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Probable Structure of Nickel(II)–Ethylenediaminetetraacetic Acid Type Complexes in Aqueous Solution

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The nuclear magnetic resonance temperature dependences for the complexes $Ni(EDTA)^{2-}$, $Ni(MED3A)^-$, Ni(EDDA), $Ni(IDA)_2{}^{2-}$, and $Ni(1,3\text{-}PDTA)^{2-}$ are reported. Racemization of $Ni(EDTA)^{2-}$ is rapid on the NMR time scale at 80°C, racemization of $Ni(1,3\text{-}PDTA)^{2-}$ is rapid at 78°C, but racemization is slow at all achievable temperatures (up to 105°C) for the other complexes. The activation energies for racemization (at the temperatures shown) are $\Delta G^\ddagger{}_{EDTA}(80°C) = 14.2$ kcal/mol, $\Delta G^\ddagger{}_{MED3A}(105°C) > 16.8$ kcal/mol, $\Delta G^\ddagger{}_{EDDA}(105°C) > 16.7$ kcal/mol, $\Delta G^\ddagger{}_{(IDA)_2}(105°C) > 16.0$ kcal/mol, and $\Delta G^\ddagger{}_{1,3\text{-}PDTA}(78°C) \approx 14$ kcal/mol. These data are interpreted to indicate predominantly pentacoordination by EDTA and 1,3-PDTA in the nickel(II) complexes. On the basis of studies of racemization of $Ni(EDTA)^{2-}$ a racemization mechanism similar to the base-catalyzed racemization of Co^{III}(EDTA) is proposed. In this mechanism, a heptacoordinate intermediate is proposed. The failure to observe certain peaks in the contact shift spectra of various nickel(II) EDTA type ligands is explained on the basis of kinetic broadening due to rapid attachment and detachment of the free carboxylate of EDTA type ligands. The rate of racemization of $Ni(EDTA)^{2-}$ is not a function of pH over the pH range $4 < pH < 12$. Cis $\rightleftharpoons$ trans isomerization of $Ni(IDA)_2{}^{2-}$ is fast at 48°C ($\Delta G^\ddagger(48°C) \approx 14$ kcal/mol) implying a rapid twist mechanism which does not lead to racemization. An unsymmetrical cis $\rightleftharpoons$ trans twist isomerization mechanism is proposed for $Ni(IDA)_2{}^{2-}$. Abbreviations used are as follows: $EDTA^{4-}$, $(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2{}^-)_2$; $MED3A^{3-}$, $^-O_2CCH_2N(CH_3)CH_2CH_2N(CH_2CO_2{}^-)_2$; $EDDA^{2-}$, $^-O_2CCH_2NHCH_2CH_2NHCH_2CO_2{}^-$; IDA^{2-}, $(^-O_2CCH_2)_2NH$; $1,3\text{-}PDTA^{4-}$, $(^-O_2CCH_2)_2NCH_2CH_2CH_2N(CH_2CO_2{}^-)_2$.

Introduction

There have been many conflicting reports on the number of coordination sites actually utilized by EDTA type ligands to coordinate metal ions. Higginson compared acid dissociation constants of metal–EDTA complexes and concluded that only five of the six possible EDTA sites were actually utilized in coordinating many divalent metal ions.[1] Subsequently, Higginson studied the mixed-complex formation of several divalent metal–EDTA ions and concluded that EDTA is hexacoordinate approximately 70% of the time[2] (75% for the case of nickel(II)). Charles,[3] on the other hand, concluded, on the basis of viscosity measurements and Kirschner's study of Cu(EDTA),[4] that most EDTA–divalent metal complexes involved hexacoordinate EDTA (or possibly tetracoordinate). Yasuda,[5] however, assigned pentadentate coordination in Co^{II}(EDTA) on the basis of his viscosity measurements. Wilkins and Yelin[6,7] utilized oxidative trapping to conclude that, in cobalt(II) complexes, the EDTA (and other similar ligands) is at least 80% hexacoordinate. Brunetti et al.[8] ascribed hexacoordination on the basis of thermodynamic data. Erickson et al.[9] in their NMR study of Ni–EDTA type complexes concluded that the coordination number of EDTA was no less than 5 but were unable to obtain a better answer.

Pentacoordination by EDTA has been indirectly assumed in several reported kinetic schemes[10,11] but has not been clearly demonstrated. This confusion exists to a large extent because it has not been possible to obtain direct measures of the solution structures of these labile complexes. The X-ray studies of Hoard et al.[13] clearly show the existence of uncoordinated carboxylates in the solid state under some conditions but, of course, do not unambiguously describe the solution structures. Hoard's work is in fact most consistent with hexacoordination at pH's where the carboxylates are deprotonated.

In this paper, evidence is provided that the EDTA complex of nickel(II) contains significant amounts of pentadentate EDTA over the pH range 4–12. This conclusion is based upon the observation of rapid racemization of $Ni(EDTA)^{2-}$ and slow racemization of similar ligands which do not have the possibility of uncoordinated acetate groups. The attack of this uncoordinated acetate appears to initiate racemization since racemization is not rapid in complexes where there is no free acetate.

Experimental Section

All of the ligands were commercial products except for MED3A and 1,3-PDTA. IDA and EDDA were recrystallized once from water. All other ligands were used without further purification. MED3A was synthesized by carboxymethylation of *N*-methylethylenediamine after the method of Smith et al.[12] The ligand was recovered as the trisodium salt by addition of sodium ethoxide to an alcoholic solution of the acid. 1,3-PDTA was graciously donated by Dr. J. Sarneski. The complexes were formed by adding equimolar amounts of ligand and anhydrous nickel chloride together with enough sodium hydroxide to neutralize the acetates. The complexes were dissolved in water, taken to dryness on a rotary evaporator, and redissolved in deuterium oxide (99.8%). This process was repeated as often as necessary to decrease the residual water content to acceptable levels. The final pH was determined with a Beckman Model SS-2 pH meter equipped with a microelectrode. The pD value was determined as pH + 0.4.[24] No high-temperature correction was made to the measured pD value.[25] The pH was varied, when necessary, by addition of 0.1 *M* sodium hydroxide or hydrochloric acid.

The contact shift measurements were made on a Hitachi R20B nuclear magnetic resonance spectrometer equipped with a Hewlett-Packard Model 230B radiofrequency amplifier to boost the radiofrequency output power for a good signal-to-noise ratio. Using this power amplifier, signal-to-noise ratios greater than 30:1 were obtained at all temperatures. The temperature was varied by means of the Hitachi Model R202VT temperature controller which was calibrated with ethylene glycol. The 300-ppm sweep width was calibrated against the internal frequency offset control and by comparison of these spectra with previously published spectra by other workers.

Results

The NMR spectral temperature dependence of $Ni(EDTA)^{2-}$ is shown in Figure 1. Essentially identical results (i.e., equivalent shifts and coalescence temperature) were obtained at pH 4 and 12. The contact shift temperature dependences of $Ni(MED3A)(H_2O)^-$, $Ni(EDDA)(H_2O)_2$, $Ni(IDA)_2{}^{2-}$, and $Ni(1,3\text{-}PDTA)^{2-}$ are shown in Figures 2–5, respectively. The spectra of all the complexes except EDTA and 1,3-PDTA obey the Curie law relationship within experimental error. The small peak at ~50 ppm in the MED3A spectra is due to an impurity. This impurity was not removed because of the small quantity of MED3A obtained and because it represents such a small fraction of the total amount of ligand that it could not prevent racemization of the rest of the

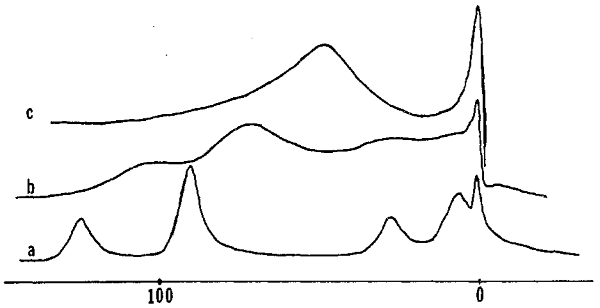

Figure 1. Contact shift temperature dependence of the Ni(EDTA) complex, pD 6.1: a, 34°C; b, 80°C; c, 105°C. Shift scale is ppm downfield of H_2O.

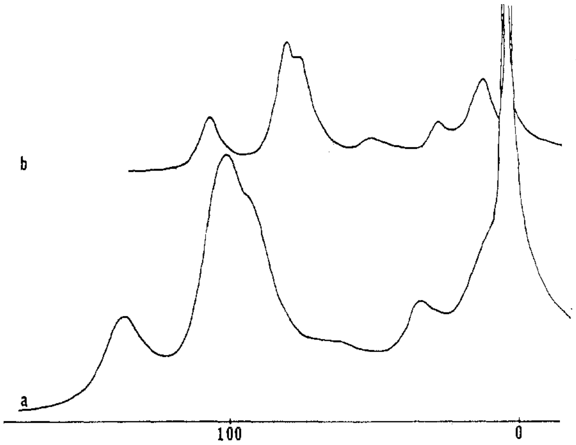

Figure 2. Contact shift temperature dependence of the Ni(MED3A) complex, pD 7.1: a, 34°C; b, 105°C. Shift scale is ppm downfield of H_2O.

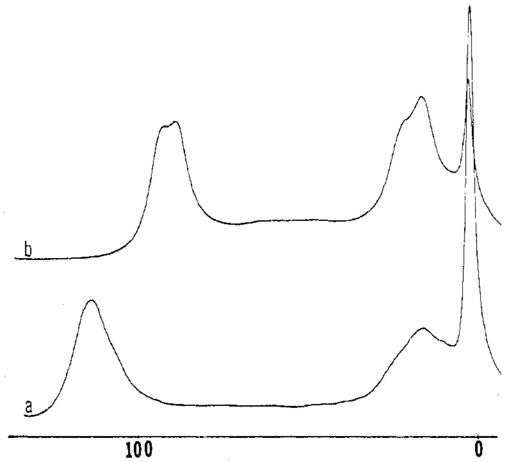

Figure 3. Contact shift temperature dependence of the Ni(EDDA) complex, pD 10.6: a, 34°C; b, 105°C. Shift scale is ppm downfield of H_2O.

complexes. The spectral assignments are tabulated in Table I.

Discussion

The room-temperature contact shift spectra of $Ni(EDTA)^{2-}$, $Ni(EDDA)(H_2O)_2$, and $Ni(IDA)_2{}^{2-}$ have previously been reported[9,19] and are consistent with the results of this study. It was previously reported, however, that no racemization of $Ni(EDTA)^{2-}$ occurs up to 100°C.[9] Upon reexamination of those previous data, it appears that the discrepancy between this earlier work and the present is due to the very poor signal-to-noise ratio of the earlier data.

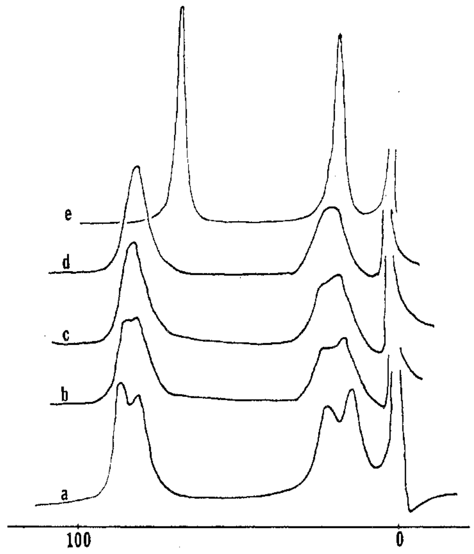

Figure 4. Contact shift temperature dependence of the $Ni(IDA)_2$ complex, pD 9.0: a, 34°C; b, 45°C; c, 48°C; d, 53°C; e, 105°C. Shift scale is ppm downfield of H_2O.

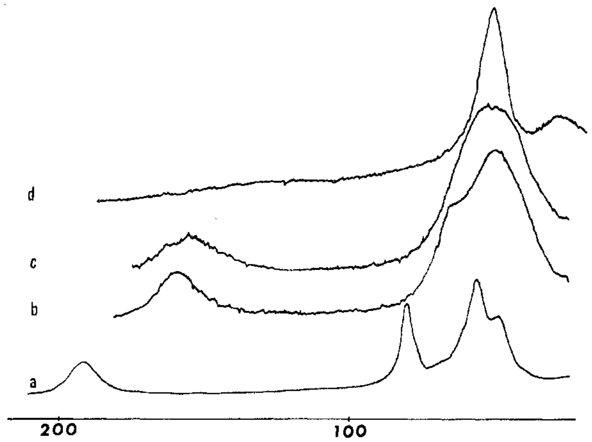

Figure 5. Contact shift temperature dependence of the Ni(1,3-PDTA) complex, pD 7.5: a, 34°C; b, 78°C; c, 87°C; d, 105°C. Shift scale is ppm downfield of H_2O; H_2O resonance not shown.

The collapse of the $Ni(EDTA)^{2-}$ spectrum at high temperature indicates that some process is occurring which averages the axial and equatorial differences of both the acetate and ethylenediamine portions of the molecule. The stereochemical consequences of $\Delta \rightleftharpoons \Lambda$ interconversion and nitrogen inversion have been previously considered in detail.[9] In this previous work, it was shown that nitrogen inversion converts in-plane (the plane refers to the

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plane) acetates to out-of-plane acetates, but neither converts equatorial acetates to axial acetates nor affects the ethylenediamine protons.[9] $\Delta \rightleftharpoons \Lambda$ conversion, on the other hand, converts in-plane axial acetates to out-of-plane equatorial acetates and also converts axial ethylenediamine protons to equatorial and vice versa. Thus, the total collapse of the spectrum to two poorly resolved peaks, shown by the data in Figure 1, clearly demonstrates that $\Delta \rightleftharpoons \Lambda$ conversion is rapid at 80°C in $Ni(EDTA)^{2-}$. One can imagine a variety of twist mechanisms similar to those proposed for tris-bidentate complexes[14-16] or one could imagine a mechanism which

Table I. Room-Temperature (310 K) Contact Shift Assignments

Complex	Shift[a]	Assignment	Ref
$\mathrm{Ni(EDTA)^{2-}}$	-5	2 axial en's	9[b]
	-25	2 axial out-of-plane acetates	
	-88	2 equatorial out-of-plane + 2 equatorial in-plane acetates	
	-117	2 equatorial en's	
$\mathrm{Ni(MED3A)^{-}}$ [c]	~ -5[d]	2 axial en's	This work
	-33	2 axial out-of-plane acetates	
	-63	Impurity	
	-93	2 equatorial out-of-plane + 1 equatorial in-plane acetates	
	-100	3 equatorial *N*-methyls	
	-133	2 equatorial en's	
EDDA	$\left.\begin{matrix}-15\\-20\end{matrix}\right\}^{e}$	2 axial acetates 2 axial en's	22[b]
	$\left.\begin{matrix}-107\\-111\end{matrix}\right\}^{e}$	2 equatorial en's 2 equatorial acetates	
$\mathrm{Ni(IDA)_2{}^{2-}}$	-15	Cis axial acetate	19[b]
	-22	Cis + trans axial acetates	
	-78	Cis + trans equatorial acetates	
	-87	Cis equatorial acetate	
$\mathrm{Ni(1{,}3\text{-}PDTA)^{2-}}$	$+13$[f]	β $\mathrm{CH_2}$	23, this work
	-3[d,f]	Axial acetates	
	-51 -58	Equatorial acetates	
	-83	Axial α CH	
	-196	Equatorial α CH	

[a] Ppm downfield from H_2O. [b] Shifts extrapolated to 310 K according to Curie law. [c] It is assumed that the vacant coordination site occupies an in-plane position. [d] Because of significant overlap with the water peak, the shift is only approximate. [e] These resonances were not completely resolved in this study. [f] Not shown in Figure 5.

involves the breaking of one or more nickel–acetate bonds followed by intramolecular rearrangements being responsible for this racemization. One can conclude, however, that a simple twist mechanism is not operative in this instance, by examining the data for Ni(EDDA) and $\mathrm{Ni(MED3A)^-}$ complexes. Both of these complexes are structurally similar to $\mathrm{Ni(EDTA)^{2-}}$ and would be expected to undergo twist racemization with comparable ease. In fact, one could rationalize that they should racemize more easily than the EDTA complex because there are fewer bonds to be stretched in the twist. What is observed, however, is that neither of these two complexes shows any significant racemization (on the NMR time scale) up to 105°C, the maximum temperature obtainable in this work. Also, the thermal racemization of $\mathrm{Co^{III}(EDTA)}$, which is believed to go via a twist mechanism, is extremely slow. Extrapolating the data of Cooke et al.[18] to 80°C yields a predicted twist rate approximately 10^{-11} times the rate of racemization observed for the Ni–EDTA complex. These facts in themselves do not, of course, disprove the twist mechanism but are consistent with an alternative mechanism proposed below.

If one uses the chemical shift differences ($\mathrm{sec^{-1}}$) between axial and equatorial substituents as a measure of the maximum rate of $\Delta \rightleftharpoons \Lambda$ conversion (assuming that a rate of 0.1 × chemical shift differences will yield observable broadening), the activation energies calculated from the Eyring equation are $\Delta G^{\ddagger}_{\mathrm{EDDA}} > 16.7$ kcal/mol and $\Delta G^{\ddagger}_{\mathrm{MED3A}} > 16.8$ kcal/mol; the activation energy for racemization of $\mathrm{Ni(EDTA)^{2-}}$calculated from the extrapolated Curie law[17] at 80°C is 14.2 kcal/mol, and for 1,3-PDTA, $\Delta G^{\ddagger} \approx 14$ kcal/mol. These data imply that the fourth acetate is an important factor in lowering the free energy of racemization. The lowering of the racemization free energy probably occurs because of strain or steric interferences which are introduced when the fourth acetate bonds to the nickel.

If one examines the data shown in Figure 4 for $\mathrm{Ni(IDA)_2{}^{2-}}$, it is apparent that some intramolecular rearrangement occurs at relatively low temperature (the two pairs of peaks collapse to two single peaks) but that the axial and equatorial differences are not averaged out by this processes. The low-temperature process is believed to be cis $\rightleftharpoons$ trans isomerization and is discussed below. The fact that the axial equatorial differences are not averaged at the highest temperature available (105°C) means that racemization via a symmetrical twist operation is slow on this time scale. Thus, it appears that the ethylenediamine or propylenediamine rings of EDTA and 1,3-PDTA, respectively, are important factors in lowering the free energy of activation for racemization.

Consideration of all of these data leads to the following conclusions about the solution structure and dynamics of $\mathrm{Ni(EDTA)^{2-}}$. In view of the great increase in rate of racemization upon addition of two acetate arms to EDDA, a simple twist mechanism is not operative since EDDA should undergo the twist operation at least as easily as EDTA. In view of the great similarity between the room-temperature $\mathrm{Ni(MED3A)(H_2O)^-}$ spectrum (Figure 2) and the room-temperature $\mathrm{Ni(EDTA)^{2-}}$ spectrum (Figure 1) (with the additional resonance due to the methyl group and impurity in MED3A) these two complexes probably have similar structures—i.e., pentacoordinated ligands and a water molecule occupying the sixth coordination site. From these data it is not possible, however, to rule out an equilibrium between hexacoordinated and pentacoordinated species. In view of the great similarity of the contact shifts of axial and equatorial protons in the Ni(MED3A) and Ni(EDTA) complexes and the great sensitivity of contact shift measurements to conformational details, it seems likely that any hexacoordinate $\rightleftharpoons$ pentacoordinate equilibrium lies far to the pentacoordinate species. Because $\mathrm{Ni(MED3A)(H_2O)^-}$ does not rapidly racemize, it can be inferred that the uncoordinated acetate plays an active role in the racemization process. Because $\mathrm{Ni(IDA)_2{}^{2-}}$ does not racemize, it is inferred that the ethylenediamine or propylenediamine ring strain and/or steric interaction are also significant factors. Further support for the importance of uncoordinated acetates is seen in the rapid racemization of $\mathrm{Ni(NTA)_2{}^{4-}}$ (NTA = nitrilotriacetic acid) in which there are certainly uncoordinated acetates available.[19] The $\Delta G^{\ddagger}$ calculated for racemization of $\mathrm{Ni(NTA)_2{}^{4-}}$ at 80°C is 13.6 kcal/mol using the data of Erickson, Ho, and Reilley.[19] This is in good agreement with the 14.2 kcal/mol reported here

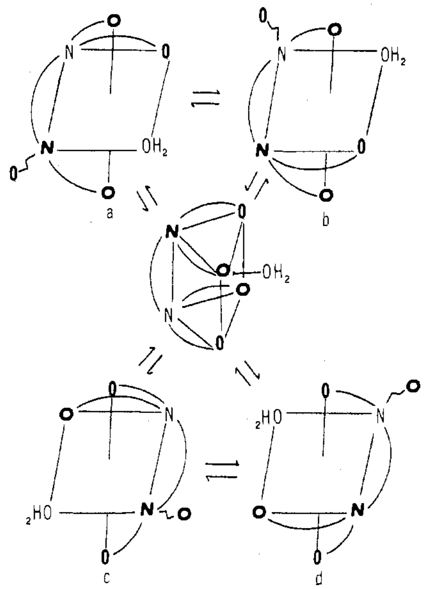

Figure 6. Proposed solution structure and racemization mechanism of the Ni-EDTA complex in aqueous solution.

for Ni(EDTA)$^{2-}$ and may indicate a similar mechanism. All of these considerations lead to the solution structure and racemization mechanism for the Ni^{II}–EDTA complex over the pH range studied, shown in Figure 6.

This proposed racemization mechanism utilizes a heptacoordinate intermediate similar to the proposed Co^{III}–EDTA–OH intermediate in the base-catalyzed racemization of Co^{III}(EDTA).[18] It is believed that coordination of the fourth acetate leads to formation of the unstable symmetrical intermediate and, hence, interconversion. Molecules which do not have uncoordinated acetates must obtain the energy thermally and, hence, are much slower reactions. Attack by a water molecule on a hexacoordinate complex to form the intermediate does not, apparently, occur to any great extent as seen by the slow racemization of Ni(IDA)$_2^{2-}$.

Thus, these data indicate that EDTA^{4-} is actually a predominantly pentacoordinate ligand in Ni(EDTA)$^{2-}$. The uncoordinated acetate greatly increases the rate of racemization of Ni(EDTA)$^{2-}$ much as attack by hydroxide ion increases the rate of racemization of Co^{III}(EDTA).[18] Although one cannot quantitatively compare the second-order hydroxide-catalyzed racemization of Co^{III}(EDTA) to the first-order thermal racemization of Ni^{II}(EDTA), it is significant to note that both occur on roughly the same time scale.[18,20] This time scale is much shorter than the normal twist racemization of Co^{III}(EDTA). It is proposed that a similar intermediate species is formed in these racemizations.

On the basis of these new data, it is possible to explain the absence of a resonance due to the in-plane axial acetate of Ni(EDTA)$^{2-}$ and other similar ligands.[9] This missing peak can now be explained as being exchange broadened by rapid direct interconversion between species a and b (or c and d) of Figure 6. This explanation was originally discounted because of a failure to observe any significant temperature dependence as noted earlier. Attempts here to observe this uncoordinated acetate peak at low temperature in deuteriomethanol were unsuccessful down to a temperature of −60°C. It seems doubtful that low-temperature studies will allow observation of this acetate peak because of excessive broadening at very low temperatures. It may be possible to observe this uncoordinated acetate by blocking the open coordination site (and, hence, a $\rightleftharpoons$ b of Figure 6) with cyanide or some other monodentate ligand. Experiments of this type are now in progress. In view of the fact that the in-plane axial acetate protons are not observed in either 1,2-PDTA, CyDTA, or

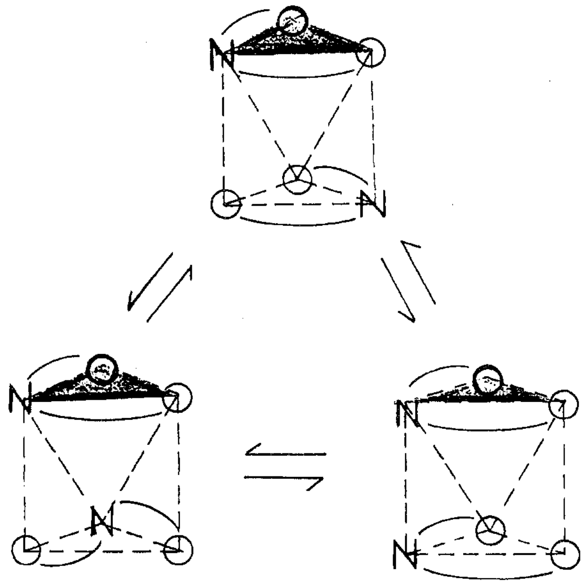

Figure 7. Proposed unsymmetrical twist mechanism for the Λ-cis $\rightleftharpoons$ trans $\rightleftharpoons$ Δ-cis isomerization of Ni(IDA)$_2^{2-}$.

BDTA complexes, it appears that all of these are also pentadentate. Racemization is not observed in 1,2-PDTA, *rac*-BDTA, or CyDTA because of strong conformational preferences. Racemization was, however, observed in Ni(*ms*-BDTA)$^{2-}$ where there is no conformational preference.[21] The free energy of activation (at 72°C) observed for Ni(*ms*-BDTA)$^{2-}$, 15.2 kcal/mol, is slightly higher than observed here for Ni(EDTA)$^{2-}$ and probably represents the increased steric interaction in the planar ring intermediate.

The previous study of deuteration rates of Ni–EDTA type complexes concluded that Ni(PDTA)$^{2-}$ (PDTA^{4-} = 1,2-propylenediaminetetraacetate) undergoes rapid nitrogen inversion (relative to the rate of deuteration) and slow $\Delta \rightleftharpoons \Lambda$ conversion.[9] This conclusion appears contradictory to the conclusions reached here, but can be rationalized if one realizes that conformational preference of the methyl group for an equatorial environment in the PDTA complex can lead to stereospecific effects similar to those observed in the previous study.[9] That is, $\Delta \rightleftharpoons \Lambda$ conversion could be rapid, but, because the Δ and Λ forms have different populations, the interconversion could appear to be slow. Differentiation between these two possibilities is extremely difficult. While it is possible that nitrogen inversion is rapid in the Ni(1,2-PDTA)$^{2-}$ case, it seems unlikely in view of the observations reported here. It is more difficult to rationalize the observed deuteration stereospecificity of Ni(*rac*-BDTA)$^{2-}$ (*rac*-BDTA = racemic 2,3-butylenediaminetetraacetic acid). The great conformational preference of the two methyl groups of this ligand for equatorial environments would lead one to conclude that $\Delta \rightleftharpoons \Lambda$ conversion effects would be very small (as discussed in ref 21). It does seem reasonable, however, that if $\Delta \rightleftharpoons \Lambda$ conversion is rapid for *ms*-BDTA, it might also be rapid for *rac*-BDTA, although the two enantiomers have different energies in the latter case. This question is not yet settled and may require some more experimental investigation.

Examination of the Ni(IDA)$_2^{2-}$ data clearly shows that Λ-cis $\rightleftharpoons$ trans $\rightleftharpoons$ Δ-cis isomerization occurs rapidly at 48°C (the peaks due to cis and trans isomers[19] coalesce at 48°C, $\Delta G^{\ddagger}$(48°C) $\approx$ 14 kcal/mol for Λ-cis $\rightleftharpoons$ trans $\rightleftharpoons$ Δ-cis isomerization). The persistence of the axial and equatorial peaks up to 105°C indicates that racemization does not occur ($\Delta G^{\ddagger}$(105°C) > 16 kcal/mol) rapidly up to this temperature, that is, the individual chelate ring conformations are not averaged. Clearly the mechanism of cis $\rightleftharpoons$ trans isomerization does not involve bond breaking, as this would also lead to racemization. It appears that cis $\rightleftharpoons$ trans isomerization occurs via a rapid intramolecular twist which does not go through a symmetrical intermediate.

The rapid cis $\rightleftharpoons$ trans isomerization of Ni(IDA)$_2^{2-}$ without racemization implies that the intermediate is not symmetrical. One possibility is that cis $\rightleftharpoons$ trans isomerization occurs by the unsymmetrical twist mechanism shown in Figure 7 in which only one of the coordinated iminodiacetates undergoes a twist. This mechanism does not racemize the complex and can occur as a low-energy process because only one ligand twists. This mechanism is not available to tris-bidentate ligands in which at least two ligands must be involved and, hence, cis $\rightleftharpoons$ trans isomerization of bis-tridentate complexes may be more rapid than racemization of tris-bidentate complexes.

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Registry No. Ni(EDTA)(H_2O)$^{2-}$, 56348-48-2; Ni(MED3A)(H_2O)$^{-}$, 56348-49-3; Ni(EDDA)(H_2O)$_2$, 21491-91-8; Ni(IDA)$_2^{2-}$, 23314-44-5; Ni(1,3-PDTA)(H_2O)$^{2-}$, 56348-50-6.

References and Notes

(1) W. C. E. Higginson, *J. Chem. Soc.*, 2761 (1962).
(2) W. C. E. Higginson and B. Samuel, *J. Chem. Soc. A*, 1579 (1970).
(3) R. G. Charles, *J. Am. Chem. Soc.*, **78**, 3946 (1956).
(4) S. Kirschner, *J. Am. Chem. Soc.*, **78**, 2372 (1956).
(5) M. Yasuda, *Bull. Chem. Soc. Jpn.*, **41**, 139 (1968).
(6) R. G. Wilkins and R. Yelin, *J. Am. Chem. Soc.*, **89**, 5496 (1967).
(7) R. G. Wilkins and R. Yelin, *J. Am. Chem. Soc.*, **92**, 1191 (1970).
(8) A. P. Brunetti, G. H. Nancollas, and P. N. Smith, *J. Am. Chem. Soc.*, **91**, 4680 (1969).
(9) L. E. Erickson, D. C. Young, F. F. L. Ho, S. R. Watkins, J. B. Terrill, and C. N. Reilley, *Inorg. Chem.*, **10**, 441 (1971).
(10) J. D. Carr and C. N. Reilley, *Anal. Chem.*, **42**, 51 (1970).
(11) D. W. Margerum and H. M. Rosen, *Inorg. Chem.*, **7**, 299 (1968).
(12) R. Smith, J. L. Bullock, F. C. Bersworth, and A. E. Martell, *J. Org. Chem.*, **14**, 355 (1949).
(13) (a) G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 556 (1959); (b) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964); (c) M. J. Jarmon, T. A. Hamon, M. D. Lind, and J. L. Hoard, *ibid.*, **3**, 34 (1964).
(14) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).
(15) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).
(16) N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).
(17) F. F. L. Ho and C. N. Reilley, *Anal. Chem.*, **42**, 600 (1970).
(18) D. W. Cooke, Y. A. Im, and D. H. Busch, *Inorg. Chem.*, **1**, 13 (1962).
(19) L. E. Erickson, F. F. L. Ho, and C. N. Reilley, *Inorg. Chem.*, **9**, 1148 (1970).
(20) D. W. Cooke and D. H. Bush, paper presented at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.
(21) D. C. Young and C. N. Reilley, *J. Coord. Chem.*, **1**, 95 (1971).
(22) F. F. -L. Ho, L. E. Erickson, S. R. Watkins, and C. N. Reilley, *Inorg. Chem.*, **9**, 1139 (1970).
(23) J. E. Sarneski and C. N. Reilley, *Inorg. Chem.*, **13**, 977 (1974).
(24) K. Mikkelsen and S. O. Nielsen, *J. Phys. Chem.*, **64**, 632 (1960).
(25) R. K. Force and J. D. Carr, *Anal. Chem.*, **46**, 2049 (1974).

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Studies of Three Nickel(II) Complexes Containing Different Macrocyclic Ligands Derived from Acetylacetone and Triethylenetetramine

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The synthetic pathways showing the relationship of the complex 12-formyl-11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II), [Ni(CHOAT)]$^+$, to the two other macrocyclic complexes 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II), [Ni(AT)]$^+$, and 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienenickel(II), [Ni(ATH)]$^{2+}$, are presented. The electrophilic and hydrolytic reactions involved in these pathways are related to the known chemistry of [Ni(AT)]$^+$. A comparative study of the three complexes and another complex containing a linear tetradentate ligand derived from acetylacetone was conducted via infrared, electronic, and PMR spectroscopy. Infrared spectra of samples of the complexes which had been selectively deuterated revealed that those species containing the 1,3-diiminate moiety exhibit the same pattern of bands in the 1600-cm^{-1} region as do selectively deuterated 1,3-diketonates. It is presumed that the same coupling phenomenon is occurring in the diiminates as has been found in the isoelectronic diketonates. Arguments are presented which account for the trends observed in the electronic spectra of the complexes. The PMR spectra reveal that all the macrocyclic complexes are conformationally fixed (relative to the NMR time scale) and that isomers of two of the three complexes are present in solution.

Introduction

Few classes of coordination compounds have served as the focus of such extensive and continuing research effort as have those prepared from the 1,3-diketones or their nitrogen analogs. For the diketones the most common mode of coordination is that where the ligand is an anionic bidentate donor containing a delocalized π system (I).[1] However, the neutral diketone also can serve as a bidentate ligand (II).[2] When the diketone is bound in this latter fashion the local character of each of the carbonyl bonds is retained. In the case of the nitrogen analogs of the 1,3-diketones two distinct classes can be specified. The members of one class, the 1,4-diazepines, have been known for many years and are readily synthesized from 1,2-diamines and 1,3-diketones.[3] The 1,4-diazepines can exhibit the delocalized (III) and localized (IV) forms seen with the diketones but they cannot serve as chelating agents due to their prohibitively unfavorable geometry. However, the other class of nitrogen analogs is eminently suited for chelation (V–VIII). To our knowledge complexes containing this class have been reported only recently and were first prepared by routes which directly involve 1,3-diketones as starting materials. The initial reports feature chelates with (1) bidentate diiminate ligands (V),[4] (2) linear ligands containing one diiminate group (V where R'' = $CH_2CH_2NH_2$, for instance),[5] (3) macrocyclic ligands containing one diiminate group (VI),[6] (4) macrocyclic ligands containing two diiminate groups (VII),[7] and (5) macrocyclic ligands containing one neutral diimine group (VIII).[8] At least three schemes to obtain chelates containing the diiminate moiety (or ligands of the 1,3-diimine class) are known which do not involve 1,3-diketones as starting materials. In one of these a chelated diiminate group is obtained directly by oxidizing a coordinated 1,3-diamine[9] and in another scheme the ligand is made from an acetylenic aldehyde and a diamine.[10] In the third scheme