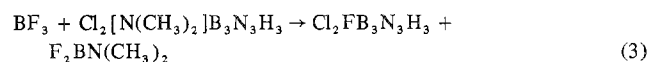


BF_3 is used instead, $\text{Cl}_2\text{FB}_3\text{N}_3\text{H}_3$ is obtained in 20% yields according to eq 3. The low yield of $\text{Cl}_2\text{FB}_3\text{N}_3\text{H}_3$ is proba-



bly related to the disproportionation of the product to form $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$ and $\text{ClF}_2\text{B}_3\text{N}_3\text{H}_3$. Both the infrared and nmr spectra of $\text{Cl}_2\text{FB}_3\text{N}_3\text{H}_3$ vary with time. Similar results⁸ have been previously observed for the compound.

The ^1H nmr data for the series of compounds $\text{Cl}_{3-x}[\text{N}(\text{CH}_3)_2]_x\text{B}_3\text{N}_3\text{H}_3$ ($x = 0-3$) are given in Table I. The chemical shift of the NH protons is dependent on the nature and the degree of substitution. In contrast, the chemical shift of the CH protons of the $\text{N}(\text{CH}_3)_2$ group is constant throughout the series. As the number of $\text{N}(\text{CH}_3)_2$ groups bound to the borazine ring increases, the NH resonance moves to higher field. However, it should be noted that an "additivity effect"¹ for each $\text{N}(\text{CH}_3)_2$ group is not observed. There is no regular change in the NH chemical shift with the degree of substitution. Similar results¹ have been noted for the series $\text{H}_{3-x}[\text{N}(\text{CH}_3)_2]_x\text{B}_3\text{N}_3\text{H}_3$. The chemical shift of the CH proton in the $\text{N}(\text{CH}_3)_2$ group remains constant throughout the series $\text{Cl}_{3-x}[\text{N}(\text{CH}_3)_2]_x\text{B}_3\text{N}_3\text{H}_3$. This observation might imply that the electron pair on the exocyclic nitrogen is delocalized into the ring to the same extent in all the derivatives. A second explanation, meta $\text{N}(\text{CH}_3)_2$ groups have little effect on each other, can also be offered. There are even oth-

er possible interpretations. Probably, very little use should be made of these observations. However, it should be noted that similar results are observed for $\text{C}_6\text{H}_5[\text{N}(\text{CH}_3)_2]$ and $\text{C}_6\text{H}_4[\text{N}(\text{CH}_3)_2]_2$.

The relative thermal stability of the compounds in the series is $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3 \sim [\text{N}(\text{CH}_3)_2]_3\text{B}_3\text{N}_3\text{H}_3 > \text{Cl}_2[\text{N}(\text{CH}_3)_2]_2\text{B}_3\text{N}_3\text{H}_3 \gg \text{Cl}[\text{N}(\text{CH}_3)_2]_2\text{B}_3\text{N}_3\text{H}_3$. A similar order was observed for the simple dimethylamino derivatives.³ This order might be related to the strengths of the boron-chlorine and boron-nitrogen (exocyclic) bonds, considering the substituent effects. The electron-donating ability of the $\text{N}(\text{CH}_3)_2$ group could weaken the boron-chlorine bond, thus increasing the possibility of producing HCl and eventually $\text{N}(\text{CH}_3)_2\text{H}_2\text{Cl}$, an observed decomposition product. When two $\text{N}(\text{CH}_3)_2$ groups are present, $\text{Cl}[\text{N}(\text{CH}_3)_2]_2\text{B}_3\text{N}_3\text{H}_3$ is so unstable that one can monitor the decomposition using successive infrared scans. There is no doubt that the instability of $\text{Cl}[\text{N}(\text{CH}_3)_2]_2\text{B}_3\text{N}_3\text{H}_3$ limits its usefulness as a synthetic intermediate.

Acknowledgments. We wish to thank the National Science Foundation, Grant No. GP-20200, for financial support of the research.

Registry No. $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$, 933-18-6; $\text{N}(\text{CH}_3)_2\text{H}$, 124-40-3; $\text{Cl}_2[\text{N}(\text{CH}_3)_2]_2\text{B}_3\text{N}_3\text{H}_3$, 51310-48-6; B_2H_6 , 19287-45-7; $\text{HCl}_2\text{B}_3\text{N}_3\text{H}_3$, 15259-40-2; $\text{Cl}[\text{N}(\text{CH}_3)_2]_2\text{B}_3\text{N}_3\text{H}_3$, 51310-49-7; $[\text{N}(\text{CH}_3)_2]_3\text{B}_3\text{N}_3\text{H}_3$, 7360-02-3; BCl_3 , 10294-34-5; BF_3 , 7637-07-2; $\text{Cl}_2\text{FB}_3\text{N}_3\text{H}_3$, 51310-50-0; $\text{ClF}_2\text{B}_3\text{N}_3\text{H}_3$, 51310-51-1.

Notes

Contribution from The Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

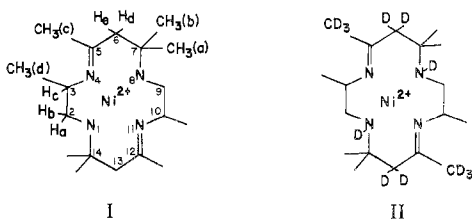
Conformations of the 3,10-meso- and (3R,10R)-3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) Complexes

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Complex I, 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) ion, exists as the non-interconvertible 3,10-meso and 3,10-racemic isomers, since the complex has two asymmetric carbons at the 3 and 10 positions.^{2,3} In this study the stereochemistry of the 3,10-meso and 3R,10R complexes has been elucidated by detailed analyses of their pmr spectra.⁴



(1) On leave from the Department of Chemistry, Fukushima University, Fukushima, Japan.

(2) (a) M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1204 (1962); (b) N. F. Curtis, D. A. Swann, T. N. Waters, and I. E. Maxwell, *J. Amer. Chem. Soc.*, 91, 4588 (1969).

(3) H. Ito and J. Fujita, *Bull. Chem. Soc. Jap.*, 44, 741 (1971).

It is known that the imine methyl protons and the methylene protons adjacent to the imine bonds in analogous macrocyclic nickel(II) complexes are easily deuterated in basic D_2O solutions⁵⁻⁷ and the appropriate deuterated ($-d_{12}$) derivatives (II) have been prepared for these studies. Spectra 1 and 2 in Figure 1 are those of the 3,10-meso complex and its deuterated derivative, respectively. Spectral parameters for both complexes are summarized in Tables I and II.

Direct evidence has not been previously reported on the positions of the methyl groups on the diaminopropane residues for the meso ligand (2,9 or 3,10). We have observed two kinds of couplings between the amine proton and the methylene protons of the five-membered chelate ring for the *trans*-dichloro- and *trans*-dicyanocobalt(III) complexes containing this ligand, indicating that the diaminopropane residue methyl groups must be located at the 3 and 10 positions.⁸

Methyl Protons. The pmr spectrum of each isomer shows three singlets and one doublet of equal intensity in the high-field region. These are due to the eight pairwise-equivalent methyl groups within each isomer. This suggests that the 3,10-meso and 3R,10R complexes have C_i and C_2 symmetry, respectively. The imine methyl protons are easily assigned

(4) Though the pmr data of these complexes were reported by Curtis, *et al.*,^{2b} their results were limited to the methyl proton resonances. Some of their assignments are shown to be incorrect by this study.

(5) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, 90, 6938 (1968).

(6) E. K. Barefield and D. H. Busch, *Inorg. Chem.*, 10, 108 (1971).

(7) V. L. Goedken and D. H. Busch, *Inorg. Chem.*, 10, 2679 (1971).

(8) T. Ito and D. H. Busch, to be submitted for publication.

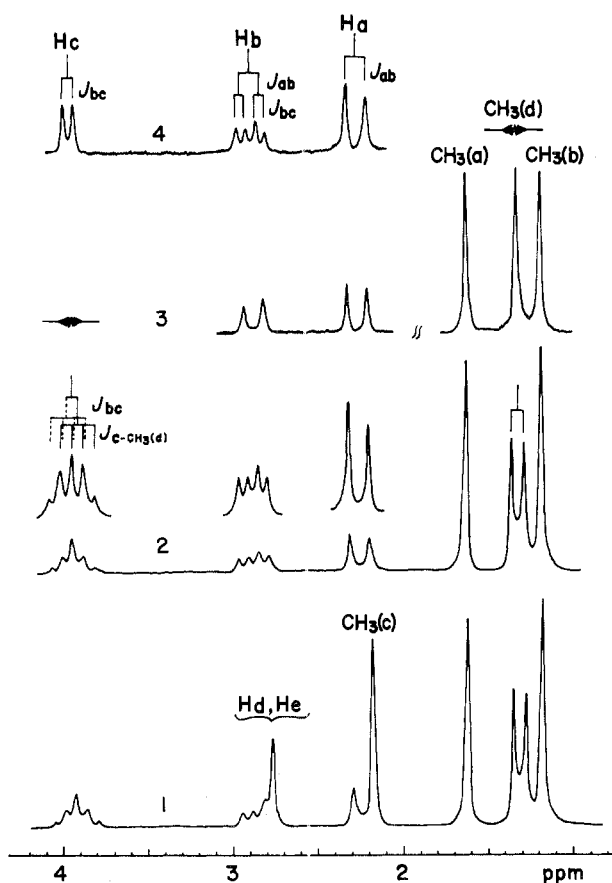


Figure 1. (1) The 100-MHz pmr spectrum of the chloride salt of the 3,10-meso complex in neutral D_2O , (2) the spectrum of the deuterated complex, (3) the double-resonance spectrum by irradiation at 3.94 ppm, and (4) the double-resonance spectrum by irradiation at 1.31 ppm.

Table I. Pmr Spectral Data for the 3,10-Meso Complex^a

| Assignment | Signal shape | Chem shift, ppm | Rel intens | Coupling const, Hz |
|-----------------|---------------------|---------------------|------------|-------------------------|
| $CH_3(a)^b$ | Singlet | 1.62 | 3 | $J_{ab} = 11.8$ |
| $CH_3(b)^c$ | Singlet | 1.17 | 3 | $J_{bc} = 6.0$ |
| $CH_3(c)$ | Singlet | 2.18 ^d | 3 | $J_{ac} \approx 0^f$ |
| $CH_3(d)$ | Doublet | 1.31 | 3 | $J_{CH_3(d)-H_c} = 7.0$ |
| H_2c^c | Doublet | 2.24 ^{d,e} | 1 | |
| H_2b^b | Doublet of doublets | 2.86 ^{d,e} | 1 | |
| H_c | Five-line multiplet | 3.94 | 1 | |
| H_d and H_e | Broad singlet | 2.77 ^d | 2 | |

^a Data for the chloride salt in D_2O . ^b Axial. ^c Equatorial. ^d Signals overlapped. ^e Observable without overlapping in deuterated complex. ^f Less than 0.5 Hz.

by comparison of the spectra of nondeuterated and deuterated samples. Specific assignments for the geminal dimethyl groups ($CH_3(a)$ and $CH_3(b)$) can be inferred from the effect of the magnetic anisotropy of d^8 transition metal ions⁵ and also from the assignments for the geminal dimethyl groups of (2*R*,9*R*)-2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) complex on the basis of the occurrence of a nuclear Overhauser effect.^{8,9} The singlet at the highest field is assigned to the equatorial methyl protons ($CH_3(b)$), and the remaining intense singlet (other than the $CH_3(c)$ singlet), to the axial member ($CH_3(a)$).¹⁰

(9) T. Ito and D. H. Busch, *J. Amer. Chem. Soc.*, **95**, 7528 (1973).

Table II. Pmr Spectral Data for the 3*R*,10*R* Complex^a

| Assignment | Signal shape | Chem shift, ppm | Rel intens | Coupling const, Hz |
|-----------------|---------------------|-------------------|------------|-------------------------|
| $CH_3(a)^b$ | Singlet | 2.20 ^d | 3 | $J_{ab} = 11.5$ |
| $CH_3(b)^c$ | Singlet | 1.18 | 3 | $J_{bc} = 5.5$ |
| $CH_3(c)$ | Singlet | 2.14 | 3 | $J_{ac} \approx 0^e$ |
| $CH_3(d)$ | Doublet | 1.55 | 3 | $J_{CH_3(d)-H_c} = 6.8$ |
| H_2c^c | Doublet | 2.21 ^d | 1 | |
| H_2b^b | Doublet of doublets | 2.60 | 1 | |
| H_c | Five-line multiplet | 3.97 | 1 | |
| H_d and H_e | Broad singlet | 2.93 | 2 | |

^a Data for the chloride salt in D_2O . ^b Axial. ^c Equatorial. ^d Signals overlapped. ^e Less than 0.5 Hz.

Methylene Protons of the Six-Membered Rings. On the basis of the deuteration experiments, the broad singlet (at 2.77 ppm for the 3,10-meso complex, at 2.93 ppm for the 3*R*,10*R* complex) can be assigned to the H_d and H_e protons.

Methine and Methylene Protons of the Five-Membered Chelate Rings. To explain the spectra due to these protons, spin-decoupling experiments have been carried out using deuterated samples. Decoupling of the $CH_3(d)$ resonance produces a three-spin system due to the protons labeled H_a , H_b , and H_c . The analyses of these ABX systems have provided not only unambiguous signal assignments but also significant information on the conformations of the five-membered chelate rings. Since the analyses of the three-spin systems for the 3,10-meso and 3*R*,10*R* complexes are quite similar, we present a detailed description only for the 3,10-meso isomer.

As is easily seen in spectrum 2 (Figure 1), the three-spin system consists of a five-line multiplet (3.94 ppm), a doublet of doublets (2.86 ppm), and a doublet (2.24 ppm). The relative integrated intensities of these three signals are equal and each is one-third that of a methyl signal. When the multiplet at 3.94 ppm is irradiated, the $CH_3(d)$ doublet at 1.31 ppm is converted to a singlet, which has the same intensity as the other two singlets (spectrum 3). Therefore the decoupled multiplet can safely be assigned to H_c . The remaining two signals are assigned to the methylene protons (2.24 (H_a) and 2.86 (H_b) ppm). The same irradiation converted the doublet of doublets (H_b) into a doublet, while it left the H_a doublet unchanged. The resulting spectrum of the H_a and H_b protons corresponds to an AB pattern with a coupling constant of 11.8 Hz, a reasonable value for geminal methylene protons.¹¹

Spectrum 4 is obtained by irradiation at the $CH_3(d)$ signal. This decoupling converts the H_c multiplet into a doublet ($J = 6.0$ Hz) with the same coupling constant as one of those in the doublet of doublets (H_b). This represents vicinal coupling and $J_{bc} = 6.0$ Hz. This double-resonance spectrum shows only eight lines in the region of the three-spin system, whereas it should consist of twelve lines plus three weak combination bands. The remaining coupling (J_{ac}), which should appear in both the H_a and H_c signals when the $CH_3(d)$ doublet is decoupled, has not been observed in measurable magnitude. This indicates that the value of J_{ac} is close to zero (less than 0.5 Hz).

The difference in chemical shifts between the extreme high-

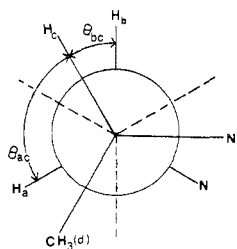
(10) The assignments for the imine methyl and the axial component of geminal dimethyl groups of the 3*R*,10*R* complex are contrary to those given by Curtis, *et al.*^{2b}

(11) A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965).

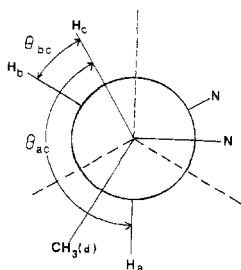
and low-field signals in the five-line multiplet due to H_c is 26.9 Hz. This value should be equal to $3J_{CH_3(d)-H_c} + J_{bc}$, if the spin-spin coupling scheme described above is correct. The observed value for this difference and the value of J_{bc} give a value for $J_{CH_3(d)-H_c}$ of 7.0 Hz, which is the same as the observed coupling constant for the $CH_3(d)$ doublet at 1.31 ppm.

Conformation of the Five-Membered Chelate Rings. There are two possible conformers for the 3,10-meso complex: those with $CH_3(d)$ equatorial and axial, respectively, to the five-membered chelate ring. Since one of the nitrogen atoms is an imine nitrogen, the five-membered chelate rings of this complex are expected to have distorted gauche forms. The vicinal spin-spin coupling for this three-spin system differs for the two conformers. The $CH_3(d)$ axial conformer would provide two distinct *distorted gauche* couplings, whereas the $CH_3(d)$ equatorial conformer would provide one *distorted gauche* and one *distorted trans* coupling. Coupling constants have been reported for other metal complexes that have structures similar to structural components of the present complexes.¹²⁻¹⁴ The reported values for gauche and trans coupling (dihedral angles θ 's are close to 60 and 180°, respectively) are approximately 3.8-4.4 and 10.0-12.4 Hz, respectively.

The observed values for J_{bc} and J_{ac} indicate that the five-membered rings are substantially distorted. The value of J_{bc} is close to, but a little larger than, those commonly observed for gauche couplings. This complex can have either of two conformational forms: one (structure III) involves an axial methyl group and the other (structure IV) an



III



IV

equatorial methyl group. It must be emphasized that the very small value of J_{ac} suggests that θ_{ac} is a good bit larger than 60° but substantially less than 120° (around 90° if the original Karplus equation¹⁵ is assumed with $J_{ac} = 0$). These facts lead uniquely to structure III. It is also concluded that the H_a (2.24 ppm) and H_b (2.86 ppm) protons are the equatorial and axial methylene protons, respectively. The difference in the chemical shifts between these two protons may be explained in terms of the magnetic anisotropy of square-planar d^8 transition metal ions.⁵ It is also worth mentioning that detailed stereochemical analysis of this structure reveals that the absolute configuration of adjacent asymmetric nitrogen and carbon atoms must be *R* and *S* or *vice versa*.

A similar analysis based on spin-decoupling experiments has been applied to the three-spin system of the deuterated 3*R*,-10*R* complex (Table II), leading to the conclusion that the five-membered chelate ring has a distorted δ gauche form

(12) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 3184 (1969).

(13) T. Ito and N. Tanaka, *J. Inorg. Nucl. Chem.*, **32**, 155 (1970).

(14) T. Ito, H. Saito, and H. Ito, *Inorg. Nucl. Chem. Lett.*, **6**, 607 (1970).

(15) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(IUPAC, 1966) with the $CH_3(d)$ group axial. This accords well with the result of the preliminary X-ray work on this isomer by Curtis, *et al.*^{2b} The observed coupling constants for the three-spin system of the 3*R*,10*R* isomer are $J_{ab} = 11.5$, $J_{bc} = 5.5$, and $J_{ac} \approx 0$ Hz. The similarity of these values to those of the 3,10-meso isomer suggests that the conformations of the two sets of five-membered chelate rings are quite similar. The absolute configuration of the secondary amine nitrogen atoms is *S*.

Experimental Section

Materials. (3*R*,10*R*)-3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) perchlorate was prepared by the template reaction,^{2a} whereas the 3,10-meso complex perchlorate was synthesized by the direct reaction of the free-ligand and salt with the nickel(II) salt.^{2b} The chlorides were prepared from the perchlorates by ion exchange (Dowex 1X8).

Deuteration Experiments. Deuteration was accomplished by dissolving the chloride salts in D_2O at pH 10-11 (anhydrous Na_2CO_3 or NaOD). The secondary amine protons, the imine methyl protons, and the methylene protons of six-membered rings exchanged within 24 hr at room temperature, as shown by the intensities of their pmr signals.

Measurements. All pmr spectra were obtained in D_2O solutions using a JEOL pmr spectrometer, Model JNM-MH-100. Chemical shifts were measured relative to sodium 2,2-dimethyl-2-silapentane-5-sulfonate internal standard.

Acknowledgment. We wish to thank the National Science Foundation for financial support of this work.

Registry No. 3,10-meso complex ion, 51349-38-3; 3*R*,10*R*-complex ion, 51349-39-4.

Contribution from the Instituto de Quimica, Universidade de Sao Paulo, Sao Paulo, Brazil, and the Department of Chemistry, University of Missouri, Columbia, Missouri 65201

Dissociation Kinetics of Pentacyanoiron(II) Complexes of Ammonia and Methylamine

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For the purpose of studying metal-to-ligand back-bonding interactions we recently investigated the aqueous kinetics of amine exchange in complexes of the general formula $Fe(CN)_5 \cdot L^{n-}$, where iron is in the oxidation state II and *L* is an aromatic N heterocycle.¹ In that work the specific rates of breakage of the bonds between iron(II) and several unsaturated amines were shown to correlate with the energies of observed metal-to-ligand electron-transfer transitions in the complexes. The relationship was ascribed to an increase in $d\pi \rightarrow p\pi$ back-bonding capacity along the series of ligands 4-methylpyridine, pyridine, isonicotinamide, and pyrazine. However, it was not possible to assess the effect of the base strengths of the leaving ligands on their rates of dissociation.

We now present a study of the dissociation kinetics of the pentacyanoiron(II) complexes of two saturated nitrogen bases, methylamine and ammonia. In these complexes back-bonding to the leaving group is impossible. The results permit the estimate of an upper limit to back-bonding stabi-

(1) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039, 2084 (1973).