Contribution from the Department of Chemistry,
University of North Carolina, Chapel Hill, North Carolina 27514

Nuclear Magnetic Resonance Studies of Configuration and Ligand Conformation in Paramagnetic Octahedral Complexes of Nickel(II). IV. Iminodiacetic Acid, N-Methyliminodiacetic Acid, and Nitrilotriacetic Acid Complexes

By L. E. Erickson,[1] F. F.-L. Ho, and C. N. Reilley

Received October 6, 1969

Proton nmr studies have been used to establish configurations, preferred conformations, and kinetic properties of paramagnetic Ni(II) complexes of IDA, MIDA, and NTA. Facial coordination has been established for IDA and MIDA in both 1:1 and 2:1 complexes. The following *cis*:*trans* isomer ratios have been determined for 2:1 complexes: IDA, 80:20; MIDA, 40:60; NTA, <10:90. Rates of intramolecular acetate scrambling have been determined from the temperature dependence of the spectrum of $Ni(NTA)_2^{4-}$ between 5 and 70°. Limits have been placed on rates of other intra- and intermolecular scrambling processes, including the scrambling of acetate groups in $Ni(NTA)(H_2O)_2^-$ which is at least an order of magnitude faster than the corresponding process in $Ni(NTA)_2^{4-}$.

Introduction

The unique characteristics of nmr spectra of paramagnetic chelates which have been employed to advantage in our previous work on Ni(II) complexes of ethylenediamines,[2] amino acids, and EDDA[3] also provide a technique for answering some interesting questions about structures, isomer distributions, and relative Ni–N and Ni–O bond lifetimes in the closely related chelating agents iminodiacetic acid (IDA), N-methyliminodiacetic acid (MIDA), and nitrilotriacetic acid (NTA). Structural conclusions are based on the empirically established generalization that axial and equatorial protons of acetate fragments of nickel(II) chelates can be distinguished on the basis of their contact shifts, with the more equatorial proton having a greater downfield shift.[3] Kinetic studies make use of the familiar coalescence of spectral lines observed when the rate of interconversion of protons in two nonequivalent sites exceeds the shift difference between the two environments. Since the shifts involved in these systems are so large, however, rates of relatively fast processes can be determined.

Spectra of paramagnetic 1:1 nickel(II) complexes of these ligands were included in Milner and Pratt's early investigation.[4] While this paper was in preparation, Pratt and Smith reported a more detailed nmr study of nickel(II) complexes of these and other closely related ligands.[5] Our conclusions as to spectral assignments and the conformational dependence of the contact shift are in substantial agreement with their findings. However, we suggest an alternative interpretation for the spectra and isomer distributions of 2:1 complexes. In addition, we have also examined the temperature dependence of the spectra and have thereby obtained kinetic data for the intramolecular scrambling processes which $Ni(NTA)_2^{4-}$ and $Ni(NTA)(H_2O)_2^-$ undergo.

Previous nmr studies of diamagnetic complexes of these ligands are also relevant to this work. These studies provided confirmation of structures of stable species isolated from reaction mixtures and information about structure and ligand scrambling kinetics. Much of the earlier literature is reviewed by Smith and Sawyer in their reports of the spectra of several Co(III), Rh(III), Pd(II), and Pt(II) complexes.[6–9] They drew some conclusions about the relative stability of certain isomer pairs. However, the ability to analyze equilibrium compositions in these more labile Ni(II) systems, which this technique provides,[3] permits more reliable analysis of equilibrium isomer distributions than comparisons of yields of isolated products.

Experimental Section

Details of preparation of D_2O solutions and spectral measurements were the same as described in previous work.[3] Commercially available IDA, MIDA, and NTA were used without further purification. Computer calculations were carried out with a GE time-sharing 235 system.

Results

Schematic spectra of several Ni(II) complexes of IDA, MIDA, and NTA are shown in Figure 1. For IDA and MIDA, spectra of both 1:1 and 2:1 complexes (more precisely, of solutions with 1:1 and 2:1 ligand:metal ratios) are shown. For NTA, the spectrum of the 1:1 complex at room temperature is included in Figure 1, but full-scale spectra of the 2:1 complex at several temperatures are shown in Figure 2. For all three ligands, spectra of solutions containing a 3:1 ligand:metal ratio are identical with those of corresponding 2:1 ratios, except for the additional peaks due to excess ligand 1–2 ppm upfield from the residual HDO peak (not shown in Figures 1 and 2). The assignment of peaks, their contact shifts, and relative areas are summarized in Table I. The

---

[1] Department of Chemistry, Grinnell College, Grinnell, Iowa. National Science Foundation Science Faculty Fellow, University of North Carolina, 1968–1969.

[2] Parts I and II: F. F.-L. Ho and C. N. Reilley, *Anal. Chem.*, **41**, 1835 (1969); **42**, 600 (1970).

[3] Part III: F. F.-L. Ho, L. E. Erickson, S. R. Watkins, and C. N. Reilley, *Inorg. Chem.*, **9**, 1139 (1970).

[4] R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88 (1962).

[5] L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, **65**, 915 (1969).

[6] B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, **7**, 922 (1968).

[7] B. B. Smith and D. T. Sawyer, *ibid.*, **7**, 1526 (1968).

[8] B. B. Smith and D. T. Sawyer, *Chem. Commun.*, 1454 (1968).

[9] B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, **8**, 379 (1969).

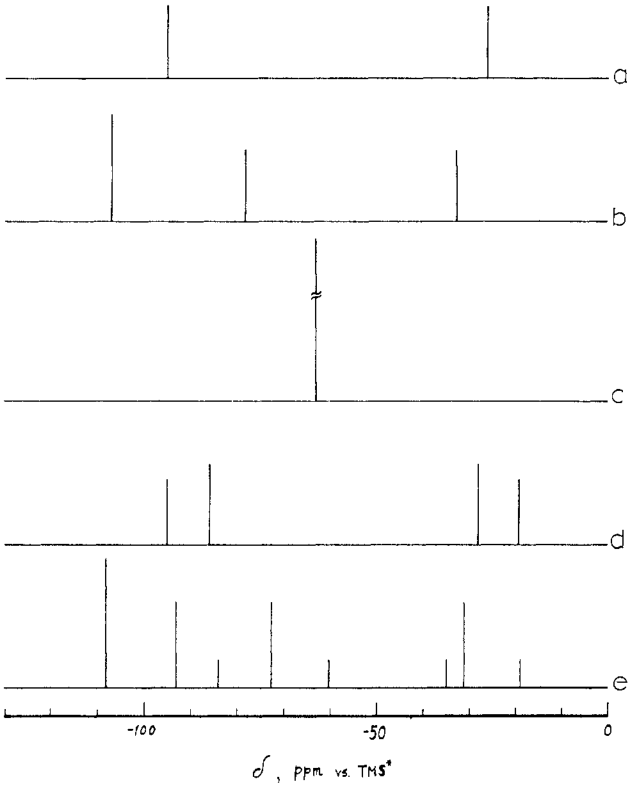


Figure 1.—Schematic nmr spectra of (a) Ni(IDA), (b) Ni(MIDA), (c) $Ni(NTA)^-$, (d) $Ni(IDA)_2^{2-}$, and (e) $Ni(MIDA)_2^{2-}$.

basis of the assignments and relevant structural considerations, which closely parallel Pratt and Smith's discusssion, will now be considered.

There are two geometric isomers possible for the 1:1 complexes of IDA and MIDA, owing to the possible *cis* and *trans* arrangements of the two acetate oxygens. These are designated facial (I) and meridional (II), respectively. There are two well-separated lines for the acetate protons of IDA and MIDA in Figure 1. Furthermore, from our previous work,[3] the upfield peak can be assigned to protons in a more axial environment in the acetate ring while the downfield peak can be identified with acetate protons in a more equatorial environment. On the basis of a rigid Dreiding model, axial and equatorial methylene protons, designated H_a and H_b, are reversed in going from facial (I) to meridional (II) forms. If both isomers were present at comparable concentrations, two pairs of peaks should

TABLE I

CONTACT SHIFTS AND SPECTRAL ASSIGNMENTS OF COMPLEXES OF IDA, MIDA, AND NTA

Complex	Contact shift[a]	Integrated area	Assignment[b]
$Ni(IDA)(H_2O)_3$	−26	2	ac (ax.)
	−95	2	ac (eq)
$Ni(MIDA)(H_2O)_3$	−33	2	ac (ax.)
	−78	2	ac (eq)
	−107	3	CH_3
$Ni(NTA)(H_2O)_2^-$	−63	6	ac
$Ni(IDA)_2^{2-}$	−19	1.8	*cis*-ac (ax.)
	−28	2.2	*cis*- + *trans*-ac (ax.)
	−86	2.2	*cis*- + *trans*-ac (eq)
	−95	1.8	*cis*-ac (eq)
$Ni(MIDA)_2^{2-}$	−19	0.8	*cis*-ac (ax.) out-of-plane
	−31	2.4	*trans*-ac (ax.)
	−35	0.8	*cis*-ac (ax.) in-plane
	−60	0.8	*cis*-ac (eq) in-plane
	−73	2.4	*trans*-ac (eq)
	−84	0.8	*cis*-ac (eq) out-of-plane
	−93	2.4	*cis*-CH_3
	−108	3.6	*trans*-CH_3

[a] In ppm downfield from the internal reference TMS*. [b] The following abbreviations are used: ac, acetate; ax., axial; eq, equatorial. In terms of structure I, the axial protons are designated H_a; the equatorial, H_b.

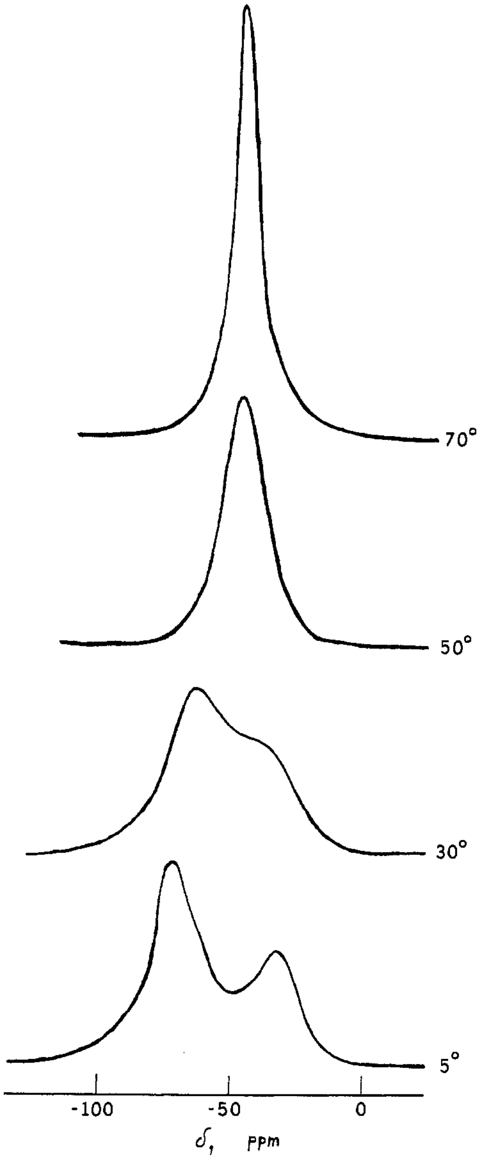
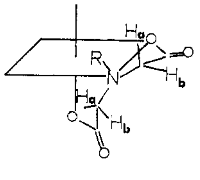
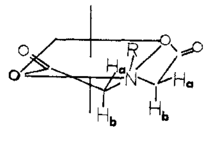


Figure 2.—Temperature dependence of the nmr spectrum of $Ni(NTA)_2^{4-}$.



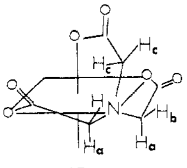
I facial



II meridional

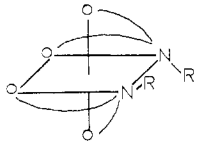
be observed unless the isomerization rate is fast on the nmr time scale. However, in that case, the observed separation between signals from H_a and H_b should be small since each proton would have a shift characteristic of an average of axial and equatorial environments. Therefore, it is most likely that the ligand in Ni(IDA) and Ni(MIDA) strongly prefers the *cis*-facial configuration. The meridional isomer is severely strained. In the mixed complex of IDA and dien (diethylenetriamine) in $Co(dien)(IDA)^+$, it was reported that only a trace of meridional IDA configuration exists in equilibrium.[8] Furthermore, in the bis complexes, $Co(IDA)_2^-$ and $Co(MIDA)_2^-$, no *trans*-meridional isomer was found.[6,10]

The situation is different for the 1:1 complex of NTA for which only a single sharp resonance at −63 ppm is observed. NTA is a potentially tetradentate ligand with two coordinating oxygens *trans* to each other and in the same plane with Ni and N. The third acetate is perpendicular to this plane. This structure would be expected to yield a three-peak nmr spectrum, corresponding to the three pairs of protons shown in III, *i.e.*, in-plane axial, in-plane equatorial, and out-of-plane. Although the out-of-plane acetate ring is probably also puckered, rapid conformational interchange would produce a single average environment for the H_c protons. However, scrambling of the acetate groups around the coordination sites in an octahedral configuration would yield a single average shift for each of the six protons. Apparently, this scrambling among equally populated states is sufficiently rapid to average out completely the magnetic environment of the acetate protons in the axial–equatorial sense so that a single peak results. However, the possibility of a structure in which all acetate protons are equivalent by symmetry cannot be ruled out entirely.

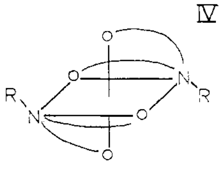


III

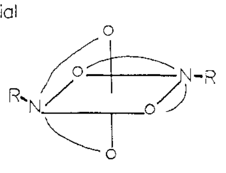
In view of the possibility of three geometric forms (IV–VI), bis complexes could give considerably more complex spectra. In the bis complex in its *cis* configuration (IV), the two acetate groups of the same ligand and are no longer identical so that four peaks, two axial and two equatorial, could result. By contrast, the *trans*-facial configuration (V) has a plane of symmetry through the two nitrogen atoms which bisects each ligand. However, each acetate group still has two nonequivalent (axial/equatorial) protons so that two peaks would be expected for this isomer. The failure to observe significant amounts of meridional isomers in 1:1 complexes suggests that the likelihood of finding any *trans*-meridional $Ni(IDA)_2^{2-}$, which would also have four peaks (two axial and two equatorial), is negligible. The spectra of 2:1 complexes of IDA and MIDA can be interpreted readily in terms of these expectations.



IV Cis-facial



V Trans-facial



VI Trans-meridional

The spectrum of $Ni(MIDA)_2^{2-}$ consists of the four equal-intensity acetate peaks expected for the *cis*-facial isomer as well as the two other equal-intensity acetate peaks expected for the *trans*-facial isomer. Correspondingly, there are two peaks of unequal intensity that can be assigned to the methyl peaks of the isomers. The *trans*:*cis* isomer ratio calculated on the basis of either acetate or methyl peaks is about 60:40. The spectrum of $Ni(IDA)_2^{2-}$ is not quite so clear-cut. It consists of four peaks, two in the axial region and two in the equatorial region, with the inner peak in each region slightly larger. This is consistent with (a) two peaks each for the *cis*- and *trans*-facial isomers, one downfield (equatorial) and one upfield (axial), or (b) the four peaks expected for *cis* (two equatorial and two axial) and a much smaller amount (20 *vs.* 80%) of *trans*-facial isomer overlapping the inner pair. The second alternative seems to be favored for two reasons. $Ni(MIDA)_2^{2-}$ does show the four acetate proton peaks expected for the *cis* isomer as well as the two acetate peaks of the *trans*-facial isomer (*trans*:*cis* = 60:40). Furthermore, *cis*-$Co(IDA)_2^-$ was found to be predominant in a 2:1 mixture of IDA and Co(III) at low temperature[11,12] even though no *cis*-$Co(MIDA)_2^-$ has been isolated.[5,10]

The fact that four acetate peaks are observed for *cis*-facial $Ni(MIDA)_2^{2-}$ and $Ni(IDA)_2^{2-}$ requires that acetate scrambling in these species is not fast on the nmr time scale since rapid scrambling would produce a single average environment for each acetate, as shown in Figure 3. The nearly equal axial–equatorial acetate proton shift differences for 1:1 and 2:1 complexes then provides additional evidence that the facial configuration predominates in the 1:1 complex since rapid averaging with an appreciable amount of meridional

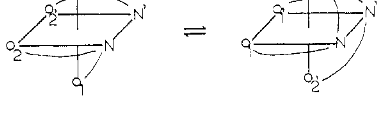


Figure 3.—Acetate scrambling in *cis*-$Ni(IDA)_2^{2-}$ (or MIDA) without Ni–N bond rupture.

---

[10] D. W. Cooke, *Inorg. Chem.*, **5**, 1141 (1966).

[11] M. Mori, M. Shibata, E. Kyuno, and F. Maryama, *Bull. Chem. Soc. Japan*, **35**, 75 (1962).

[12] C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **8**, 1145 (1969).

sonfiguration would decrease the observed average separation.

For the 2:1 complex of NTA, the temperature dependence of the spectrum (Figure 2) suggests a temperature-sensitive scrambling of acetate groups. Like Ni(IDA)$_2^{2-}$, both *cis*-facial and *trans*-facial isomers are possible. However, both steric and electrostatic interactions between free acetate groups of the two ligands attached to a given nickel atom should be greater than in Ni(MIDA)$_2^{2-}$, for which *trans*:*cis* ratio is 60:40. This interaction would be minimized in the *trans*-facial isomer so that it is not unreasonable to expect this isomer to predominate. The spectrum of this isomer (Figure 4) should consist of one upfield peak from four axial ring protons, one downfield peak from four equatorial ring protons, and one peak for the four equivalent protons of the free acetate group. The latter should be 20–30 ppm downfield from the average of chelated acetate peaks since breaking the Ni–O bond has been shown to produce a downfield shift of CH$_2$ protons in an acetate fragment.[3] This accounts for the appearance of the spectrum obtained at 5° where the free and equatorial peaks overlap at −70 ppm and the axial proton peak is at −30 ppm. As the temperature rises, both peaks become very broad and finally coalesce to a single sharp peak at 70°. The chemical shift of this peak provides additional confirmation of the correctness of the spectral assignment. Taking into account the $1/T$ dependence of the chemical shift required by the Curie law, the average chemical shift of the three types of protons at 70° calculated from the shifts at 5° is −46 ppm (*vs.* −45 ppm observed). Finally, since the same spectral behavior was observed with excess ligand present (which gave rise to a separate peak at −3 ppm) the scrambling process must be intramolecular.

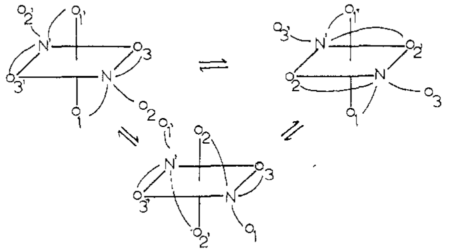


Figure 4.—Acetate scrambling in *trans*-Ni(NTA)$_2^{4-}$.

The line shapes at intermediate scrambling rates were analyzed in terms of the following model (see Figure 4 and structure III). From the point of view of a particular acetate proton, acetate scrambling has the effect of interchanging three equally probable environments, which could be designated axial, equatorial, and free (labeled a, b, and c, respectively, in III). The system can then be characterized by three chemical shifts and a single rate constant, k, the rate constant for the interchange of any two isomers. Experimental curves were matched to computer-generated spectra for three-site scrambling, assuming that the high-temperature line width adequately characterized the natural line widths (and corresponding T_2) for each of the three sites. Rate constants at the three accessible temperatures are summarized in Table II. The following activation parameters were calculated from the temperature dependence of k: $\Delta H^{\ddagger} = 9$ kcal, $\Delta S^{\ddagger} = -13$ eu. Rate constants determined by this approach are estimated to be accurate to only ±30% since no attempt was made to take into account other contributions to the temperature dependence of line widths which could result in systematic errors, especially at temperatures well removed from coalescence. Such errors would lead to substantial errors in the activation parameters.

TABLE II

RATE CONSTANTS FOR ACETATE SCRAMBLING IN Ni(NTA)$_2^{4-}$

Temp, °C	k, sec^{-1}	Temp, °C	k, sec^{-1}
5	5×10^3	50	3×10^4
30	1.2×10^4	70	6×10^4

Discussion

Isomer Distributions in Ni(II) and Corresponding Diamagnetic Complexes.—The following statements summarize our conclusions regarding isomer distributions in these complexes. (1) For 1:1 complexes of IDA and MIDA, facial coordination is preferred over meridional by at least a factor of 10 to 1. (2) For 2:1 complexes of IDA, MIDA, and NTA, there is no evidence for meridional coordination, and the following *cis*:*trans* equilibrium ratios are found: IDA, 80:20; MIDA, 40:60; NTA <10:90. These observations are similar to those reported by other workers for analogous Co(III) and Rh(III) complexes. For example, Cook and Legg[13] found only trace amounts of meridional coordination in Co(dien)(IDA)$^+$, and no meridional isomers were found for Co(IDA)$_2^{2-}$ or Co(MIDA)$_2^{2-}$ [10] or for the corresponding Rh(III) complexes.[6] Both *cis* and *trans* 2:1 IDA complexes of Co(III)[10] and Rh(III)[6] have been prepared, but only *trans*-MIDA complexes of the same metals have been isolated. In view of the greater solubility of the *cis* isomer, the conclusion that the *trans* isomers are more stable than the *cis* isomers probably reflects a failure to reach equilibrium. In fact, the relative amount of *cis*-Co(IDA)$_2^-$ is known to increase as the temperature is lowered,[11] and recent work indicates that it is the preferred isomer[12] at room temperature. These isomer distributions for 2:1 isomers differ significantly from those suggested by Pratt and Smith.[5] For Ni(IDA)$_2^{2-}$, they suggested that the *cis* and *trans* isomers are present in comparable amounts while for Ni(MIDA)$_2^{2-}$ they obtained a *trans*:*cis* ratio of ~85:15. The former conclusion was based on an alternative spectral assignment (peaks at −28 and −86 to *trans* and −19 and −95 to *cis*) while the latter was based on a different value for the ratio of areas with the same assignment we have given. From their published spectra, it appears that for Ni(IDA)$_2^{2-}$ they may have taken ratios of C–H peak areas without taking into account the fact that the *cis* isomer has four C–H peaks while the *trans* has only two. This would decrease their ratio to 74:26.

[13] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

The 4:1 ratio of *cis* to *trans* $Ni(IDA)_2^{2-}$ is just the ratio expected from probability considerations since there are four positions *cis* to a coordinated nitrogen and only one *trans*. This result is perhaps not surprising if one considers that the only significant interligand interaction is between N–H protons, which are *gauche* in *cis*-$Ni(IDA)_2^{2-}$ (IV). In our previous work on Ni(EDDA)(gly) and related complexes, we have shown that steric interaction between N–H protons occupying adjacent coordination sites is negligible.[3] For MIDA, steric interaction between adjacent CH_3 groups significantly reduces the relative stability of the *cis* isomer. For NTA, both steric effects and electrostatic repulsion between $CH_2CO_2^-$ fragments reduce the equilibrium concentration of *cis* isomer to a negligible level.

If one assumes that all of the extra stability of the *trans* isomer of $Ni(MIDA)_2^{2-}$ results from the energy of repulsion of the two *gauche* methyl groups and that $\Delta S°$ $(trans \rightarrow cis) = R \ln 4$ for both IDA and MIDA, the *cis*:*trans* equilibrium ratio for $Ni(MIDA)_2^{2-}$ can be used to estimate the energy (enthalpy) of interaction of the two *gauche* CH_3 groups in $Ni(MIDA)_2^{2-}$. That is, with these assumptions, we can write $-RT \ln (40/60) = \Delta H° - RT \ln (80/20)$, which yields 1.07 kcal/mol for $\Delta H°$ for this interaction. An interaction of this magnitude would probably lead to considerable distortion of acetate ring conformations as compared to $Ni(MIDA)(H_2O)_3$. In attempting to avoid each other, the methyl groups should move further away from the N–Ni–N plane. The in-plane acetates would, thereby, become more nearly planar while the out-of-plane acetates would probably become more puckered. This is the basis of the detailed assignments of peaks given in Table I. (It should be noted that only the number of peaks and their relative intensities were used to establish isomer distributions.) Thus, the pair of peaks at −35 and −60 ppm (centered at −48 ppm) are assigned to in-plane acetates while the pair at −19 and −84 ppm (centered at −52 ppm) are assigned to out-of-plane acetates. This distortion also decreases the downfield shift of CH_3 to −93 ppm (*vs.* −108 ppm for the *trans* isomer and −107 ppm for the 1:1 complex).

Conformational Implications.—Pratt and Smith discussed the dihedral angle dependence of the contact shift for these complexes and included a rough sketch of contact shift *vs.* dihedral angle from their data. It is of interest to compare the extent of distortion from planarity of acetate fragments, as reflected in the contact shift difference for the two methylene protons, for these complexes with those of EDDA complexes. For $Ni(EDDA)(H_2O)_2$, in which acetate groups occupy out-of-plane positions, ethylene proton contact shifts are −19 and −120 ppm. This difference is somewhat greater than for $Ni(IDA)(H_2O)_3$ (−26 and −95 ppm) and the other complexes considered in this paper. This implies that the distortion from planarity is probably somewhat greater for the acetate group of EDDA complexes. However, judging from the steepness of the shift *vs.* dihedral angle plot for ϕ near 150° (~3 ppm/deg) the difference is not great. The difference is further reduced if some adjustment is made to take into account the smaller average shift for $Ni(IDA)(H_2O)_3$ (−60 *vs.* −70 ppm) which probably reflects a somewhat weaker Ni–N bond.

Relative Ni–N and Ni–O Bond Lifetimes.—Although rate constants are reported for only one process, the scrambling of acetate groups in $Ni(NTA)_2^{4-}$, limits can be placed on the rates of some other processes.[14] For $Ni(NTA)(H_2O)_2^-$, the single peak observed at room temperature persists at 5°. This requires that the intramolecular displacement of a water molecule by an acetate group in $Ni(NTA)(H_2O)_2^-$ is faster than the rate of displacement of one acetate group by another in $Ni(NTA)_2^{4-}$. In view of the great tendency for IDA and MIDA to coordinate facially, a significant concentration of a facially coordinated three-coordinate species, designated $Ni(NTA)(H_2O)_3^-$, probably persists for the 1:1 NTA complex. Eigen[15] has demonstrated that the rate of formation of many metal complexes is governed by the rate at which a water molecule is lost from the first coordination sphere of the ion-pair intermediate. For $Ni(H_2O)_6^{2+}$, the first-order rate constant for this process at 25° is $\sim 10^4$ sec^{-1} for several ligands. It seems reasonable that this should be close to the rate of the process $Ni(NTA)(H_2O)_3^- \rightarrow Ni(NTA)(H_2O)_2^-$. This is not fast enough to account for the failure to observe separate peaks for the three types of acetate protons expected for $Ni(NTA)(H_2O)_2^-$. The expected separation between peaks would be about 4000 Hz at 100 MHz (based on $Ni(NTA)_2^{4-}$) so that a rate constant in excess of $\sim 10^4$ sec^{-1} is required to produce total averaging. The single peak observed at 5° required that $k > 10^4$ sec^{-1} at 5°. Thus, the rate constant for acetate scrambling at 25° must be at least 10^5 sec^{-1}. The slower displacement of a chelated acetate by a free acetate in *trans*-$Ni(NTA)_2^{4-}$ is not surprising since the displaced acetate is one of the relatively strongly bound acetates of a facially coordinated tridentate NTA. The product of this displacement is the mixed bidentate–tetradentate complex which Rabenstein and Kula[16] have proposed as an intermediate in the scrambling and displacement of NTA ligands of $Zn(NTA)_2^{4-}$.

The rate of acetate scrambling in four-coordinate, square-planar *trans*-$Pd(NTAH)_2$ at pH 3.5 has been determined.[8] Rate constants are about two orders of magnitude smaller than those of the 2:1 nickel complex, but the activation energies are comparable (~9 kcal). By contrast, for $Pt(NTAH)_2$, failure to observe coalescence of acetate proton signals at 100° requires that the rate of acetate scrambling is at least two orders of magnitude less than that of $Pd(NTAH)_2$.[8,9]

The rate of acetate scrambling in $Ni(IDA)_2^{2-}$ and $Ni(MIDA)_2^{2-}$ is considerably less than for the corresponding NTA complex. As others have noted,[6] this,

---

(14) R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Am. Chem. Soc.*, **85**, 2930 (1963); R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964).

(15) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 153.

(16) D. L. Rabenstein and R. J. Kula, *J. Am. Chem. Soc.*, **91**, 2492 (1969).

no doubt, reflects the absence of a free acetate group in these complexes. An upper limit can be placed on this rate. Since separate peaks separated by ~10 ppm are observed for corresponding protons in *cis* isomers, the rate constant for acetate scrambling must be significantly less than 10^3 sec^{-1}.

Finally, the observation of separate peaks for complex and free excess ligand requires that the Ni–N bond lifetimes also are $<10^{-4}$ sec. Upper limits for these rates could be readily determined by using deuterated excess ligand to follow the incorporation of free ligand into the complexes.

Acknowledgment.—The authors wish to acknowledge financial support from the National Institutes of Health, Grant GM-12598, and the National Science Foundation, Grant GP-13786. We also wish to acknowledge the National Science Foundation, Grant GP-6880, for the purchase of the Varian HA-100 nmr spectrometer used in these studies.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR, INDIA

Syntheses and Solution Equilibria of Some Nickel(II) Chelates

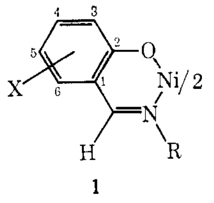
BY T. S. KANNAN AND A. CHAKRAVORTY

Received October 21, 1969

The syntheses of a number of nickel(II) complexes derived from various imines of 2-hydroxyacetophenone, 2-hydroxypropiophenone, and 2-hydroxybutyrophenone are described. Normally a nonaqueous chelation reaction is required for the syntheses. Unlike the salicylaldimine complexes, the present chelates do not form paramagnetic associated species in noncoordinating solvents like chloroform or benzene. In pyridine solution an equilibrium exists between a pseudooctahedral pyridine adduct and the parent planar species. This equilibrium has been thermodynamically characterized by variable-temperature spectroscopic and magnetic measurements. In several cases the paramagnetic pyridine adduct could be isolated in the crystalline state. It is concluded that steric factors are important in determining the population of the pseudooctahedral state in pyridine solution. An important conclusion is that the tendency to attain paramagnetism is uniformly less in the present complexes than in the corresponding salicylaldimine chelates. Some copper(II) complexes of the present ligands are also synthesized and examined spectroscopically. Their behavior is qualitatively similar to that of the salicylaldimines.

Introduction

The complexes derived from Schiff bases form a vast and fruitful area of research in coordination chemistry. More than one review article[1,2] concerning this general area have appeared in the last few years. The most widely investigated among Schiff base complexes are probably those derived from salicylaldimines. In particular, the bis chelates **1** show interesting stereochemical patterns. The behavior of complex **1** depends largely on the nature of group R. When R is a straight-chain alkyl group, the solids are usually diamagnetic but their solutions in, *e.g.*, chloroform and benzene, exhibit the equilibrium[3,4]



1
$(\text{R-sal})_2\text{Ni}$

$$\underset{\text{(planar)}}{\text{monomer } (S = 0)} \rightleftharpoons \underset{\text{(pseudooctahedral)}}{\text{associated species } (S = 1)} \qquad (1)$$

When R = aryl, the solids are either diamagnetic or paramagnetic depending upon the nature of the aryl group.[5,6] In solution (*e.g.*, in chloroform) they also exhibit equilibrium 1 heavily shifted toward the right unless steric factors prevent this.[5] When R is an α-branched alkyl group, conformational equilibria involving planar (S = 0) and tetrahedral (S = 1) geometries occur in solution.[7,8]

In contrast to extensive research on the salicylaldimine chelates **1**, surprisingly little is known about the corresponding chelates, **2**. Many years ago Pfeiffer, *et al.*,[9] reported the synthesis of $(\text{H–hac})_2\text{Ni}$. Harris, *et al.*,[10] later synthesized $(\text{Me–hac})_2\text{Ni}$ and $(\text{OH–hac})_2\text{Ni}$. Holm and coworkers[11] recently reported the nmr data on the complex $(\textit{sec}\text{-Bu–hac})_2\text{Ni}$. Apart from these there are no reports on the syntheses and studies of the complexes **2**. This probably stems from problems involved in the synthesis of **2**. The simple synthetic methods[1] that are generally applicable to salicylaldimines are in many cases of no avail in the syntheses of 2-hydroxyacetophenimine and other type **2** complexes.

---

[1] R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).

[2] L. Sacconi, *Coord. Chem. Rev.*, **1**, 126 (1966); S. Yamada, *ibid.*, **1**, 415 (1966).

[3] R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961).

[4] H. C. Clark, K. Macvicar, and R. J. O'Brien, *Can. J. Chem.*, **40**, 822 (1962).

[5] R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).

[6] L. Sacconi and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 1750 (1963).

[7] L. Sacconi, P. Paoletti, and M. Ciampolini, *ibid.*, **85**, 411 (1963).

[8] R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963).

[9] P. Pfeiffer, E. Buchholz, and O. Bauer, *J. Prakt. Chem.*, **129**, 163 (1931).

[10] C. M. Harris, L. Lenzer, and R. L. Martin, *Australian J. Chem.*, **11**, 331 (1958).

[11] R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, **89**, 6104 (1967).