solvent was found to be 950, based on $i = 3$, which compares well with the theoretical value of 929 for the assumed structure. The molar conductance of this complex in acetonitrile is 288 ohm^{-1} at 25°, in excellent agreement with the value of 286 ohm^{-1} determined for the di-univalent electrolyte $Ni(en)_3(BF_4)_2$ in this solvent.

Stereomodels of the *meso* and racemic forms of the reduced complex indicate that the *meso* form of the macrocyclic ligand can fold to leave two vacant *cis* sites on octahedral nickel(II), whereas the racemic form cannot assume such an unstrained nonplanar configuration. Moreover, the racemic form cannot fold without bringing at least one of the methyl groups into close proximity with members of the macrocyclic rings. The fact that the yellow α isomer does not form a *cis* oxalate adduct (a property which is made use of in separation of the isomers) strongly implies that the red β isomer is the *meso* form and the yellow α isomer is the racemic form.

It is surprising that the *meso* isomer is produced in yields so far exceeding those of the racemic form. This may be related to the mechanism of hydrogenation. If one assumes a model for the hydrogenation process involving attack by the complex on activated hydrogen adsorbed on the catalytic substrate, then two possible explanations can be advanced for the preponderant yield of the *meso* isomer. The hydrogenation proceeds very rapidly (about 50% conversion in the first hour) and it may be that both >C=N– groups are reduced on the same contact with the substrate, producing the *meso* form. Alternatively, it may be that the nonplanar methyl group of half-reduced complex sterically inhibits contact between the substrate and the side of the complex from which it protrudes, again leading to the *meso* product.

The properties of $\beta\text{-}Ni(CRH)^{2+}$ and its derivatives have been studied more extensively than those of $\alpha\text{-}Ni(CRH)^{2+}$ owing to the relative abundance of the former. Unlike the unreduced complex $Ni(CR)(ClO_4)_2$, whose aqueous solutions are fully paramagnetic ($\mu = 3.45$ BM at 20°), $\beta\text{-}Ni(CRH)(ClO_4)_2$ exhibits only a partial paramagnetism in coordinating solvents. At 20° this complex has moments of 2.08 BM in pyridine, 2.66 BM in acetonitrile, and 2.11 BM in water. The temperature dependence of the susceptibility in water is consistent with an equilibrium of the type (to be reported in detail elsewhere)[10,11]

$$\underset{\text{(tetragonal, high spin)}}{Ni(CRH)(H_2O)_2^{2+}} \rightleftharpoons \underset{\text{(planar, low spin)}}{Ni(CRH)^{2+}} + 2H_2O$$

with $\Delta H = 4400$ cal/mol and $\Delta S = 15.8$ eu.

$\beta\text{-}Ni(CRH)(NH_3)_2(ClO_4)_2$ and $\beta\text{-}Ni(CRH)en(ClO_4)_2$ are formed by the addition of either ammonium hydrox-

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[11] A detailed review on anomalous magnetic moments of Fe, Co, and Ni has appeared: E. K. Barefield, S. M. Nelson, and D. H. Busch, *Quart. Rev.* (London), **22**, 457 (1968).

ide or ethylenediamine to an aqueous solution of β-Ni(CRH)$(ClO_4)_2$. The infrared spectrum of β-Ni(CRH)$(NH_3)_2(ClO_4)_2$ shows bands at 3380, 3320, 1627, and 1235 cm^{-1}, assignable to the stretching and deformation modes of NH_3. β-Ni(CRH)en$(ClO_4)_2$ shows infrared bands at 3360, 3240, and 1612 cm^{-1} assignable to the $-NH_2$ stretching and deformation modes of the ethylenediamine. These are violet paramagnetic complexes with moments of 3.10 BM for the ammonia complex and 3.11 BM for the ethylenediamine complex. The macrocyclic ligand in β-Ni(CRH)en$(ClO_4)_2$ is presumably folded, as in the oxalate adduct. It is possible that the macrocyclic ligand also folds in the ammonia complex to allow the ammonia molecules to coordinate without interaction from the N–H hydrogens of the macrocycle.

β-Ni$(CRH)^{2+}$ forms a series of tetragonal derivatives with coordinating anions. The anhydrous thiocyanate, chloride, bromide, and iodide derivatives are paramagnetic complexes with room-temperature moments of 3.06, 3.06, 3.13, and 2.79 BM, respectively. The low value of μ_{eff} for Ni(CRH)I_2 will be the subject of a later paper. The addition of azide ion to aqueous solutions of β-Ni(CRH)$(ClO_4)_2$ results in the precipitation of the mixed salt β-Ni(CRH)$N_3(H_2O)ClO_4$. The infrared spectrum of this complex shows a sharp –O–H band at 3400 cm^{-1}, a strong antisymmetric azide stretching band at 2070 cm^{-1}, and the ν_3 and ν_4 fundamentals of perchlorate ion at 1090 and 621 cm^{-1}, respectively. This derivative is paramagnetic with a room-temperature moment of 3.11 BM. The complex presumably has a molecule of water coordinated at one axial site and an azide ion at the opposite site.

The nitrite derivative Ni(CRH)$(NO_2)_2 \cdot H_2O$ is also paramagnetic with a moment of 3.07 BM at room temperature (solid state). The infrared spectrum of this complex indicates the presence of both N- and O-coordinated nitrite ion. For nickel(II) complexes of N-coordinated nitrite ion, Goodgame and Hitchman reported a symmetric N–O– stretch (ν_{as}) at ~1350 cm^{-1} and a very strong antisymmetric stretch (ν_s) at ~1300 cm^{-1}.[12] For O-coordinated nitrite ion ν_s is reported to be ~1350 cm^{-1} and ν_{as} is in the region of 1100–1250 cm^{-1}. Interpretation of the infrared spectrum of β-Ni(CRH)$(NO_2)_2 \cdot H_2O$ in this region is somewhat difficult owing to the presence of C–H bands of the macrocyclic ligand; however, a comparison of the spectra of β-Ni(CRH)Br_2 and β-Ni(CRH)$(NO_2)_2 \cdot H_2O$ reveals additional bands in the spectrum of the latter at 1356, 1300, and 1220 cm^{-1}. The band at 1356 cm^{-1} can be assigned to ν_{as} of $-NO_2^-$ or $-ONO^-$ or both; and the bands at 1300 and 1220 cm^{-1}, to ν_s of $-NO_2^-$ and ν_s of $-ONO^-$, respectively. Electronic spectral studies support the conclusion that both nitro and nitrito coordinations occur in this compound.[10,13]

The dissimilarity of the two axial sites in β-Ni$(CRH)^{2+}$ indicated by the occurrence of both O- and N-coordinated nitrites is an instructive example of some of the chemistry peculiar to these rigid macrocyclic complexes. Stereomodels of *meso*-Ni(CRH) indicate that neither of the axial sites is subject to serious steric hindrance from the hydrocarbon components of the ligand. It is most likely that the dissimilarity between the two axial sites is the result of interactions involving the N–H hydrogens. In *meso*-Ni$(CRH)^{2+}$ at least two and probably all three N–H hydrogens extend on the same side of the plane of the complex and presumably prevent N coordination of the nitrite ion at this site. It is probable that this sort of interaction also hinders coordination by water at this site. This assumption is consistent both with the formation of the mixed salt Ni(CRH)$N_3(H_2O)ClO_4$ and with the partial paramagnetism of aqueous β-Ni$(CRH)^{2+}$, as contrasted to the fully paramagnetic aqueous Ni$(CR)^{2+}$ ion. On the basis of donor strengths of the macrocycles, a converse relationship would be expected for Ni$(CRH)^{2+}$ and Ni$(CR)^{2+}$.

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[12] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **5**, 1303 (1966).

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