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Elucidation of Structural Relationships and Assignment of ^{1}H NMR Spectra of Transition-Metal Cyclidene Complexes by 2-D NMR Techniques

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The complete ^{1}H NMR spectra of five nickel cyclidene macrocyclic complexes are assigned by using DEPT (distortionless enhancement by polarization transfer) and 2-D NMR techniques: ^{1}H–^{13}C shift correlation, COSY (correlated shift), and NOESY (nuclear Overhauser enhanced correlated shift). The ^{1}H NMR assignments are consistent with the complexes having an overall saddle shape with the two saturated six-membered rings (composed of nickel, two nitrogens, and a trimethylene chain) adopting a chair and a boat configuration similar to those observed in the X-ray crystal structures of these complexes. The ^{1}H NMR spectra can distinguish between two possible configurations for the bridging moiety (lid-off and lid-on). The vinyl methyl groups, labeled as O and N, have a chemical shift separation greater than 0.35 ppm for a lid-off configuration and less than 0.15 ppm for a lid-on configuration. The complex [2,9,10,17,19,25,33,34-octamethyl-3,6,13,16,20,24,27,31-octaazapentacyclo[16.7.7.$2^{8,11}$.$2^{3,6}$.$2^{13,16}$]-octatriaconta-1,8,10,17,19,24,26,31,33-nonaene–$\kappa^4 N$]nickel(II) hexafluorophosphate (V) has a bridge that consists of durene (tetramethylbenzene) supported by two piperazine rings. Those protons on the piperazine rings that are in close proximity to the arene ring are shifted upfield due to shielding contributions of the ring currents.

Introduction

The broad family of transition-metal complexes with the cyclidene ligands has provided the opportunity to study a variety of phenomena. These include template-directed synthesis reactions,[1] dioxygen binding and activation,[2,3] and host–guest chemistry.[4–7] A large inventory of these complexes presently exists and many have been fully characterized by a variety of techniques including X-ray crystallography and infrared, UV–visible, ESR, ^{13}C NMR, and ^{1}H NMR spectroscopy.[8,9] Due to the number of protons in these complexes and the concomitant ambiguities in their assignments, ^{1}H NMR has been of limited use in their characterization. Total assignment of the proton spectra of the cyclidene complexes would make available a highly sensitive probe capable of furnishing a great deal of structural information. NMR spectrometers operating below 300 MHz are incapable of resolving the numerous overlapping signals typically seen in the proton NMR spectra of these complexes. Even when the overlap of signals can be resolved, accurate assignments are extremely difficult. Two-dimensional NMR techniques provide the means to eliminate signal overlap and yield additional information that is critical to solving this challenging problem. In this paper is described the complete assignment of the proton NMR spectra of five cyclidene complexes (Figure 1) using the NMR technique called DEPT (distortionless enhancement by polarization transfer) and the 2-D NMR techniques: ^{1}H–^{13}C shift correlation, COSY (correlated shift), and NOESY (nuclear Overhauser enhanced correlated shift).[10–12,14] These assignments have resulted in conclusions regarding intramolecular spatial relationships within the cyclidene complexes.

Results and Discussion

The absolute assignments of resonances in the proton NMR spectra of the cyclidene complexes, whose structures are shown in Figure 1, have awaited the development of NMR field strengths that are high enough, and techniques that are powerful enough, to facilitate adequate resolution and bases for the assignment of signals. The complexity of the problem may be apparent if one realizes that the cyclidene complexes reported here have as many as 45 protons. In addition to the identification of detailed structural features, such as lid-on and lid-off isomerism,[1,13] information concerning solution behavior, notably inclusion complex formation, may be accessible from proton spectra. This would be strictly analogous to the previously reported use of chemical shift change in ^{13}C NMR absorptions as a probe for investigating host–guest association.[5] However, since ^{1}H NMR spectroscopy is inherently more sensitive than ^{13}C, these spectra may be more useful in delineating the subtle changes that occur during inclusion complex formation.

The first step in assigning the signals in the proton spectra has been to assign the resonances in the far less complicated ^{13}C spectra. The cyclidene complexes, almost exclusively, possess mirror symmetry; therefore, the number of carbon resonances is relatively low. Off-resonance decoupled ^{1}H–^{13}C NMR and ^{13}C enrichment studies have been used in this regard, and the assignment of the majority of the ^{13}C resonances has been accomplished previously.[2,4] An additional technique that helps rapid general identification of ^{13}C signals is DEPT.[12] The phase properties of the magnetization of quaternary carbon atoms and of CH, CH_2, and CH_3 groups may be displayed by the proper choice of the pulse angle, θ.[10] An example is shown in Figure 2. The resonances of the methylene carbons adjacent to nitrogen atoms in the complex are commonly found in the region of 40–60 ppm. The signals corresponding to those methylenes not adjacent to nitrogen are located from 28 to 35 ppm, and methyl group signals are consistently found in the range of 15–22 ppm unless they are adjacent to an electronegative atom, as are the methyl groups on the nitrogens in complexes I and II whose resonances appear at 40 ppm. As expected, quaternary carbon resonances reside at much lower fields. Once assignment of the ^{13}C spectra is completed, 2-D ^{1}H–^{13}C correlated shift experiments can be used to assign the proton signals to the carbon atoms to which they are bonded.[10,14]

When the Larmor frequencies of the two different nuclei can be related through scalar coupling, this heteroscalar correlated 2-D NMR experiment is ideal for making assignments.[12] The result of applying this method to complex I is shown in Figure 3. The abscissa in the correlation diagram corresponds to the

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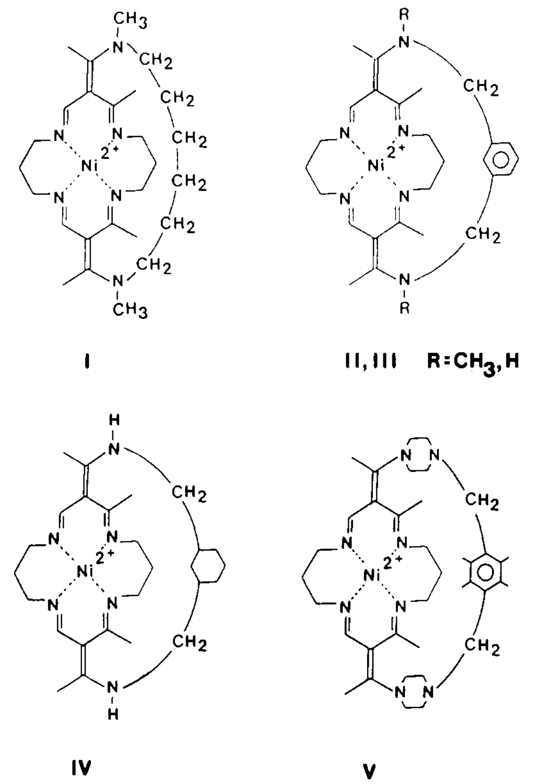


Figure 1. Flat projections of five transition-metal cyclidene complexes.

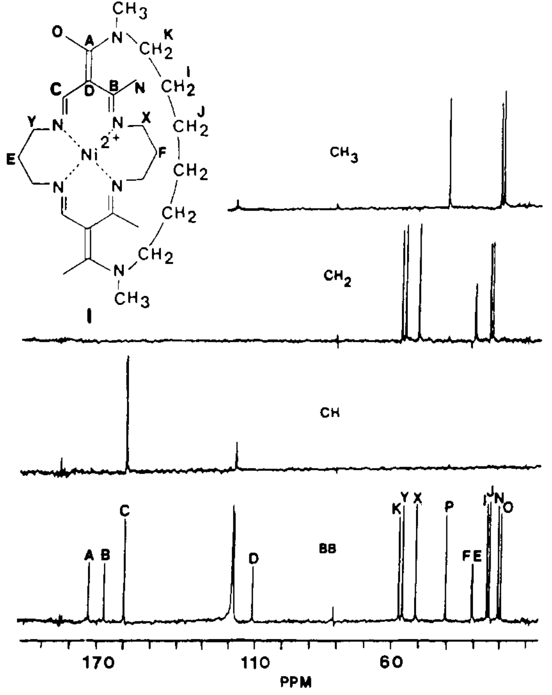


Figure 2. Broad-band proton-decoupled and DEPT carbon-13 NMR (FT; 20.12 MHz) spectra of I in CD$_3$CN.

$\delta(^{13}C)$ values, while the ordinate shows the $\delta(^{1}H)$ values. Due to the correlative nature of the technique, assignments made previously in the ^{13}C spectrum may be translated directly into assignments of proton signals. Figure 3 shows the expanded region for the $\delta(^{13}C)$ values from 10 to 60. An additional resonance occurs at 160 ppm and corresponds to the lone methine carbon, C. The proton of the methine carbon C has been assigned to the signal at 7.45 ppm in the ^{1}H NMR spectrum of I by using this technique. The carbon atom signal at 57 ppm, which corresponds to the methylene carbon K, is related to the proton resonances at approximately 3.3 and 3.7 ppm. Each of the remaining signals in the ^{13}C spectrum may also be correlated with their respective proton resonances simply by drawing a perpendicular line to the ordinate and reading the ^{1}H chemical shift. However, due to the limitations of data collection in the ^{1}H–^{13}C correlated shift experiment (e.g., 2000 data points), an overlap of methylene proton signals occurs, and unambiguous assignment cannot be made of every proton in a given spectrum.

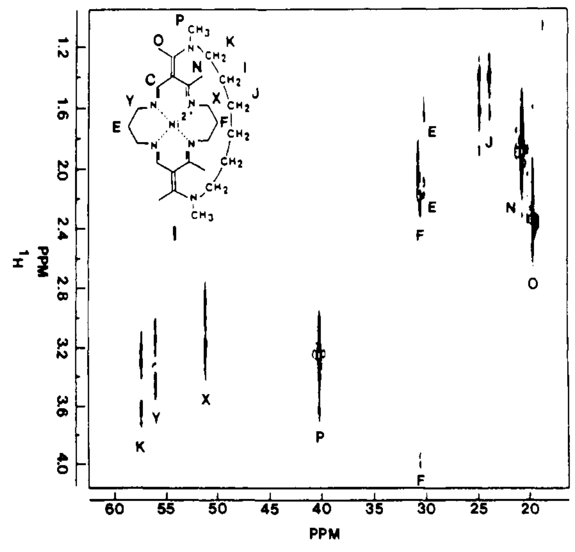


Figure 3. 2-D ^{13}C–^{1}H correlation diagram of I in CD$_3$CN (FT; ^{1}H, 300 MHz; ^{13}C, 75.46 MHz).

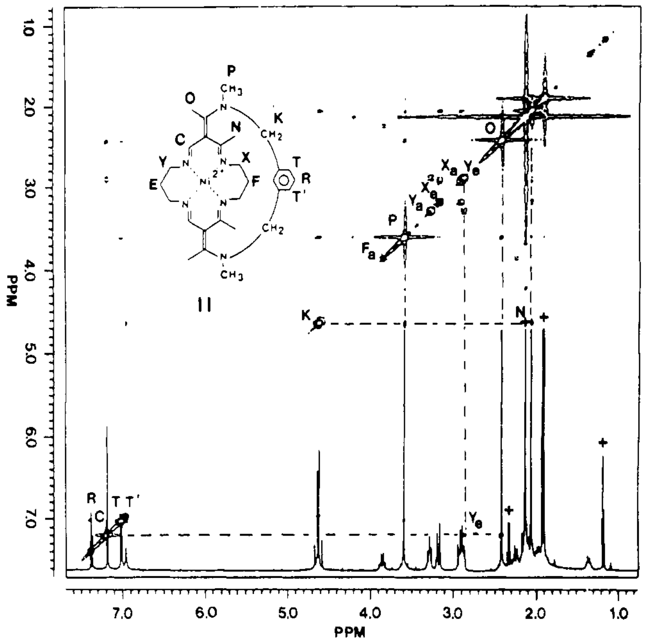


Figure 4. Homoscalar correlated 2-D ^{1}H NMR (FT; 500 MHz) spectrum of II in CD$_3$CN (NOESY experiment; + = solvent impurity).

At this juncture, the protons on C, K, I, J, N, O, and P of complex I may be assigned with confidence (Table I). Further, the protons on C, K, N, and O of complex II have been assigned (Table I). The remaining methylene carbon signals at 30 ppm and from 48 to 57 ppm are not easily distinguished since their carbon resonances were not previously assigned and because there was a large degree of signal overlap in these regions. When these situations prevail, 2-D NOESY and COSY experiments may be used to assign the remaining protons and indistinguishable carbon atoms in the ^{13}C NMR spectra.

The NOESY contour correlation plot for complex II is given in Figure 4. The peaks along the diagonal may be viewed as looking down on the proton NMR spectrum. For clarity, the proton NMR spectrum is also shown in the normal manner along

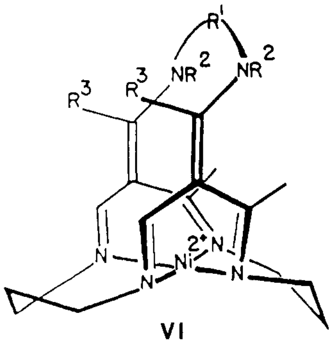
Table I. ^{1}H NMR Chemical Shift Data[a] and Assignments for Complexes I–V

	δ					
protons[b]	I	II	III[c]	IV	V	code
C	7.45	7.21	7.59, 7.32	7.51	7.32	*d*
K_e (K_a)	3.73 (3.38)	4.65	4.83, 4.52	3.72 (2.90)	3.89	*f, h, i*
F_e	2.28	2.27	~2.4	2.34	2.20	*e*
F_a	3.95	3.89	3.89→4.01	3.91	3.87	*i*
X_e	3.20	3.20	3.31, 3.07	3.22	3.09	*e*
X_a	2.88	2.92	2.89	2.81	2.77	*h*
Y_e	3.17	2.88	3.17	3.14	3.14	*h*
Y_a	3.48	3.31	3.47	3.49	3.49	*f*
E_e	2.18	2.08	~2.1	~2.2	2.07	*h*
E_a	1.69	1.39	1.95, 1.60	1.61	1.56	*g*
Q			8.15, 6.60	6.30		*k*
Z, Z′					2.27, 2.26	*d*
P	3.20	3.62				*d*
O	2.38	2.44	2.31, 2.29	2.29	2.31	*d*
N	1.88	2.16	2.21, 2.09	2.15	1.84	*d*
R		7.39	7.49	0.73		*j*
S		6.98	7.02	1.82, 1.33		*k*
T, T′		7.04, 7.03	7.37, 7.35 7.25, 7.24	1.73, 0.90		*e*
I	1.68				3.68	*g, h*
J	1.40				3.33, 2.98	*h, k*
M_e					1.79	*h*
M_a					1.53	*h*
L					2.87	*h, i*

[a] Proton NMR spectra were acquired with a Bruker-AM 500 NMR spectrometer operating at 500.13 MHz and using 32K data points. [b] Chemical shifts are versus 1.930 ppm as determined for the solvent CD_3CN. In several of the spectra there appear a triplet at ~1.1 and a multiplet at 3.5 ppm; this is assigned to ethanol used in solvent recrystallization. In addition, water is present at ~2.2 ppm. [c] The chemical shifts listed for this complex are at the centers of complex multiplets. Due to asymmetry, more than one set of peaks may be assigned to the signal. [d] Singlet. [e] Doublet multiplet. [f] Triplet multiplet. [g] Broad multiplet. [h] Complex multiplet. [i] Chemical shifts listed are the centers of the AB quartet. [j] Triplet. [k] Broad singlet.

the abscissa. The off-diagonal elements in the NOESY experiment represent correlations due to dipolar coupling between protons and are limited to detection distances of 4 Å or less. Due to the 2-D nature of the experiment, the off-diagonal elements occur as mirrored pairs on either side of the diagonal proton spectrum. Protons that are dipole coupled to each other may be observed by selecting a peak on the diagonal and drawing a line that is parallel to the base line to an off-diagonal element and then proceeding 90° back to the diagonal (dashed lines in Figure 4). Drawing an additional perpendicular line to the ordinate or abscissa of the contour plot allows the corresponding chemical shift of the dipole coupled atoms to be read.

When considering dipolar interactions in the cyclidene complexes, it is important to be aware of the overall saddle shape of the macrocycle that has been revealed by X-ray crystallographic data and is shown in structure VI. From the 2-D ^{1}H–^{13}C correlation experiments discussed previously, the signal at 7.21 ppm in the proton spectra of complex II has been assigned to the methine proton, C. It may be seen from the off-diagonal elements in Figure 4 that dipolar coupling is occurring between this proton and protons located at 2.88 and 2.44 ppm. When a molecular model of the complex is constructed, it is clear that the nearest neighbors, through space, to proton C are located on carbons Y and O. The protons on the methyl group O were previously assigned at approximately 2.4 ppm for complex I; therefore, the proton at 2.88 ppm must correspond to the equatorial proton on Y, Y_e. However, there is no detectable correlation observed for the axial proton of Y (Y_a) with C. This result is reasonable on the basis of X-ray crystallographic results and molecular models that show proton C is closer to Y_e than Y_a. An additional example may be seen by observing that the protons on K (4.65 ppm) show dipolar correlations with P and N (Figure 4). This is consistent with the assignments discussed previously and dramatically depicts the saddle shape of the cyclidene complex. Other dipolar interactions, and therefore tentative assignments that may be made, include P with T and T′, S with K, P with O, N with X, and, perhaps most importantly in terms of the final assignments, Y with what could be E. This observation, together with the strong Y and O dipolar coupling, provides the means to distinguish between the two "sides" of the macrocycle (i.e., Y and X).



VI

Results from COSY experiments may be used to resolve the remaining protons and serve as a cross check for assignments already made. COSY contour diagrams are analyzed in a manner strictly analogous to that used with NOESY plots; however, they reveal interactions that are the result of spin–spin coupling. As an example, the diagonal peak at 3.89 ppm of complex II (Figure 5) has three off-diagonal elements that indicate this single proton (via integration) is coupled to protons at 3.20, 2.88, and 2.28 ppm. Exploiting the data obtained on complex I with 2-D ^{1}H–^{13}C correlation and DEPT experiments discussed previously, we find the proton at 3.89 ppm is on a carbon whose chemical shift is 30 ppm. This carbon is assigned to either E or F on the macrocycle. Therefore, the three off-diagonal elements described above in Figure 5 may be attributed to coupling with the two protons X or Y and the third correlation accounts for the other proton of the same carbon E and F. Since Y was already assigned by using NOESY, the interactions observed must be due to the two protons on X and the other F proton. Additional correlations confirm this conclusion. The X protons are expected to couple with each other, and this is clearly seen in Figure 5. The Y_e and Y_a protons are seen to couple, as do the E_e and E_a protons. The remaining assignments in the aromatic region and any other correlations may be cross-checked by use of the NOSEY and COSY techniques. The final assignments for complex I and II are listed in Table I; the assigned proton spectrum of II is shown in Figure 6.

The assignments of protons for complexes I and II reveal that the methylene protons on the saturated chelate rings of the parent macrocycle are fixed in axial and equatorial sites. The protons

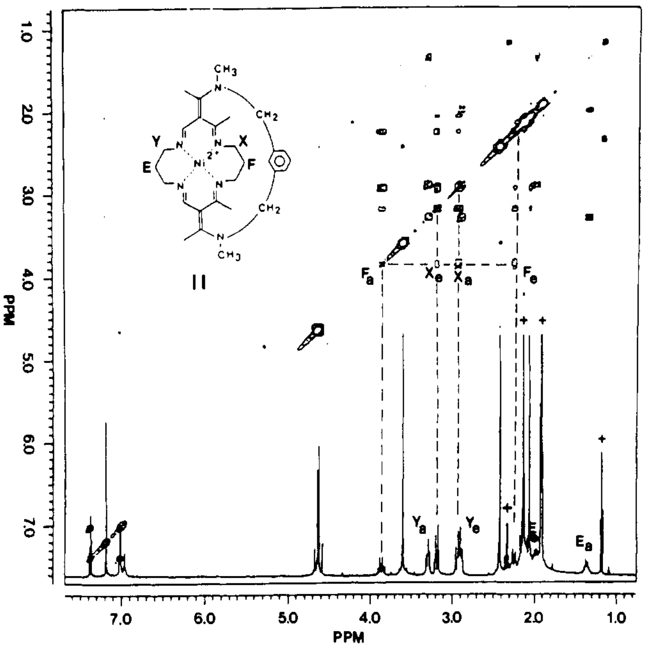


Figure 5. Homoscalar correlated 2-D ^{1}H NMR (FT; 500 MHz) spectrum of II in CD_3CN (COSY experiment).

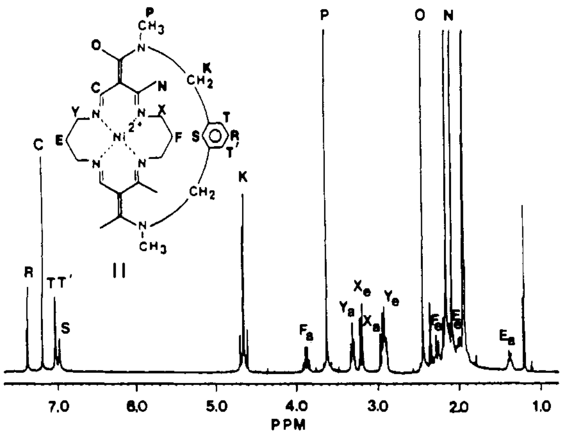


Figure 6. ^{1}H NMR (FT; 500 MHz) spectrum of II in CD_3CN.

F_a and F_e in both complexes depict a feature common to the spectra of all five cyclidenes studied here. The six-membered rings containing the X–F–X carbons are in the boat conformation, with a large separation between the axial and equatorial protons (1.6–1.7 ppm). The boat conformation is presumably a result of steric constraints caused by the methyl carbon N. This conformation draws the axial proton on F into close proximity to the dipositive metal atom, and significant deshielding takes place, resulting in a downfield shift to 3.9 ppm for F_a, in complex II. Such deshielding has been observed in other nickel complexes where methyl groups interact with the nickel.[15] This was explained by comparison to d^8 square-planar platinum(II) complexes where a large deshielding effect for protons situated above the plane was predicted.[16] In contrast, the E protons are at much higher field, the difference in their chemical shifts is small (~0.5 ppm), and the equatorial proton is farther downfield than the axial proton. The Y_a proton lies downfield of the Y_e proton, opposite of what would be expected in a cyclohexane ring. This is again due to deshielding of the axial proton due to interaction with the nickel.

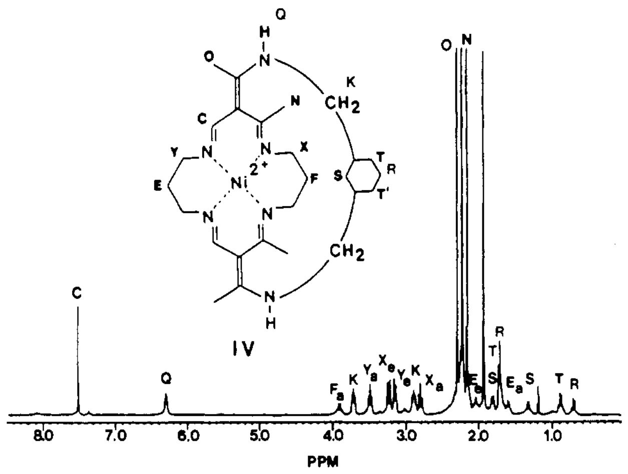
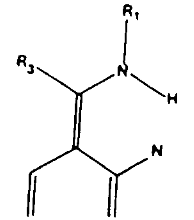


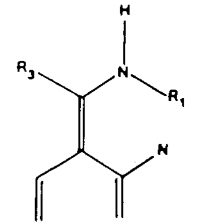
Figure 7. ^{1}H NMR (FT; 500 MHz) spectrum of IV in CD_3CN.

These axial and equatorial assignments for E, F, X, and Y are also supported by homonuclear decoupling experiments that allow the determination of coupling constants. These coupling constants can then be examined in a manner similar to that applied to cyclohexane rings. The F_a–X_a proton coupling is about 13 Hz while the F_a–X_e and F_e–X_a proton coupling constants are about 3 Hz. This is consistent with expected constants of 6–14 Hz for axial–axial and 0–6 Hz for axial–equatorial vicinal coupling constants.[17] The coupling constant for E_a–Y_a is 9 Hz. The E_a–Y_e and E_e–Y_e coupling constants are on the order of 6–7 Hz, while that of E_e–Y_a is about 2 Hz. This suggests a flattening of the six-membered ring, which causes the dihedral angles between vicinal axial–axial and axial–equatorial protons to be similar. This ring flattening is observed in the X-ray crystal structure.[4]

The assigned proton spectra of complex IV, in which the bridge is the *cis*-1,3-cyclohexanediylbis(methylene) moiety, is listed in Table I and is shown in Figure 7. The structure of this species has been confirmed by X-ray crystallography and by ^{13}C NMR experiments to involve the isomeric lid-on structure VII, while complexes I and II adopt the lid-off configuration VIII. It is clear from X-ray crystallographic data that there is a profound difference in cavity shape between the two species.[18] The cavity of the lid-on isomer is 7.56 Å high and 5.20 Å wide, while the cavity in the lid-off species is 5.02 Å high and 7.37 Å wide. It has been previously noted in the ^{1}H-coupled ^{13}C NMR spectra that the chemical shifts of methyl groups N and O can be used to distinguish between lid-on and lid-off isomers in the absence of X-ray structural information.[13] This identification of isomer type is also possible by using the ^{1}H NMR signal from the same two methyl groups (N and O) as the probe. The separation of the N and O methyl proton peaks is consistently greater than 0.35 ppm when the complex is of the lid-off isomer type (complexes I and II). When the isomer type is lid-on, the separation is less than 0.15 ppm (complex IV and other lid-on complexes not discussed here).



VII



VIII

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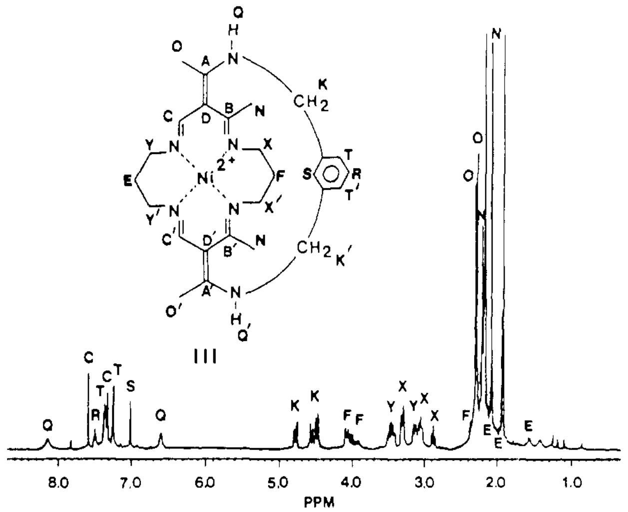

Figure 8. ^{1}H NMR (FT; 500 MHz) spectrum of III in CD_3CN.

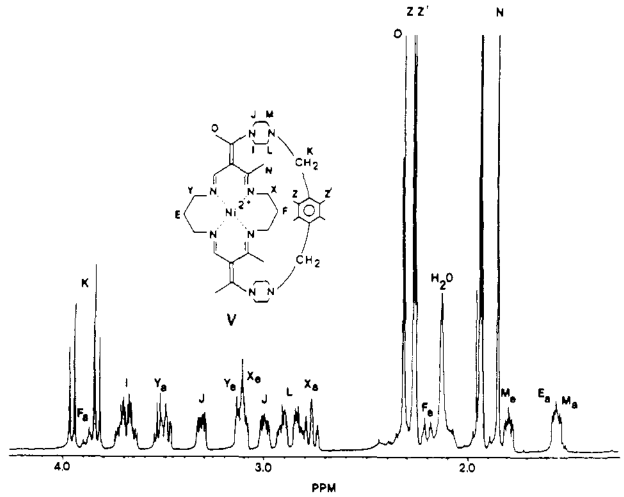

Figure 9. ^{1}H NMR (FT; 500 MHz) spectrum of V in CD_3CN.

The proton NMR spectrum of complex III presents special problems. From the multiple peaks seen in the proton NMR (Figure 8), either the molecule does not have mirror symmetry or the sample is a mixture of species. The relatively small differences in chemical shifts between the doubled peaks support the former possibility and suggest that the loss of symmetry is due to some very small, nonfluxional structural perturbation. The relative chemical shifts of the protons are consistent with previous determinations, including the chair–boat conformational dichotomy of the E and F carbons. Rotation about one of the A–D double bonds would produce asymmetry, but this modification would undoubtedly have a much larger impact on the coupling of the methyl protons than can be accounted for in the proton spectrum. The X-ray crystal structure of the complex shows what appears to be a symmetryic cavity.[18] The ^{13}C NMR spectrum of complex III contains several additional signals that cannot be accounted for on the basis of the number of carbon atoms; however, the spectrum suggests a lid-on isomer.[13] NOSEY and COSY contour plots of the complex do not reveal any outstanding features that may account for the asymmetry of the complex.

A plausible solution to this apparent enigma may be found in the N and O methyl protons used to assign the lid-on and lid-off isomers. There are four distinct peaks corresponding to the N and O protons. One set is split by 0.1 ppm, indicating that the isomer is lid-on. The other set of N and O methyl protons is split by 0.22 ppm. This splitting falls between the range of the standard of greater than 0.35 ppm determined for lid-off and less than 0.15 ppm for lid-on. It is possible that complex III possesses both lid-on and lid-off planar nitrogen moieties on opposite sides of the complex. This phenomenon would account for the asymmetry of the complex and the observation of slightly different environments as seen for the majority of the protons in the proton spectra. The protons that would be most affected by such a conformational change are K and Q (the protons on nitrogen). The two NH protons, Q, on either side of the macrocycle, are clearly in significantly different environments as indicated by their chemical shifts of 6.6 and 8.15 ppm. The proposed structural relationships may be seen with the aid of molecular models of the complex and are consistent with the NMR spectral observations.

Finally, the ^{1}H NMR spectrum of complex V has been assigned by using the techniques described, and these assignments are listed in Table I. Figure 9 shows the region from 1.4 to 4.2 ppm; the peak due to the lone methine proton, C, at 7.32 ppm is not shown. There are similar features in the ^{1}H NMR spectrum of this vaulted complex when compared to those of the lacunar cyclidene complexes (I–IV). The familiar chair–boat conformations of E and F are indicated since the peaks for the protons of these carbon atoms reside at approximately the same chemical shifts as those of the analogous protons in the other cyclidene complexes. This is consistent with the crystal structure of the complex, which shows that E residues in a chair conformation and F is a boat conformation.[4] The protons labeled K show a typical A–B splitting pattern from 3.8 to 4.0 ppm. The protons on X and Y give peaks at similar positions relative to those of complexes I–IV. Absolute assignment of the peaks for the protons on I, J, L, and M is more complicated due to the symmetry of the piperazine rings. From the COSY experiment, the protons on the carbon atoms adjacent to each other on the piperazine rings may be assigned due to the strong spin coupling. The signal at 3.68 ppm (four protons via integration) is spin–spin coupled to the protons resonating at 2.87 ppm (four protons by integration). Further, two protons whose peaks reside at 3.30 ppm reveal coupling with two protons at 2.98 ppm and also with two protons whose peaks occur at 1.79 and 1.53 ppm. These proton resonances correspond to the other "half" of the piperazine ring.

The large upfield shift of the protons at 1.79 and 1.35 ppm (M) from the other three sets of protons of the piperazine ring (J, I, and L) indicates a strong shielding contribution unique to M. With the aid of molecular models, it may be seen that a single proton on the piperazine ring is in very close proximity to the durene (tetramethylbenzene) ring. Using crystallographic data of a similar complex[4] in order to approximate the position and distance of this proton from the durene ring and using a table of predicted values of shielding contributions for ring currents,[20,21] one can predict a value of −1.7 ppm for the shielding contribution. This is relatively close to the observed −1.2 ppm shift of M, upfield from free piperazine. With M assigned, the nearest-neighbor proton may be assigned to J. I and L are assigned in a similar manner.

Conclusions

The 2-D techniques have been used to unambiguously assign the resonances in the ^{1}H NMR spectra of five cyclidene complexes. Several three-dimensional structural relationships are exhibited, and the proton spectra have been assigned. A number of features are common to all five cyclidenes studied. The chair and boat conformations of macrocyclic ring components are apparent from the ^{1}H NMR spectra and agree with the results of X-ray crystallographic data. The saddle-shaped nature of the cyclidene ligand is observed with dipolar coupling of protons by using NOESY experiments. The identification of lid-on and lid-off isomers of the complexes may be routinely performed with NMR measurements even at low magnetic fields.

Experimental Section

Synthesis of the Bridged Ni(II) Cyclidenes. [2,3,10,11,13,19-Hexamethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-κ^4N]nickel(II) Hexafluorophosphate (I). This

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complex was prepared by a published procedure.[1]

[2,3,11,12,14,20-Hexamethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,5,7,9(28),12,14,19,21,26-nonaene-κ^4N]nickel(II) Hexafluorophosphate (II). This complex was prepared by a published procedure.[8]

[2,12,14,20-Tetramethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,5,7,9(28),12,14,19,21,26-nonaene-κ^4N]nickel(II) Hexafluorophosphate (III). This complex was prepared by published procedures and carefully purified to ensure no dimer was present.[8]

(5*R,9*S**)-[2,12,14,20-Tetramethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,12,14,19,21,26-hexaene-κ^4N]nickel(II) Hexafluorophosphate (IV).** This complex was prepared by published methods.[19]

[2,9,10,17,19,25,33,34-Octamethyl-3,6,13,16,20,24,27,31-octaazapentacyclo[16.7.7.2^{8,11}.2^{3,6}.2^{13,16}]octatriaconta-1,8,10,17,19,24,26,31,33-nonaene-κ^4N]nickel(II) Hexafluorophosphate (V). This complex was also prepared by published methods.[4]

Physical Measurements. Proton NMR spectra were acquired by using Bruker WM300, Bruker AM500, and Nicolet NT500 spectrophotometers. All NMR spectra were obtained in acetonitrile-d_3. The ^{1}H–^{13}C shift correlation measurements were acquired on a Bruker WM300 spectrometer with SI = 4K, $TD_1 = 256$, $P_{90}H = 44$ μs, and $P_{90}C = 29$ μs. The 2-D NOESY and COSY experiments were acquired on a Bruker AM500 with the Bruker Coco-NOESY Shift-Correlated 2-D sequence with a 0.5-s mixing time. The SW = 4000 Hz and SI = 16K. This program allows for the COSY data to be acquired during the mixing time and has been adapted from Haansnoot et al.[22,23] The ^{13}C DEPT experiments were carried out on a Bruker NR-80 spectrophotometer with a sweep width of 4500 Hz and PW = 35 μs; the data were acquired over 16K data points.

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Binding of Pentaammineruthenium(II) Residues to the Tris(bipyrazine)ruthenium(II) Cation

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A series of $[\{(NH_3)_5Ru\}_n(bpz)]^{2n+}$ (bpz = bipyrazine; $n = 1, 2$) and $[Ru(bpz)_3\{Ru(NH_3)_5\}_n]^{(2+2n)+}$ ($n = 1, 3, 6$) complexes have been synthesized and characterized by means of electronic spectra, ^{1}H NMR spectroscopy, cyclic voltammetry, and spectroelectrochemistry. The complexes are very stable and inert in aqueous solution. The peripheral pentaammineruthenium(II) groups in the tris(bipyrazine) series exhibit strong absorption bands in the visible region, around 490 and 660 nm, ascribed to metal-to-ligand charge transfer transitions. The attached ions can be reversibly oxidized, with formal potentials of approximately 0.65 V versus NHE, in comparison to 0.52 V for the $[\{(NH_3)_5Ru\}_n(bpz)]^{2n+}$ complexes. No evidence of intervalence bands with $\epsilon > 100$ M^{-1} cm^{-1} has been observed in the near-IR region of mixed-valence species. The spectroscopic and electrochemical data are consistent with a very weak interaction between the peripheral pentaammineruthenium(II) groups.

Introduction

Ruthenium(II) complexes of bipyrazine (bpz) are of special interest in coordination chemistry, because of their pronounced photochemical activity and of the existence of six peripheral nitrogen atoms available to bind Lewis acids and transition-metal ions.[2–10] Recently, we reported a detailed kinetic and spectroscopic study on a series of di- to heptanuclear tris(bipyrazine)ruthenium(II) pentacyanoferrate(II) complexes in aqueous solution.[11] In this work, we extend the investigation to a series of pentaammineruthenium(II) derivatives, including the $[Ru(NH_3)_5(bpz)]^{2+}$ and $[\{Ru(NH_3)_5\}_2(bpz)]^{4+}$ species in solid state and in aqueous solution. Electrochemical and electronic spectroscopic data reveal that the several pentaammineruthenium(II) groups are essentially uncoupled to one another and to the central ruthenium atom.

Experimental Section

The bipyrazine ligand was prepared by the pyrolysis of the bis(2-pyrazinecarboxylato)copper(II) complex at 270–290 °C, under an argon atmosphere, as described in the literature.[3,12] The solid was recrystallized from toluene, yielding pale yellow crystals, mp 186–190 °C (lit.[13] mp 190 °C).

The complexes $[Ru(bpz)_3](PF_6)_2$ and $[Ru(NH_3)_5(H_2O)](PF_6)_2$ were prepared by literature methods.[2,14] $[Ru(NH_3)_5(bpz)](PF_6)_2$ and $[\{Ru(NH_3)_5\}_2(bpz)](PF_6)_4$ were obtained by reacting 0.20 mmol of bpz with 0.20 or 0.40 mmol of $[Ru(NH_3)_5(H_2O)](PF_6)_2$ in boiling acetone (25 mL) under an argon atmosphere. After 30 min, the deep purple solution was evaporated to dryness at 55 °C under a vigorous stream of argon. The black residue was kept under vacuum for 1 day and then washed with toluene. The compounds were recrystallized by dissolving in a small volume of 1:1 water–acetone solution and allowing the solvent to evaporate very slowly under reduced pressure. Anal. Calcd for $[Ru(NH_3)_5(bpz)](PF_6)_2$: C, 15.15; H, 3.33; N, 19.87. Found: C, 14.6; H, 3.2; N, 19.7. Calcd for $[\{Ru(NH_3)_5\}_2(bpz)](PF_6)_4 \cdot C_3H_6O$: C, 11.31; H,

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