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Stereochemistry of the Nickel(II) Complexes of the Macrocycle *meso*-2,12-Dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene

BY EI-ICHIRO OCHIAI[1] AND DARYLE H. BUSCH

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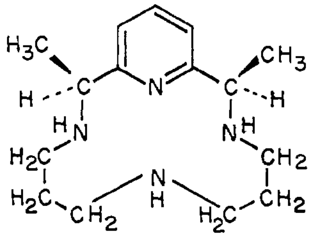
In an earlier paper[2] concerned with the stereochemistry of the cobalt(III) complexes of *meso*-CRH (structure I) it was shown that there are six conceivable configurational isomers in coordinated planar CRH. These arise because of the three tetrahedral secondary nitrogen atoms in the structure. Of the six possible isomers, only two are probable because of the bond angle strain and intraligand steric hindrance in the other structures. The most probable form (II) (see Figure 3) is rather free from bond angle strain and steric hindrance and, moreover, can assume a conformation in which both of the six-membered chelate rings are in the stable chair form. This structure is characterized by the presence of all three of the secondary amine hydrogen atoms on the same side of the plane of coordination. Another form (III) which has the nitrogen atom *trans* to the pyridine nitrogen inverted appears to suffer rather large strain (Dreiding stereomodels) and so is less stable than form II. However, it is also predicted on the basis of conformation relationships that the structure which is obtained by folding form III with retention of configuration at all nitrogen atoms is more stable than that which is obtained by the folding of form II. This means that for the folded or *cis* form, in octahedral coordination, the arrangement of nitrogen configurations found in form III is more stable than that in form II.



I

As reported elsewhere,[3] the hydrogenation over platinum oxide at room temperature of [Ni(CR)](ClO_4)$_2$, where CR is 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene gives rise to a principal product in the form of red crystals and a minor yellow product. The former contains the *meso* ligand (*meso* with respect to the asymmetric carbon atoms) and the latter contains the racemic ligand.[3] Only the *meso* form is of concern here. The red isomer of the *meso*-CRH complex is called the α isomer, α-[Ni(CRH)](ClO_4)$_2$. This compound is allowed to react with sodium oxalate in boiling neutral water and gives a violet dimeric oxalato complex [{Ni(CRH)}$_2$(C_2O_4)](ClO_4)$_2$·H_2O in 15–20 min. Upon treating this oxalato complex with perchloric acid, a yellow complex is obtained. It has the formula [Ni(CRH)](ClO_4)$_2$ and is called the β isomer. This isomer, β-[Ni(CRH)](ClO_4)$_2$, gives rise to the same dimeric oxalato complex upon reaction with sodium oxalate, but the reaction is much more facile, occurring at room temperature in a few minutes.

In acetone solution the β isomer remains unchanged over a few hours, but it converts to the α isomer upon the addition of base. Lutidine was selected because of its reluctance to coordinate. However, the α isomer does not convert to the β isomer in basic media.

In addition to these chemical differences, the isomers also show a few differences in physical properties. The infrared spectra show substantial differences, especially in the ν(N–H), ν(C–H), and δ(C–H) bonds, as shown in Figure 1. The electronic spectra in the visible region are shown in Figure 2. These differences in physical and chemical properties indicate that these two substances actually are isomers.

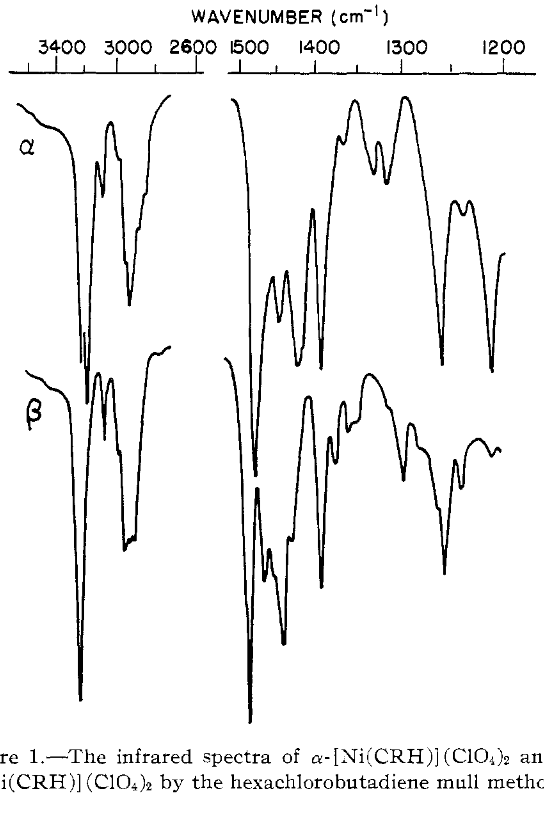


Figure 1.—The infrared spectra of α-[Ni(CRH)](ClO_4)$_2$ and β-[Ni(CRH)](ClO_4)$_2$ by the hexachlorobutadiene mull method.

The fact that the β isomer converts to the α isomer in basic media while the reverse reaction does not occur requires (1) that the α and β isomers differ from one another in the configuration of at least one of the

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[2] E. Ochiai and D. H. Busch, *Inorg. Chem.*, **8**, 1474 (1969).

[3] J. L. Karn, Thesis, The Ohio State University, 1966; J. L. Karn and D. H. Busch, *Inorg. Chem.*, **8**, 1149 (1969).

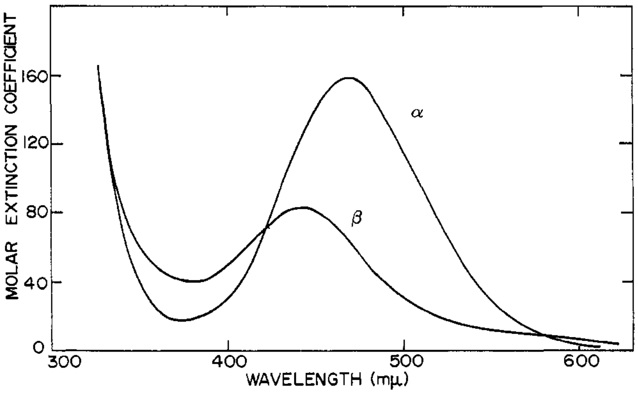

Figure 2.—The electronic spectra of α-$[\mathrm{Ni(CRH)}](\mathrm{ClO_4})_2$ and β-$[\mathrm{Ni(CRH)}](\mathrm{ClO_4})_2$ in acetone at room temperature.

secondary amine nitrogens[4] and (2) that the α isomer is substantially more stable than the β isomer. These considerations lead to the assignments of structure I to the α isomer and structure II to the β isomer. This assignment is consistent with the theoretical expectation that form II is more stable than form III when the *meso*-CRH is coordinated in the planar fashion. The readiness with which the β isomer (III) forms the oxalato *cis* complex, in which CRH is folded, is consistent with the structural assignments. Structure III (the β isomer) can be folded into the most stable *cis* form without the inversion of any of the nitrogen atoms. To effect the same transformation the α isomer (II) must undergo inversion of that nitrogen atom in the position *trans* to pyridine. This is a slow process in neutral aqueous media. Therefore, this reaction requires heating in order to proceed in reasonable time. The role of the basicity of sodium oxalate in the formation of the oxalato complex when this must be accompanied by the inversion of nitrogen configuration has been discussed earlier.[2] The configurational relationships are summarized in Figure 3.

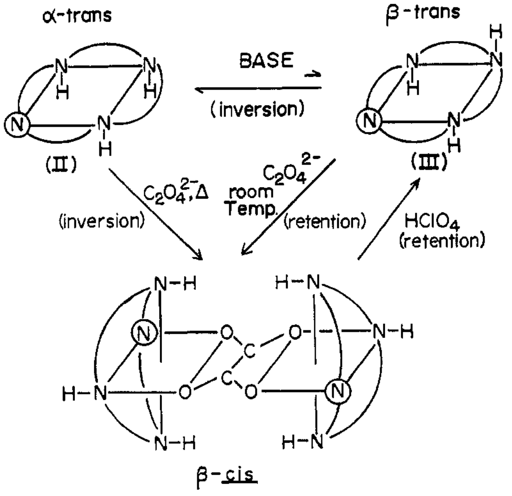

Figure 3.—The stereochemistry of $[\mathrm{Ni(CRH)}]$ complexes.

Experimental Section

Preparation of α-$[\mathrm{Ni(CRH)}](\mathrm{ClO_4})_2$.—This compound was prepared by hydrogenation of $[\mathrm{Ni(CR)}](\mathrm{ClO_4})_2$ according to the method of Karn.[3] In the process (H_2 over platinum oxide catalyst), a minor product $[\mathrm{Ni}(\textit{rac}\text{-}\mathrm{CRH})](\mathrm{ClO_4})_2$ was also formed, but only the major isomer $[\mathrm{Ni}(\textit{meso}\text{-}\mathrm{CRH})](\mathrm{ClO_4})_2$ is discussed in the text and hereafter in this report. The crude product was recrystallized from hot water. In recrystallization, care should be taken not to heat for a prolonged period in air because it has been observed that the coordinated CRH ligand is oxidized to form a new ligand with one C=N bond under these conditions. The product was isolated as red needles or plate crystals. *Anal.* Calcd: C, 34.62; H, 5.04; N, 10.77. Found: C, 34.41; H, 5.10; N, 10.80. Molar conductivity (in H_2O): 221 mho cm^2/mol (2:1 electrolyte).

Preparation of β-*cis*-$[\{\mathrm{Ni(CRH)}\}_2\mathrm{C_2O_4}](\mathrm{ClO_4})_2$.—This compound was also prepared by the method of Karn.[3] It exists as violet crystals. *Anal.* Calcd: C, 41.36; H, 5.64; N, 12.06. Found: C, 41.42; H, 5.83; N, 11.82.

Preparation of β-$[\mathrm{Ni(CRH)}](\mathrm{ClO_4})_2$.—The violet oxalato complex (1.0 g) was suspended and shaken in 30 ml of perchloric acid solution (2:1 concentrated $HClO_4$–H_2O). In a few minutes, yellow crystals separated from the slurry and the shaking was continued until all of the violet material disappeared. The yellow crystals were collected on a filter funnel, washed with water and ethanol, and air dried. *Anal.* Calcd: C, 34.62; H, 5.04; N, 10.77. Found: C, 34.88; H, 5.10; N, 10.98. Molar conductivity (in H_2O): 212 mho cm^2/mol (2:1 electrolyte).

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[4] J. Halpern, A. M. Sargeson, and K. P. Turnbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966); D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967); L. G. Warner, N. J. Rose, and D. H. Busch, *ibid.*, **89**, 703 (1967).

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Observations on Reactions of $(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_9)$ Isomers with Electrophiles

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Several substitution reactions were attempted on the newly discovered "π-sandwich" cobalt(III) complex containing the $C_5H_5^-$ and $B_7C_2H_9^{2-}$ anions, $(\pi\text{-}C_5H_5)Co(\pi\text{-}1,6\text{-}B_7C_2H_9)$ (I).[1] It was the intent of this study to investigate substitution reactions similar to those which were successful with ferrocene and other metallocenes and to see if the carborane cage or the cyclopentadiene ring of compound I is more reactive with electrophiles.

Acetylation

Friedel–Crafts acylation of compound I with acetyl chloride and aluminum chloride in methylene chloride solvent produced an acetyl derivative, $(C_5H_5)Co(B_7C_2H_8COCH_3)$ (II). The infrared spectrum of the red compound II contained a sharp carbonyl absorption band at 1630 cm^{-1}.

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[1] M. F. Hawthorne and T. A. George, *J. Am. Chem. Soc.*, **89**, 7114 (1967).