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Nuclear Magnetic Resonance Studies of Configuration and Ligand Conformation in Paramagnetic Octahedral Complexes of Nickel(II). V. Complexes of Ethylene(dinitrilo)-*N,N,N′,N′*-tetraacetate, 1,2-Propane(dinitrilo)-*N,N,N′,N′*-tetraacetate, and *trans*-1,2-Cyclohexane(dinitrilo)-*N,N,N′,N′*-tetraacetate

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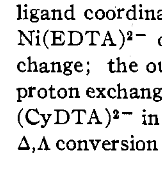
Received June 22, 1970

The pmr spectra of paramagnetic octahedral complexes of nickel(II) with ethylene(dinitrilo)-*N,N,N′,N′*-tetraacetate (EDTA), 1,2-propane(dinitrilo)-*N,N,N′,N′*-tetraacetate (PDTA), and *trans*-1,2-cyclohexane(dinitrilo)-*N,N,N′,N′*-tetraacetate (CyDTA) are reported. The spectra are interpreted on the basis of the well-established dependence of hyperfine coupling constant upon dihedral angle. It is postulated that the in-plane axial acetate protons do not contribute to the spectra of any of the complexes, and the cyclohexane ring protons nearest the metal are also not observed. All the chelate rings are puckered, but the acetate chelate rings of Ni(EDTA)$^{2-}$ are not as puckered as those in Ni(EDDA). The out-of-plane acetate rings of Ni(CyDTA)$^{2-}$ are the most nearly planar of the acetate rings studied. It is surmised that the average ligand coordination number is between 5 and 6 with Ni(CyDTA)$^{2-}$ having a greater fraction of hexadentate species than Ni(EDTA)$^{2-}$ or Ni(PDTA)$^{2-}$. The acetate protons are found to undergo stereospecific base-catalyzed deuterium exchange; the out-of-plane acetate protons exchange about 10^4 times faster than the in-plane acetate protons, and an axial proton exchanges about three times faster than an equatorial proton. No significant nitrogen inversion was observed for Ni(CyDTA)$^{2-}$ in 1 week at 100°. However, nitrogen inversion is the mode of acetate scrambling in Ni(PDTA)$^{2-}$, while Δ,Λ conversion and nitrogen inversion contribute equally to acetate scrambling in Ni(EDTA)$^{2-}$.

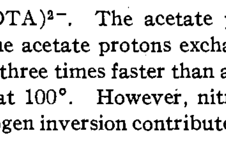
Introduction

In spite of extensive study by a variety of techniques, several interesting questions regarding structural and kinetic properties of metal chelates of the familiar hexadentate chelating agents EDTA, PDTA, and CyDTA have not yet been answered. This nmr study was undertaken to answer some of these questions for nickel(II) complexes of these ligands. The questions posed were the following.

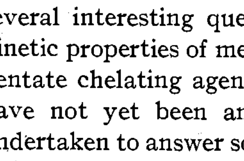
(1) What species are present in solution? Optical and coordination isomers must both be considered. The former category includes both ligand-centered and metal-centered isomers, if the ligand is asymmetric. Structures of the four isomers possible with these three ligands are shown in I–IV. For EDTA, $R_1 = R_2 =$ H, so that I = II and III = IV and only two equally probable species (Δ or Λ) are possible.[2] For PDTA, $R_1 =$ H and $R_2 = CH_3$. For racemic PDTA, four species are thus possible and the ratio of Δ-*l* to Λ-*l* is not likely to be one.[3] With optically active PDTA, only one Δ–Λ pair is possible. Only *trans-dl*-CyDTA will be considered. For this ligand, R_1, R_2 = C_4H_8, the remainder of the cyclohexane ring. The steric requirements of the cyclohexane ring permit only one isomer, which can be designated Δ-*l*, for the optically pure ligand. Because nmr spectra do not distinguish between mirror image isomers, the number of isomers distinguishable by nmr will be the same whether racemic or optically pure ligands are used. Thus, for Ni(EDTA)$^{2-}$ and Ni(CyDTA)$^{2-}$, only one distinguishable species is expected; for Ni(PDTA)$^{2-}$, two are expected. In all of the above structures, the distinction between in-plane and out-of-plane acetate groups (with reference to the N–Ni–N plane) is maintained. For Ni(PDTA)$^{2-}$, the two in-plane and two out-of-plane acetates are distinguishable, in principle.



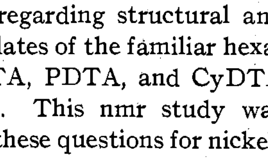
I Δ-l



II Δ-d



III Λ-l



IV Λ-d

The possibility of a significant concentration of five-coordinate species containing a coordinated water molecule must also be considered.[4] Available evidence is not conclusive, but it is clear that of the two possible five-coordinate species (V and VI) the one in which the water molecule occupies an in-plane position (V) would be strongly favored. This is the site of

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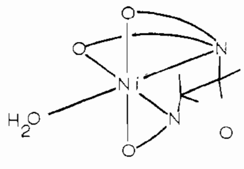
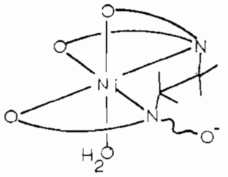
(2) The symbols Δ and Λ will be used to designate the absolute configurations of the complexes. The assignments are based on the corresponding Ni(EDDA) isomers in which the two acetates are both out of plane. A more appropriate, but more cumbersome, symbolism is described in a later section of this paper and in *Inorg. Chem.*, **9**, 1 (1970).

(3) F. P. Dwyer and F. L. Garvin, *J. Amer. Chem. Soc.*, **83**, 2610 (1961).

(4) A. P. Brunetti, G. H. Nancollas, and P. N. Smith, *ibid.*, **91**, 4680 (1969), have reviewed earlier work critically in presenting thermodynamic data which indicate a coordination number of 6 for EDTA in Ni(EDTA)$^{2-}$.



V



VI

water coordination in the acid salt.[5] Furthermore, EDDA acetate groups show a strong tendency to coordinate out of plane.[6]

(2) What is the conformation of each of the five-membered acetate (ac) and ethylenediamine (en) rings? The en ring conformation of chelated CyDTA is determined by the conformational requirements of the cyclohexane ring. The en ring in the other chelates no doubt adopts a similar conformation. For PDTA, the strong tendency for CH_3 to be equatorial can be expected to have a large effect on the Δ/Λ equilibrium ratio.[3] The conformation of the acetate rings is less certain. X-Ray data suggest a nearly planar out-of-plane ring in the solid state, but the conformation in solution may be quite different.[5] For either type of ring, puckering of the five-membered ring makes one methylene proton pseudoaxial and the other pseudoequatorial. This axial–equatorial designation, though not strictly appropriate, will be employed throughout.

(3) How fast and by what mechanisms do the isomers (optical or coordination) interconvert? These questions are particularly important to consider, because the nmr technique employed in this work cannot distinguish between isomers that are being rapidly interconverted. Interchange of in-plane and out-of-plane acetate groups, referred to an *acetate scrambling*, is particularly interesting. It can be achieved either with or without Ni–N bond rupture. The latter corresponds to a Δ,Λ (I → III) conversion: the former requires lone-pair inversion while the Ni–N bond is broken, does not lead to a configuration change, and is detectable only if in-plane and out-of-plane acetate groups can be distinguished. An assessment of the relative importance of these pathways has been made for some diamagnetic complexes.[7] It is based on the ability to answer still another question.

(4) What is the stereochemistry of acetate proton exchange? Base-catalyzed deuterium-exchange rates of acetate protons of $Ni(EDTA)^{2-}$ were determined by Terrill and Reilley[8] by observing the decrease in nmr absorption of acetate proton signals of free excess EDTA (fivefold excess) in the presence of $Ni(EDTA)^{2-}$. The determination required the assumption that the rate of exchange of ligand molecules is much greater than the rate of proton exchange. This assumption was subsequently confirmed by Carr and Reilley[9] by following the incorporation of acetate-deuterated $EDTA^{4-}$ into $Ni(EDTA)^{2-}$ in the mid-pH range. For several Co(III) complexes, acid- and base-catalyzed deuteration of out-of-plane acetates is several orders of magnitude faster than that of in-plane acetates.[10,11] Furthermore, the deuteration is stereospecific with one out-of-plane acetate proton being more labile than the other. In none of these cases was any exchange detected for en CH_2 protons. Thus, a convenient method is available for distinguishing between ac and en protons, between in-plane and out-of-plane ac protons, and between the two CH_2 protons of a given acetate group.

Our previously reported nmr studies have enabled us to answer similar questions about paramagnetic nickel(II) complexes of substituted ethylenediamines,[12,13] amino acids,[14] and other aminocarboxylate ligands.[14,15] These studies and a recent report by Pratt and Smith[16] have established, on a semiquantitative basis, the conformation dependence of CH_2 proton shifts in five-membered en and ac rings. For both types of rings, the more equatorial proton has a much larger downfield shift than the more axial proton. On this basis, it is clear that the earlier tentative spectral assignment reported by Pratt and Milner[17] for $Ni(EDTA)^{2-}$ and $Ni(PDTA)^{2-}$ cannot be correct. Similarly, on the basis of our study of complexes of IDA MIDA, and NTA, it is reasonable to expect the I → III conversion to be slow enough to observe separate nmr spectra of nonidentical Δ and Λ isomers, while the I → V conversion is probably too fast to see anything more than a weighted-average spectrum for five-coordinate and six-coordinate species.[15]

In analyzing the kinetics and stereochemistry of proton exchange, spectra of both paramagnetic NiY^{2-} and of diamagnetic Y^{4-}, released from NiY^{2-} by treatment with excess KCN, were analyzed. The KCN treatment is particularly convenient, since it yields a solution of diamagnetic $Ni(CN)_2^{2-}$ and free ligand. Thus the spectrum of diamagnetic free ligand can be obtained without requiring further separation or purification. In this way, we were able to obtain information that is not available in the spectrum of either species alone. Without this complementary information, it is doubtful that the spectra of the complexes would ever have been completely interpreted.

Experimental Section

Sample Preparation.—Anhydrous reagent grade nickel chloride and commercially available H_4EDTA, H_4PDTA, and H_4CyDTA were used to prepare solutions of the complexes. In a typical preparation 1 mmol of $NiCl_2$ (as 0.1 *M* stock solution) was added to 1 mmol of the ligand. Standardized aqueous KOH

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[5] G. S. Smith and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 556 (1959); C. L. Fox and J. L. Lambert, *Inorg. Chem.*, **8**, 2220 (1969); J. L. Hoard, G. S. Smith, and D. M. Lind in "Advances in the Chemistry of Coordination Compounds," Macmillan, New York, N. Y., 1961.

[6] For a recently reported exception, however, see P. J. Garnett, D. W. Watts, and J. I. Legg, *Inorg. Chem.*, **8**, 2534 (1969).

[7] R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964); J. L. Sudmeier and C. N. Reilley, *Inorg. Chem.*, **5**, 1047 (1966).

[8] J. B. Terrill and C. N. Reilley, *Anal. Chem.*, **38**, 1876 (1966).

[9] J. D. Carr and C. N. Reilley, *ibid.*, **42**, 51 (1970).

[10] J. B. Terrill and C. N. Reilley, *Inorg. Chem.*, **5**, 1988 (1966).

[11] See J. L. Sudmeier and G. Occupati, *ibid.*, **7**, 2524 (1968), for a comparable study of an EDDA complex of Co(III).

[12] F. F.-L Ho and C. N. Reilley, *Anal. Chem.*, **41**, 1835 (1969).

[13] F. F.-L. Ho and C. N. Reilley, *ibid.*, **42**, 600 (1970).

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

[15] L. E. Erickson, F. F.-L. Ho, and C. N. Reilley, *ibid.*, **9**, 1148 (1970).

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

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

was then added to neutralize the protons released and the whole solution was rotary evaporated to dryness under vacuum. After treating with 1–2 ml of D_2O and reevaporating 1–2 times, 2 ml of D_2O was added to yield a 0.5 M solution.

For kinetic runs, 5 mmol of metal and ligand were used and slightly less than the total calculated base was added until after the preliminary D_2O treatment. The concentration of KOD used in final dilution (in a 10-ml volumetric flask) was chosen to yield a final solution which was 0.5 M in Ni(II) and ligand and 0.1 M in excess KOD.

Kinetic Runs.—The contents of the stock solution were transferred to several nmr tubes equipped with pressure caps and placed in a refluxing water bath (100°) or a constant-temperature water bath (71.7°) or were left at room temperature or in a 6° refrigerator. The high-temperature samples were placed in an ice bath immediately after removal and their spectra were recorded promptly.

Immediately after recording spectra, samples (0.5 ml) were transferred to a small test tube containing about 2 mmol of KCN to liberate the ligand (and produce $Ni(CN)_4^{2-}$). Spectra of the KCN-treated solutions were run shortly after treatment to avoid error resulting from the much slower exchange of acetate protons of free ligand.

Recording Spectra.—Spectra of paramagnetic complexes were recorded with a Varian HA-100 nmr spectrometer as described earlier.[12] Spectra of diamagnetic free ligands were recorded with either Varian HA-100 or Varian A-60A spectrometers.

Results

Spectral Assignments.—Spectra of 0.5 M D_2O solutions of $Ni(EDTA)^{2-}$, $Ni(PDTA)^{2-}$, and $Ni(CyDTA)^{2-}$ are shown in Figure 1. Details of the upfield portion of the $Ni(CyDTA)^{2-}$ spectrum are shown in Figure 2. The residual HDO proton peak occurs at about −5 ppm in this and all following illustrations.

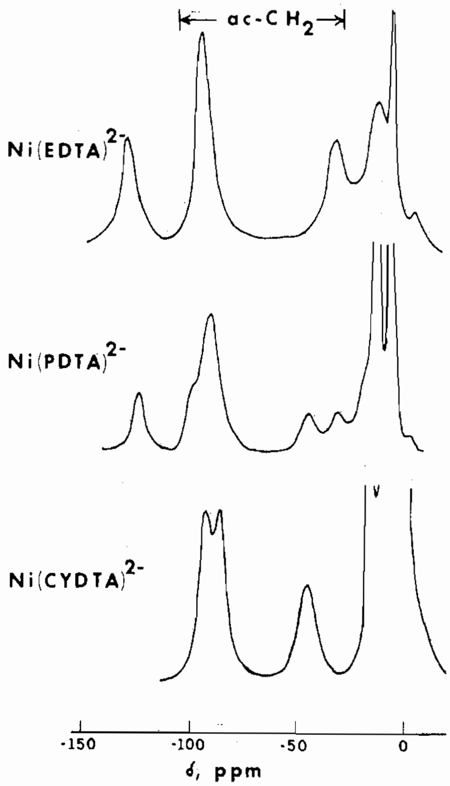


Figure 1.—The 100-MHz spectra of nickel complexes in D_2O at room temperature.

The spectrum of $Ni(EDTA)^{2-}$ consists of four peaks. The three at −10, −31, and −126 ppm are approximately equal in area, while the peak at −96 ppm is about twice as large. Since the two peaks at −31 and −96 ppm disappear on deuteration in 0.1 N KOH–D_2O, these can be assigned to acetate protons. The peaks at −10 and −126 ppm can then be assigned to axial and equatorial en CH_2 protons, respectively. The acetate portions of the spectra of $Ni(PDTA)^{2-}$ and $Ni(EDTA)^{2-}$ are similar, except that the more upfield portion is split into two equal-intensity peaks (−33 and −44 ppm) and the larger downfield peak (∼−90 ppm) shows some structure. The extreme downfield peak is only about half the size of the corresponding peak of $Ni(EDTA)^{2-}$. Since it is not affected by deuterium exchange, it and the remaining large peak at −11 ppm can be assigned to en protons and the methyl group. For $Ni(CyDTA)^{2-}$, the acetate portion of the spectrum is again similar, with the larger absorption occurring as two equal-intensity peaks at −83 and −93 ppm and the smaller as a somewhat broader but equal-area peak at −48 ppm. The remaining relatively sharper peaks of approximately equal area at −17, −9, −3, and +1 ppm are assigned to cyclohexane ring protons. The deuteration experiments which led to the above assignments and which also permitted the more detailed assignments, which are summarized in Table I and Figure 2, will now be considered.

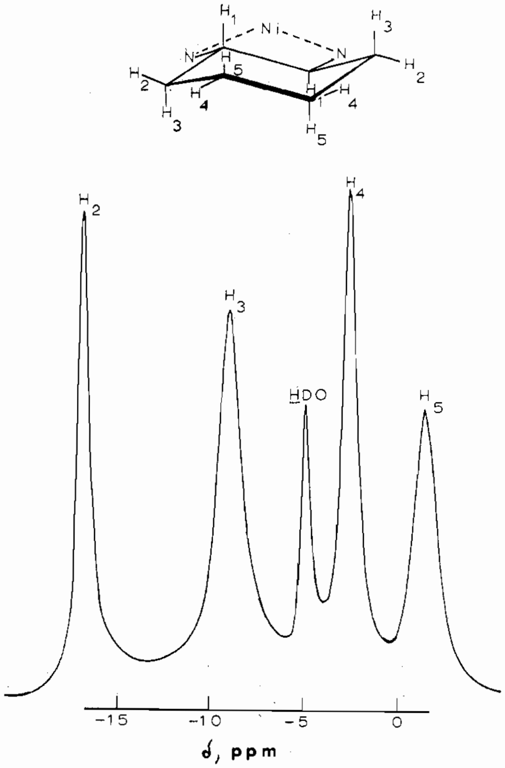


Figure 2.—Spectrum and assignment of contact shifts of cyclohexane ring protons of $Ni(CyDTA)^{2-}$.

Deuteration Studies and Complete Spectral Assignments for $Ni(CyDTA)^{2-}$.—The rate and stereo-

TABLE I

SPECTRAL ASSIGNMENTS FOR NICKEL(II) COMPLEXES AT 30° AND pH 8–10

Contact shift[a]	Assignment
	$Ni(EDTA)^{2-}$
−10	2 axial en CH_2
−31	2 axial out-of-plane ac CH_2 ($H_a{}^o$)
−96	2 equatorial out-of-plane ac CH_2 ($H_e{}^o$) 2 equatorial in-plane ac CH_2 ($H_e{}^i$)
−126	2 equatorial en CH_2
	$Ni(PDTA)^{2-}$
−11	2 axial en CH_2 + 3 methyl
−33	1 axial out-of-plane ac CH_2 ($H_a{}^o$)
−44	1 axial out-of-plane ac CH_2 ($H_a{}^o$)
−90, −96	2 equatorial out-of-plane ac CH_2 ($H_e{}^o$) 2 equatorial in-plane ac CH_2 ($H_e{}^i$)
−125	1 equatorial en CH_2
	$Ni(CyDTA)^{2-}$
+1	2 protons of cyclohexane ring (H_5)
−3	2 protons of cyclohexane ring (H_4)
−9	2 protons of cyclohexane ring (H_3)
−17	2 protons of cyclohexane ring (H_2)
−48	2 axial out-of-plane ac CH_2 ($H_a{}^o$)
−83	2 equatorial out-of-plane ac CH_2 ($H_e{}^o$)
−93	2 equatorial in-plane ac CH_2 ($H_e{}^i$)

[a] Shifts are given in ppm relative to internal TMS*. Negative shifts are downfield from the reference; estimated uncertainty, ±1–2 ppm.

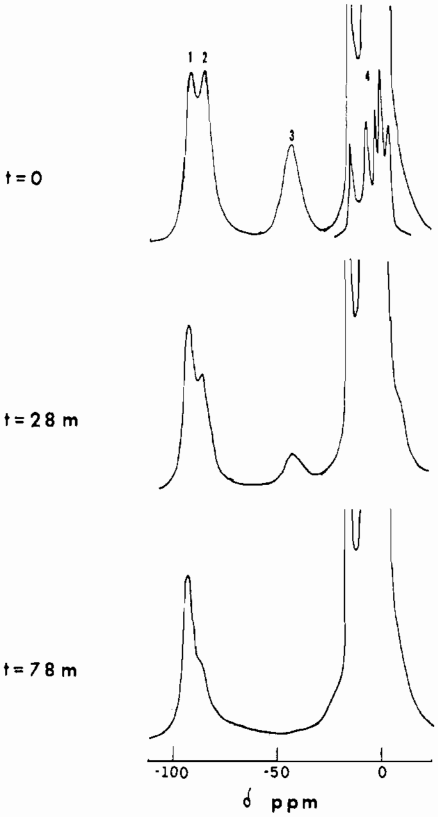


Figure 3.—Proton exchange for $Ni(CyDTA)^{2-}$ at 71.7° and pD 13.

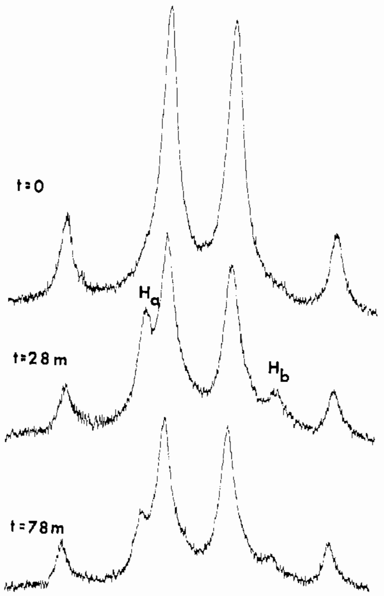


Figure 4.—Proton exchange of $Ni(CyDTA)^{2-}$ revealed by spectral changes in the KCN-liberated free ligand. Only the acetate portion of the spectrum is shown.

specificity of acetate proton deuteration of each of the three complexes in 0.1 *N* KOD–D_2O were investigated. Spectra both of paramagnetic complexes and of the corresponding diamagnetic free ligand (released from the complex by treament with excess KCN) were recorded after samples had been heated for varying times. Because deuteration studies of $Ni(CyDTA)^{2-}$ provided the basis for a plausible complete assignment of acetate proton peaks they will be considered first.

The spectral changes resulting from heating $Ni(CyDTA)^{2-}$ in 0.1 *N* KOD–D_2O are shown in Figure 3. Spectra of the KCN-liberated free ligand of corresponding samples are shown in Figure 4. The following changes are observed. First, in the spectra shown in Figure 3, only two of the three acetate-designated proton peaks disappear upon heating. Second, of these two, the upfield disappears more rapidly than the downfield peak by a factor of about 3. Third, as shown in Figure 4, in the KCN-liberated free ligand, one of the two monodeutero acetate species predominates at intermediate times. Fourth, after heating long enough to eliminate the two acetate proton peaks completely, the intensity of the ac CH_2 AB pattern of the free ligand has decreased only 50%. Fifth, on long heating at 100°, the remaining acetate-designated peak disappears slowly. Sixth, none of the remaining four cyclohexane-designated peaks is affected even by long heating at 100°.

Pseudo-first-order rate constants for the disappearance of the −83 and −48-ppm peaks were determined by plotting ln (peak height) *vs.* time to obtain a half-life $t_{1/2}$, and calculating k from $k = 0.693/t_{1/2}$. Rate constants at several temperatures are given in Table II. For the −93-ppm peak, which disappeared much more slowly, a rate constant was obtained only at 100° and pH 14. However, an Arrhenius plot of log k *vs.* $1/T$ was prepared to obtain the activation energies and entropies (from the Eyring absolute rate equation) which are given in Table III. These data were used to calculate the k value reported for the −83-ppm peak at 100°.

TABLE II

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR EXCHANGE OF ACETATE PROTONS IN 0.1 *N* KOD–D_2O

Temp, °C	Chem shift of obsd peak, ppm	k, sec^{-1}
	$Ni(CyDTA)^{2-}$	
71.7	−83	2.3×10^{-4}
71.7	−48	7.2×10^{-4}
100 (extrap)	−83	8.4×10^{-3}
71.7	−83	9.6×10^{-4} [a]
29 ± 1	−83	1.3×10^{-5} [a]
6 ± 1	−83	1.9×10^{-6} [a,b]
71.7	−48	2.9×10^{-3} [a]
29 ± 1	−48	3.9×10^{-5} [a]
100	−93	3.6×10^{-6} [c]
	$Ni(EDTA)^{2-}$	
100.0	−96	1.8×10^{-3}
71.7	−96	3.0×10^{-4}
29 ± 1	−96	5.5×10^{-6}
6 ± 1	−96	6×10^{-7} [b]
100.0	−31	2.3×10^{-3}
71.7	−31	3.8×10^{-4}
29 ± 1	−31	7.7×10^{-6}
6 ± 1	−31	4×10^{-7} [b]
	$Ni(PDTA)^{2-}$	
71.7	−90	1.2×10^{-4}
71.7	−96	1.1×10^{-4}
71.7	−44	4.3×10^{-4}

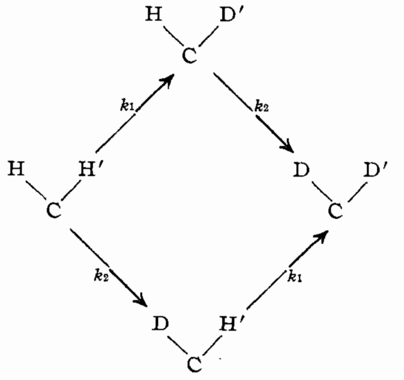
[a] All data are for a single solution in ~0.2 *N* KOD, but the OD^- concentration is not accurately determined. [b] Based on the spectrum of a single refrigerated sample recorded at 160 hr after mixing. [c] pH 14.

TABLE III

ACTIVATION PARAMETERS FOR ACETATE PROTON EXCHANGE OF Ni(II) COMPLEXES

Complex	E_a, kcal	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, cal deg^{-1}
$Ni(EDTA)^{2-}$	18.8 ± 0.5	18.2 ± 0.5	−17 ± 2
$Ni(CyDTA)^{2-}$	19.5 ± 0.5	18.9 ± 0.5	−14 ± 2

The spectra of free ligand show clearly that only half of the acetate protons are readily deuterated. In analogous Co(III) complexes, out-of-plane acetate protons exchange much more rapidly.[10] Thus, the two peaks at −48 and −83 ppm must represent out-of-plane acetate protons. The acetate deuteration process can then be represented schematically as



where the indicated equality in rates for

$$CHH' \xrightarrow{k_1} CHD'$$

and

$$CDH' \xrightarrow{k_1} CDD'$$

follows if secondary isotope effects are negligible. For this system relative concentrations of the four species are given by

$$(CHH') = e^{-(k_1+k_2)t} \quad (1)$$

$$(CHD') = e^{-k_2 t} - e^{-(k_2+k_1)t} \quad (2)$$

$$(CDH') = e^{-k_1 t} - e^{-(k_2+k_1)t} \quad (3)$$

$$(CDD') = 1 - (CHH') - (CHD') - (CDH') \quad (4)$$

According to this scheme, the rate constants obtained directly from the decrease in peak heights of the two out-of-plane acetate proton peaks (at −83 and −48 ppm) correspond to k_1 and k_2. These values were used to test several predictions of the model. For example, the half-life for the disappearance of CHH′, $t_{1/2}$, is equal to the time for the total intensity of the acetate absorption of the free $CyDTA^{4-}$ ligand to reach three-fourths of its initial intensity. According to the above scheme, $t_{1/2} = 0.693/(k_1 + k_2)$. The agreement between the $t_{1/2}$, obtained from the spectra of $CyDTA^{4-}$, and that calculated from k_1 and k_2, obtained from spectra of the complex, is good. For example, in one run for which $k_1 = 0.00072$ and $k_2 = 0.00023$ sec^{-1}, $t_{1/2}$ estimated from the $CyDTA^{4-}$ AB pattern was 840 sec *vs.* 720 sec calculated from $k_1 + k_2$. Furthermore, the ratio of CHD′ to CDH′ in the free ligand (which is equal to the ratio of intensities of H_a to H_b in Figure 4) is consistent with that predicted from eq 2 and 3. For the data shown in Figure 3 the ratio of monodeuterio isomers should increase from 3.0 at short times to 3.5 at t = 78 min. Finally, the per cent deuteration was calculated on the assumption that the two peaks which disappear rapidly on deuteration each represent two protons. This was then compared with the per cent deuteration based on integration of the spectrum of the free ligand. Results are given in Table IV. Again the agreement is excellent. The uniformly smaller values obtained from the integration probably reflect small saturation effects.

TABLE IV

COMPARISON OF THE NUMBER OF REMAINING ACETATE PROTONS CALCULATED FROM THE SPECTRA OF PARAMAGNETIC $Ni(CyDTA)^{2-}$ WITH THE NUMBER CALCULATED FROM THE SPECTRA OF CORRESPONDING KCN-LIBERATED FREE $CyDTA^{4-}$

Time of heating at 71.7°, min	No. of acetate protons			
	$Ni(CyDTA)^{2-}$ spectrum			$CyDTA^{4-}$ spectrum[a]
	Out-of-plane	In-plane	Total	
0	4.0	4.0	8.0	7.7
5	3.4	4.0	7.4	7.0
10	3.0	4.0	7.0	6.6
14	2.6	4.0	6.6	6.0
28	1.9	4.0	5.9	5.4
42	1.4	4.0	5.4	5.0
78	0.7	4.0	4.7	4.6
150	0	4.0	4.0	3.8
210	0	4.0	4.0	3.7

[a] Based on the integration of the $CyDTA^{4-}$ spectra and the assumption that the area of the cyclohexane ring proton peaks corresponds to 10 protons. All values ±5%.

In summary, these experiments show that only half of the acetate protons (presumably those out of plane) deuterate and that one of the out-of-plane protons is more readily deuterated than the other. They also identify three of the expected four acetate proton peaks. However, some important questions remain unanswered. Where is the remaining ac CH_2 peak? The three acetate-designated peaks have about equal areas and each has been shown to correspond to two protons. Furthermore, why are only four equal-intensity peaks observed for the five pairs of cyclohexane ring protons? These questions have not been answered, but the validity of the above conclusions and a basis for further refinement of the assignments have been provided by the following acetate-scrambling experiments. Reconversion of free $CyDTA^{4-}$ + $Ni(CN)_4^{2-}$ to $Ni(CyDTA)^{2-}$ was achieved by several treatments of the KCN-treated $Ni(CyDTA)^{2-}$ solution with excess HCl followed by evaporation to dryness and readjustment to pH 7. When this was done with a 50% deuterated sample, all three acetate-designated peaks were restored with the same *relative* intensities as in the undeuterated sample at the same concentration, but each was only about 50% of normal intensity. When the same experiment was done with a sample that was initially partially deuterated to the extent that about 60% of the −83-ppm peak and about 20% of the −48-ppm peak remained, the two downfield peaks reestablished their initial *relative* intensities at about 80% of an unexchanged sample while the intensity of the −48-ppm peak increased to about 60% of the intensity of the corresponding peak in an unexchanged sample. These two experiments show that when the complex is decomposed and reassembled, protons responsible for the two downfield peaks (−93 and −83 ppm) scramble while protons responsible for the −48-ppm peak scramble with the two other acetate protons (presumably of the in-plane type) that do not exchange readily in D_2O at high pH and do not give rise to any absorption in the normal acetate region of the spectrum. Because the relative intensities of cyclohexane-designated peaks are unaffected in these experiments, the possibility that one of these is the missing acetate peak is ruled out.

A detailed examination of the stereochemistry of complexes of these hexadentate ligands and of possible acetate-scrambling processes permits us to complete spectral assignments and to establish unequivocally the identity of the protons which are not seen in the spectrum of the paramagnetic complex. A portion of the structure of these complexes showing the four nonequivalent protons of the two acetate groups attached to one nitrogen is shown in Figure 5. For $Ni(CyDTA)^{2-}$, R_1 and R_2 constitute the remaining portion of the cyclohexane ring. The axial–equatorial nature of each acetate proton (subsequently justified) is noted explicitly by an a or e subscript. In-plane and out-of-plane acetate protons, identified in Figure 5 by an i or o superscript, can be interchanged by a Δ,Λ conversion or by nitrogen inversion. The latter requires prior breaking of an Ni–N bond and two M–O bonds. As discussed by Sudmeier and Reilley, the two processes have different stereochemical consequences (Figure 5). However, for $Ni(CyDTA)^{2-}$ the rigid cyclohexane ring does not allow Δ,Λ conversion, so acetate scrambling can only occur by a N-inversion process. Because we have shown that protons responsible for the two peaks at −83 and −93 ppm are interchanged when the complex is decomposed and reassembled, these peaks must correspond either to H(1) and H(3) or to H(2) and H(4). Conversely, the −48-ppm peak and the missing peak must correspond to the other pair. Furthermore, since it has been established that out-of-plane acetates of $Ni(CyDTA)^{2-}$ exchange readily, the peaks at −83 and −48 ppm must correspond to H(1) and H(2). Finally, the average shift of H(1) and H(2), −65 ppm, is typical of acetate fragments of several amino acids and other ligands, for which the more equatorial proton invariably has the larger downfield shift. There may be some uncertainty about the preferred conformation of the out-of-plane acetate ring, but H(3) is clearly the more equatorial in-plane proton. We, therefore, assigned the −93-ppm peak to H(3) and proceeded with the above restrictions to complete the assignment as follows: $H_e^o(1) = -83$, $H_a^o(2) = -48$, $H_e^i(3) = -93$ ppm, while $H_a^i(4)$ is not observed. We concluded further, as shown in Figure 5, that the sense of the acetate ring deformation is the same for both acetate rings so that acetate scrambling with N inversion interchanges in-plane and out-of-plane axial and in-plane and out-of-plane equatorial protons.

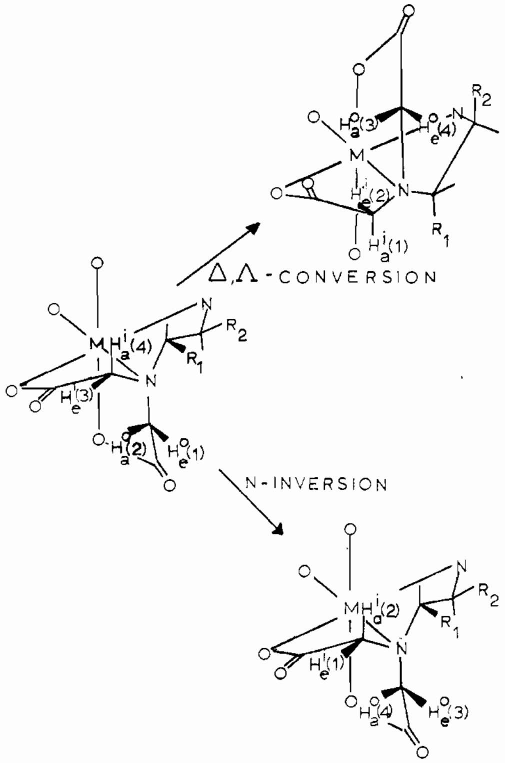


Figure 5.—Stereochemical consequences of Δ,Λ conversion and N inversion of six-coordinate EDTA.

It was of interest to determine the rate of N inversion in solution. A half-deuterated sample was adjusted to pH 7 and heated at 100° for 1 week. No change was observed in the spectrum. The result showed that N inversion in $Ni(CyDTA)^{2-}$ is very slow and that the slow observable decrease in the 93-ppm peak at high pH is due to in-plane acetate proton exchange rather than to acetate scrambling by N inversion.

The assignment of the upfield portion of the spectrum of $Ni(CyDTA)^{2-}$ shown in Figure 2 is based on the following propositions. Because there are only four peaks for five pairs of protons, one pair does not contribute to the observed spectrum. The close structural similarity between H_1 and $H_a{}^i$ (see Figure 5) suggests that H_1 may not give rise to a detectable peak. The remaining peaks were then assigned, with some reservation, to H_2–H_5 on the assumption that the contact shift would decrease rapidly with number of intervening bonds and would be greater for an equatorial than for an axial proton in a given CH_2 group. All four peaks in this part of the spectrum are much sharper than any acetate peaks, but there is almost a twofold difference in line width between the +1 or −9 and −3 or −17 ppm peaks.

Deuteration Rates and Spectral Assignments for $Ni(EDTA)^{2-}$.—The spectral changes resulting from heating $Ni(EDTA)^{2-}$ in 0.1 *N* KOD–D_2O are shown in Figure 6. The peak at −96 ppm decreases at essentially the same rate as the peak at −31 ppm and both approach zero intensity. Pseudo-first-order rate constants, given in Table II, were calculated from plots of log (peak height) *vs.* time for both peaks. The slight difference in rate constants obtained from the two peaks is barely outside experimental error. Activation energies and entropies calculated from the temperature dependence of the rate constants are given in Table III. In spectra of KCN-liberated $EDTA^{4-}$, the single acetate proton peak also decreases to zero intensity and at a rate which is approximately equal to the rate of decrease of either peak in the spectrum of the complex. The remaining $Ni(EDTA)^{2-}$ peaks (at −126 and −10 ppm) are unaffected by exchange.

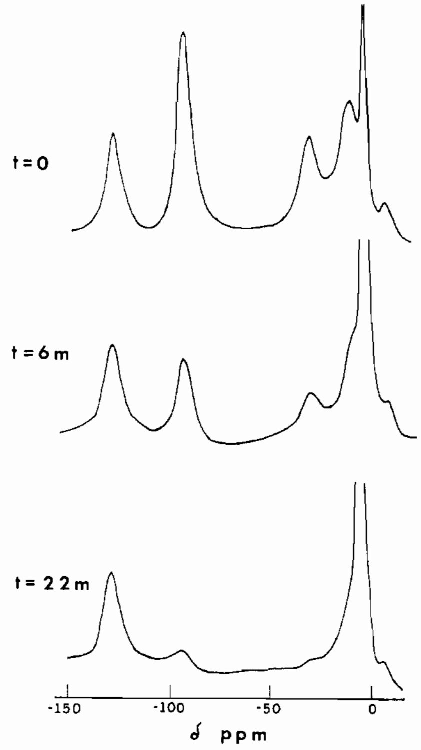


Figure 6.—Proton exchange for $Ni(EDTA)^{2-}$ at 100° and pD 13.

These exchange studies and the close similarity between acetate portions of the spectra of $Ni(EDTA)^{2-}$ and $Ni(CyDTA)^{2-}$ suggest that the larger peak at −96 ppm corresponds to the overlap of peaks of $H_e{}^o$ and $H_e{}^i$ protons while the −31-ppm peak corresponds to $H_a{}^o$ protons (Figure 5). The remaining two peaks can be assigned to axial (−10 ppm) and equatorial (−126 ppm) en CH_2 protons.

Deuteration Rates and Spectral Assignments for $Ni(PDTA)^{2-}$.—The spectral changes associated with deuteration of $Ni(PDTA)^{2-}$ in 0.1 *N* KOD–D_2O are shown in Figure 7. Like $Ni(CyDTA)^{2-}$, the upfield peaks at −33 and −44 ppm decrease more rapidly than downfield peaks at about −90 ppm. However, like $Ni(EDTA)^{2-}$ and unlike $Ni(CyDTA)^{2-}$, all acetate-designated peaks approach zero intensity. First-order rate constants, given in Table II, were calculated from both the −90-ppm peak and the −44-ppm peak. The −33- and −44-ppm peaks decreased at similar rates, but accurate measurements were more readily made for the −44-ppm peak. As with $Ni(CyDTA)^{2-}$, the ratio of disappearance rates of upfield and downfield acetate peaks is about 3.

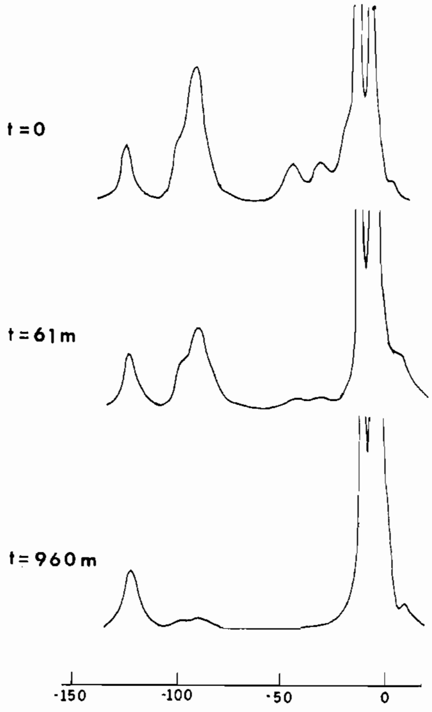


Figure 7.—Proton exchange for $Ni(PDTA)^{2-}$ at 71.7° and pD 13.

Spectra of corresponding KCN-liberated $PDTA^{4-}$

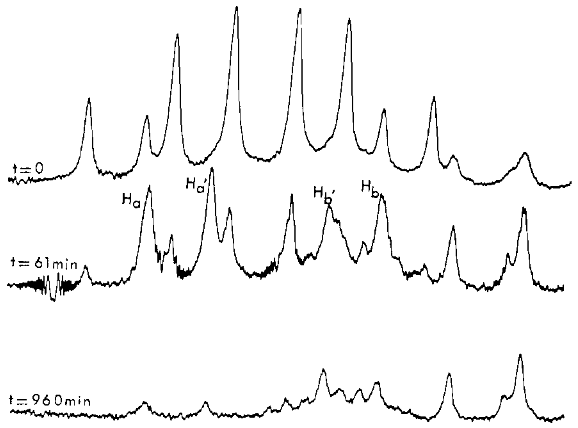


Figure 8.—Proton exchange in Ni(PDTA)$^{2-}$ revealed by spectral changes in the KCN-liberated free ligand. The methyl portion of the spectrum is not shown.

are shown in Figure 8. At $t = 0$, the spectrum consists of two overlapping symmetric AB quartets for the two different types of acetate protons plus the highly structured pattern of the CH–CH$_2$ portion of the ethylenediamine skeleton. The more upfield CH$_3$ peak is not included. In the spectrum of the 61-min sample, the intensities of the original AB quartets have decreased considerably and the four peaks of monodeuterio isomers are evident. The latter are designated $\mathrm{H_a}$ and $\mathrm{H_b}$ for the acetate protons attached to one PDTA^{4-} nitrogen and $\mathrm{H_{a'}}$ and $\mathrm{H_{b'}}$ for the other. The $\mathrm{H_{b'}}$ peak overlaps one of the strong peaks of an original AB quartet. Two important observations are illustrated by the 61-min trace. The two AB quartets decrease at about the same rate, but the two monodeuterio species associated with each quartet are not present at equal concentrations. The first observation shows that the two types of acetate groups of PDTA^{4-} deuterate at the same rate; the second indicates some stereospecificity in the deuteration of a particular acetate group. As noted also for Ni(EDTA)$^{2-}$, acetate proton exchange is complete in a reasonable time.

The spectral assignments indicated by these experiments and by comparison of acetate portions of the spectra of the three ligands are summarized in Table I. The asymmetry introduced by the methyl group eliminates any equivalence among the eight acetate protons. Thus the single $\mathrm{H_a^o}$ peak observed for Ni(EDTA)$^{2-}$ and Ni(PDTA)$^{2-}$ appears as two smaller equal-intensity peaks at −33 and −44 ppm. Similarly, the strong peak at −90 and shoulder at −96 ppm can be assigned to the two $\mathrm{H_e^o}$ and two $\mathrm{H_e^i}$ protons. The small peak at −125 ppm must then correspond to equatorial en protons while the single large sharp peak at −10 ppm and its downfield shoulder correspond to axial en protons and the methyl group.

Discussion

Effects of Δ,Λ Conversion and N Inversion on Spectral Changes Accompanying Deuterium Exchange.

—The ability to obtain complementary information by examining spectra of both the paramagnetic complex and that of the KCN-liberated free ligand, which has permitted the complete analysis of the spectra of these complexes, also makes it possible to distinguish between alternative mechanisms of deuteration in Ni(EDTA)$^{2-}$ and Ni(PDTA)$^{2-}$. To assist in analyzing these experiments, it is convenient first to introduce an appropriate shorthand notation and to consider all possible alternative pathways for the deuteration.

The following notation (*cf.* Figure 5) will be used for the complete description of each proton required for this analysis. The four nonequivalent protons of the two acetate groups attached to one nitrogen are designated, for example, $(\mathrm{H}_e^o H_a^o \mathrm{H}_e^i H_a^i)$, where the o or i superscript denotes out-of-plane or in-plane acetate protons and the a or e subscript describes the preferred conformation of the proton. The first two protons are those of one acetate; the third and fourth, of the other. Assuming rapid nitrogen inversion *for the free ligand*, the first and third protons are equivalent in the KCN-liberated free ligand.[18] The second and fourth are similarly equivalent. This equivalence is emphasized by italicizing or not italicizing equivalent protons. For example, H_a^o denotes the out-of-plane axial proton which is equivalent to H_a^i in the KCN-liberated free ligand. The stereochemistry of the complex can be included in the description by including a Δ or Λ prefix, *e.g.*, $\Delta\text{-}(\mathrm{H}_e^o H_a^o \mathrm{H}_e^i H_a^i)$. Finally a given position in the scheme always refers to the same ligand proton. With this notation, the stereochemical consequences of Δ,Λ conversion and of N inversion can be represented as shown in Scheme I (*cf.* Figure 5).

SCHEME I

$$\begin{tikzcd}
\Delta\text{-}(\mathrm{H}_e^o H_a^o \mathrm{H}_e^i H_a^i) \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & \Delta'\text{-}(\mathrm{H}_e^i H_a^i \mathrm{H}_e^o H_a^o) \arrow[d, leftrightarrow] \\
\Lambda\text{-}(\mathrm{H}_a^i H_e^i \mathrm{H}_a^o H_e^o) \arrow[r, leftrightarrow] & \Lambda'\text{-}(\mathrm{H}_a^o H_e^o \mathrm{H}_a^i H_e^i)
\end{tikzcd}$$

In Scheme I, vertical arrows indicate Δ,Λ conversion; horizontal arrows, N inversion. With the additional provision that only out-of-plane acetates can be deuterated in the times considered in these experiments and that the axial and equatorial out-of-plane acetate protons ($\mathrm{H_a^o}$ and $\mathrm{H_e^o}$, respectively) are deuterated at different rates, this scheme can be used to analyze the spectral changes expected for the variety of situations which might be encountered during deuterium exchange in these complexes. Because either Δ,Λ conversion or N inversion or both could be fast compared to the rate of deuteration, four extreme cases are possible.

Case I. No Δ,Λ Conversion and No N Inversion.—In the early stages of deuteration, this situation is represented as shown in Scheme II. Under these circumstances, the peak assigned to $\mathrm{H_a^o}$ disappears at a rate characterized by a rate constant designated k_a^o;

SCHEME II

Monodeuterio isomers

$$\begin{tikzcd}
 & \Delta\text{-}(\mathrm{H}_e^o D_a^o \mathrm{H}_e^i H_a^i) \\
\Delta\text{-}(\mathrm{H}_e^o H_a^o \mathrm{H}_e^i H_a^i) \arrow[ur, "k_a^o"] \arrow[dr, "k_e^o"'] & \\
 & \Delta\text{-}(\mathrm{D}_e^o H_a^o \mathrm{H}_e^i H_a^i)
\end{tikzcd}$$

Monodeuterio isomers	Rel abund for $k_a^o/k_e^o = 3$
$\Delta\text{-}(\mathrm{H}_e^o D_a^o \mathrm{H}_e^i H_a^i)$	>3
$\Delta\text{-}(\mathrm{D}_e^o H_a^o \mathrm{H}_e^i H_a^i)$	1

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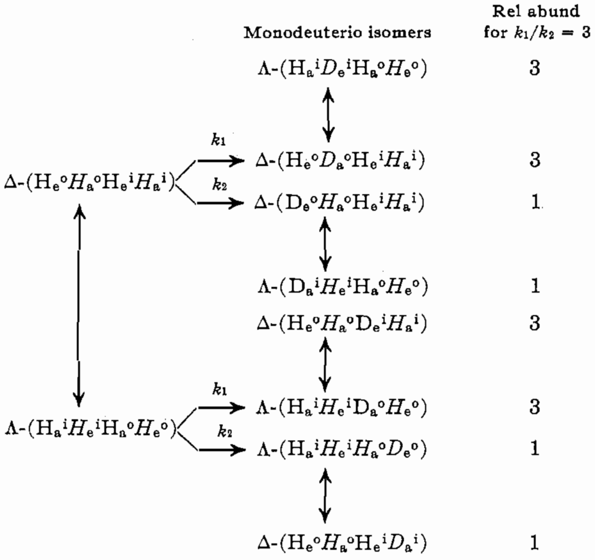
[18] J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1704, 1968 (1964).

the peak assigned to H_e^o, by k_e^o. In the KCN-liberated free ligand, the ratio of monodeuterio species increases from k_a^o/k_e^o to a very large value as the deuteration proceeds, and deuteration proceeds until 50% of the total acetate protons have been deuterated. This corresponds to the situation encountered in Ni(CyDTA)$^{2-}$ before any appreciable exchange occurs for in-plane acetate protons.

Case II. Fast Δ,Λ Conversion and No N Inversion.—The resultant spectral changes follow from a consideration of Scheme III, which indicates the expected distribution of the eight possible monodeuterio isomers. Since H_a^o and H_e^i are interconverted by Δ,Λ conversion, peaks arising from these two protons decrease at equal rates characterized by k_1. Similarly, peaks from H_e^i and H_a^o decrease at equal rates as determined by k_2.

SCHEME III

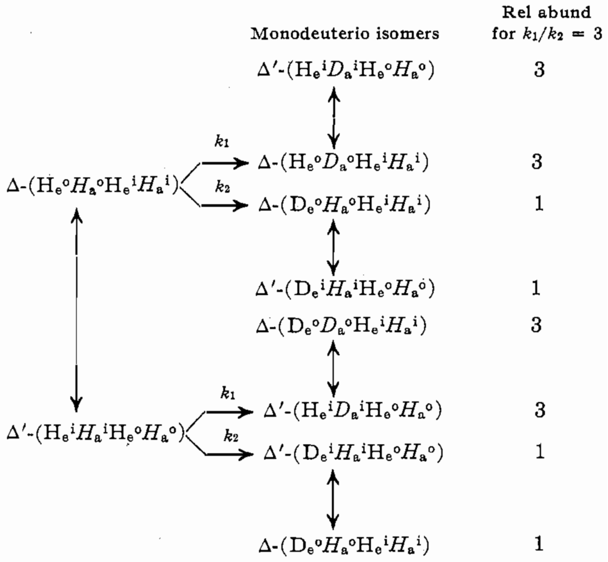


For example, if $k_1/k_2 = 3$, the rate of decrease in the H_a^o or H_e^o peaks would exceed the rate of decrease of the H_a^i or H_e^o peaks by a factor of 3. In the KCN-liberated free ligand monodeuterio isomers of the (H*D*H*H*) type and those of the (D*H*H*H*) type would be equally probable.

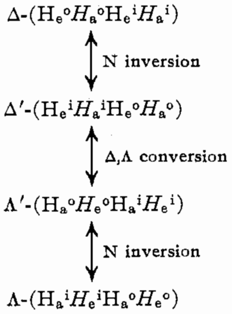
Case III. No Δ,Λ Conversion and Fast N Inversion.—The expected distribution of monodeuterio isomers is indicated by Scheme IV. Because H_a^o and H_a^i are interconverted by N inversion, peaks arising from these two protons decrease at equal rates characterized by k_1. Similarly, peaks from H_e^o and H_e^i decrease at equal rates as determined by k_2. All peaks approach zero intensity. In the KCN-liberated free ligand, the concentration of monodeuterio isomers of the (D*H*H*H*) type would exceed that of the (H*D*H*H*) type by a ratio of 3:1 or more if $k_1/k_2 = 3$.

Case IV. Both Δ,Λ Conversion and N Inversion Are Fast Compared to the Rate of Deuteration.—As shown in Scheme V, all four protons have an equal chance of being in any of the four possible environments. Therefore, peaks arising from the four types of protons disappear at the same rate. Similarly, no stereospecificity is observed in the KCN-liberated free ligand. The expected spectral changes arising during deuteration for these four cases are summarized in Table V.

SCHEME IV



SCHEME V



Relative Rates of Deuterium Exchange. Δ,Λ Conversion and N Inversion.—The foregoing analysis provides the basis for an assessment of deuterium-exchange mechanisms in the three complexes. For Ni(CyDTA)$^{2-}$, in-plane and out-of-plane acetates maintain their identity, even for the relatively long times required to observe exchange of in-plane acetate protons. A Δ,Λ conversion is ruled out by the stereochemical restrictions imposed by the cyclohexane ring. This is clearly an example of case I. For the other two complexes, the situation is more complicated.

For Ni(EDTA)$^{2-}$, the complete exchange of all acetate protons requires either simple Δ,Λ conversion (case II) or complete scrambling by Δ,Λ conversion and N inversion (case IV). Assuming no significant exchange for in-plane acetates and an axial/equatorial stereospecificity ratio similar to Ni(CyDTA)$^{2-}$, the near equality of exchange rates observed for the −96- and −31-ppm peaks argues for case IV. If Δ,Λ conversion is rapid, the following protons are rapidly interconverted: H_e^o and H_a^i, H_a^o and H_e^i. Because only out-of-plane acetate protons exchange at a reasonable rate, the peak at −31 ppm (H_a^o) would disappear at a rate typical of H_a^o; half of the peak at −96 ppm (H_e^i), at a

TABLE V

SPECTRAL CHANGES EXPECTED DURING DEUTERATION OF ACETATE PROTONS OF METAL COMPLEXES OF EDTA-TYPE LIGANDS

Conditions	Predicted spectral changes for acetate protons: Paramagnetic complex	Predicted spectral changes for acetate protons: Free ligand (KCN liberated)
Case I: no Δ,Λ conversion; no N inversion	Peaks H_a^o and H_e^o go to zero intensity at rates k_a^o and k_e^o, respectively. Peaks H_a^i and H_e^i unaffected	Total intensity decreases by 50%; monodeuterio species are not equally probable
Case II: fast Δ,Λ conversion; no N inversion; no Δ,Λ isomer preference	Peaks H_a^o and H_e^i decrease at rate determined by k_1; peaks H_a^i and H_e^o, by k_2. All peaks approach zero intensity	Total intensity approaches zero; monodeuterio species are equally probable throughout course of reaction
Case III: no Δ,Λ conversion; fast N inversion	Peaks H_a^o and H_a^i decrease at rate determined by k_1; peaks H_e^o and H_e^i, by k_2. All peaks approach zero intensity	Total intensity approaches zero; monodeuterio species are not equally probable
Case IV: fast Δ,Λ conversion; fast N inversion; no Δ,Λ isomer preference	Peaks H_a^i, H_e^i, H_a^o and H_e^o all decrease at the same rate and approach zero intensity	Total intensity approaches zero; no stereospecificity is observed in monodeuterio species

rate typical of H_e^o; and half of the peak at −96 ppm (H_e^i), at a rate typical of H_a^o. Since the rate of H_a^o exchange would be substantially greater than the rate of H_e^o exchange, the disappearance of the peak at −96 ppm would be characterized by two different rate constants and the first-order plot would not be linear. In fact, the plots were linear for 3–4 half-lives and yielded a first-order rate constant not significantly smaller than the ones obtained from the −31-ppm peak at the same temperature. We thus conclude that acetate scrambling in $Ni(EDTA)^{2-}$ occurs by breaking of the Ni–N bond in addition to the two Ni–O bonds with subsequent N inversion and re-formation of complex. In the last step, Δ and Λ isomers are formed with equal probabilities.

It should be pointed out that, although the rate of nitrogen inversion is greater than the rate of deuterium exchange, it is not fast enough to produce the complete averaging of en and ac CH_2 protons that is observed for some more labile diamagnetic complexes.[7] Even at 90°, the spectrum shows separate peaks for the different types of protons. Furthermore, Δ,Λ conversion could also be occurring without Ni–N bond rupture. The rate of the N-inversion process is simply much greater than the rate of deuteration so that simple Δ,Λ conversion is not detectable in these experiments.

For $Ni(PDTA)^{2-}$, the spectrum is consistent with almost complete configurational stereospecificity. Only a single methyl peak is observed and the equatorial en CH peak at −125 ppm is about half the size of the corresponding peak in $Ni(EDTA)^{2-}$. This is, of course, expected for the more stable configuration in which the methyl group is equatorial.

The strong preference for one configuration does not rule out Δ,Λ conversion as a possible pathway for acetate scrambling, but the kinetic data indicate that exchange in $Ni(PDTA)^{2-}$ closely approximates case III, *i.e.*, fast N inversion without significant Δ,Λ conversion. Of course, N inversion is not likely to occur without some Δ,Λ conversion, but since the equilibrium favors one configuration strongly, the situation corresponds very nearly to case III. The ratio of rates of disappearance of peaks at −44 (or −33) and −90 ppm corresponds closely to that observed for $Ni(CyDTA)^{2-}$. However, unlike $Ni(CyDTA)^{2-}$, for $Ni(PDTA)^{2-}$ all acetate protons exchange readily. With rapid N inversion, H_e^o and H_e^i scramble as do H_a^o and H_a^i (Scheme IV). The rate constant calculated from the −90-ppm peak corresponds to exchange of the former (when in the H_e^o site); from the −44- or −33-ppm peaks, to the latter (when in the H_a^o site). The preference of one monodeuterio isomer over the other in the KCN-liberated $PDTA^{4-}$ is consistent with this model. Furthermore, the rate of disappearance of AB quartets of $PDTA^{4-}$ corresponds exactly to that calculated from the spectra of $Ni(PDTA)^{2-}$ and the assumed model.

Referring to Scheme IV, it can be seen that a particular acetate group (first two or last two protons) can be deuterated in only one of the two isomers having significant abundance. The deuteration of a specific acetate group can thus be represented

$$\begin{tikzcd}
 & & \Delta'\text{-(monodeuterio complex)} \\
\Delta\text{-(complex)} \arrow[r, leftrightarrow, "\text{fast}"] & \Delta'\text{-(complex)} \arrow[ur, "k_1"] \arrow[dr, "k_2"] & \\
 & & \Delta'\text{-(monodeuterio complex)}'
\end{tikzcd}$$

for which the rate of disappearance of a given AB pattern (R) is given by

$$R = -(k_1 + k_2)(\Delta'\text{-(complex)} = -(k_1 + k_2)(\text{total complex})/2$$

where k_1 and k_2 correspond to the rate constants obtained from $Ni(PDTA)^{2-}$ spectra. The disappearance of a particular AB pattern of KCN-liberated $PDTA^{4-}$ should thus be a first-order process with the observed first-order rate constant equal to $(k_1 + k_2)/2$. For the data given in Table II, $(k_1 + k_2)/2 = 2.8 \times 10^{-4}$ *vs.* 2.9×10^{-4} sec^{-1} observed for the first-order rate of disappearance of the more downfield AB pattern.

The small but significant difference in exchange rates observed for the three complexes can also be accounted for entirely in terms of the above classification schemes. The rate constants determined for $Ni(CyDTA)^{2-}$ can be taken as "normal" values for protons of the four types. These are designated k_e^o, k_a^o, etc. Then for $Ni(EDTA)^{2-}$, where rapid scrambling among all four sites occurs, a weighted-average rate constant can be calculated as

$$k_{av} = {}^1/_4k_e^o + {}^1/_4k_a^o + {}^1/_4k_e^i + {}^1/_4k_a^i \cong {}^1/_4k_e^o + {}^1/_4k_a^o$$

Similarly for $Ni(PDTA)^{2-}$, where only Δ and Δ' (or Λ and Λ') species are rapidly averaged, appropriate average rate constants are for equatorial protons

$$k_{av} = {}^1/_2 k_e{}^o + {}^1/_2 k_e{}^i \cong {}^1/_2 k_e{}^o$$

and for axial protons

$$k_{av} = {}^1/_2 k_a{}^o + {}^1/_2 k_a{}^i \cong {}^1/_2 k_a{}^o$$

A comparison of average rate constants calculated in this way and corresponding observed rate constants is given in Table VI. The close agreement between calculated and observed values suggests very close similarity in structure and bonding of acetate fragments of the three ligands.

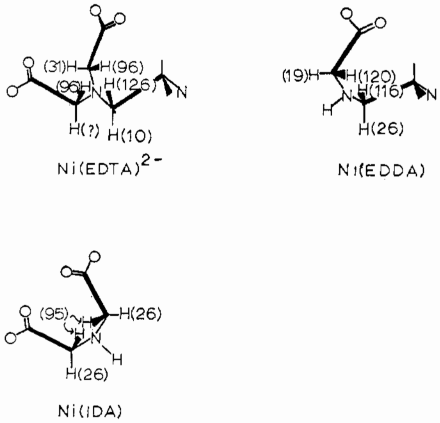
TABLE VI

COMPARISON OF OBSERVED AND CALCULATED WEIGHTED-AVERAGE RATE CONSTANTS FOR DEUTERIUM EXCHANGE OF NiY^{2-} AT 71.7° AND 0.1 *N* KOD

Complex	$10^4 k_{obsd}$, sec^{-1}	$10^4 k_{av}$, sec^{-1}
$Ni(CyDTA)^{2-}$	9.6 ($k_a{}^o$)	. . .
	2.9 ($k_e{}^o$)	. . .
$Ni(EDTA)^{2-}$	3.0	3.1
$Ni(PDTA)^{2-}$	4.3 (ax.)	4.8
$Ni(PDTA)^{2-}$	1.2 (eq)	1.4

It is of interest to compare the proton-exchange rates determined directly from the nmr spectra of the paramagnetic complex with those obtained by Terrill and Reilley[8] by examination of the spectra of diamagnetic free ligand in equilibrium with a much smaller concentration of 1:1 complex (5:1 ratio of free ligand to complex). They reported a second-order rate constant at 95° of 0.017 M^{-1} sec^{-1} for solutions which were 0.5 *M* in excess ligand and 0.1 *M* in $Ni(EDTA)^{2-}$. This value compares favorably with the value 0.020 M^{-1} sec^{-1} for 0.5 *M* $Ni(EDTA)^{2-}$ at 100° reported in this work.

Acetate Ring Conformations in Related Ni(II) Complexes.—A comparison of acetate ring conformations of the three related ligands IDA, EDDA, and EDTA is of interest in itself and provides the basis for analyzing the coordination number of the species in solution and the observed stereospecificity of proton exchange. Corresponding portions of structures of 1:1 complexes of these three ligands, as viewed from the outside looking down the N–Ni bond, are shown in Figure 9. The numbers in parentheses are the observed downfield contact shifts of the corresponding protons. The likely preferred conformation for each ring is shown, but other conformations no doubt also contribute to the weighted average spectral parameters. In every case, the substantial difference in the contact shift of the two methylene protons indicates substantial deformation from planarity and a preference for one conformation.[12–16] The larger shift difference for out-of-plane acetate protons of Ni(EDDA) compared to $Ni(EDTA)^{2-}$ requires an increase in the distortion of the out-of-plane acetate ring when the strain associated with formation of the in-plane chelate ring is not present.



Ni(EDTA)$^{2-}$

Ni(EDDA)

Ni(IDA)

Figure 9.—Preferred conformations of coordinated ligands. The numbers in parentheses are the contact shifts of each proton in ppm downfield from TMS*.

Although *cis*-$Ni(IDA)_2{}^{2-}$ and $Ni(EDTA)^{2-}$ differ only by having the connecting CH_2–CH_2 link in the latter, the conformational effect of such a connection is not trivial. Referring to Figure 9, the acetate protons of $Ni(IDA)_2{}^{2-}$ and $Ni(EDTA)^{2-}$ can be described as "inside" or "outside" of a V-shaped trough formed by the two chelated acetate rings (with the N–Ni bond forming the common base). It is clear from the symmetry of the complex and from scale models that the "inside" protons are equatorial for both acetates of $Ni(IDA)_2{}^{2-}$.[15,16] By contrast, for $Ni(EDTA)^{2-}$, the "inside" proton is equatorial for the in-plane acetate, but it is axial for the out-of-plane acetate. That is, the out-of-plane acetate ring of $Ni(EDTA)^{2-}$ assumes the conformation of the corresponding acetate ring of Ni(EDDA) rather than of $Ni(IDA)_2{}^{2-}$.

In terms of the notation recently recommended to designate absolute configurations and conformations of octahedral complexes,[19] the configuration of $Ni(EDTA)^{2-}$ shown in Figure 9 would be designated "skew chelate pairs, ΛΔΛ" while the preferred conformations of out-of-plane ac and in-plane ac and en rings would be designated (λλδ), respectively. For $Ni(IDA)_2{}^{2-}$, the preferred conformations of the corresponding rings would be designated (λδ–); for Ni(EDDA), (λ–δ).

Stereospecificity of Acetate Proton Exchange.—For both acid- and base-catalyzed exchange and for both Co(III) and Ni(II) complexes, the rate of deuteration of out-of-plane acetate groups exceeds that of in-plane acetate groups by several orders of magnitude. However, $Ni(CyDTA)^{2-}$ is the only complex for which this ratio has actually been evaluated. For $Ni(CyDTA)^{2-}$, the ratio of out-of-plane to in-plane deuteration rates at 100°, based on extrapolated lower temperature data and corrected for (OD^-), is about 10^4. This probably corresponds to a pK_a difference of 5–6 units for these protons[20] and is a clear indication of relative strengths of out-of-plane and in-plane Ni–O bonds.

Within each acetate group, whether in-plane or out-of-plane, the more axial (upfield) proton is more labile toward exchange. For out-of-plane protons, the degree of stereospecificity, as reflected in the axial/equatorial exchange rate ratio, is about 3 for both $Ni(CyDTA)^{2-}$

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[19] *Inorg. Chem.*, **9**, 1 (1970).

[20] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter X.

and Ni(PDTA)$^{2-}$. This ratio is probably closely related to the distortion from planarity of the out-of-plane chelate ring, suggesting similar average ring distortions for the two complexes.

Contact shift data indicate a greater distortion from planarity for Ni(EDDA) than for Ni(EDTA)$^{2-}$ or Ni(CyDTA)$^{2-}$ (out of plane). On that basis, we would expect the stereospecificity ratio of Ni(EDDA) to be greater than 3. Unfortunately, a relatively labile Ni–N bond permits rapid N inversion which precludes a direct experimental evaluation of the ratio for Ni(EDDA). For Co(en)(EDDA)$^+$ and similar Co(III) complexes, Sudmeier and Occupati determined a ratio of about 100 for OD$^-$-catalyzed acetate proton exchange,[11] but Ni(II) and Co(III) complexes are probably not directly comparable. This is emphasized by the unexpected equality of the axial/equatorial exchange rate ratio (~10) for acid-catalyzed exchange in Co(CyDTA)$^-$ and Co(en)(EDDA)$^+$.[10,11]

Ligand Coordination Number: 6 or 5?—In assigning spectra and analyzing the deuterium-exchange experiments for Ni(II) complexes of these potentially hexadentate ligands, we have considered only six-coordinate species. Available evidence is ambiguous at best. Brunetti, Nancollas, and Smith based their recent conclusion that Co(II), Ni(II), and Cu(II) complexes of EDTA^{4-} are all hexadentate on thermodynamic data for the reaction $MY^{2-} + H^+ \rightarrow MHY^-$.[4] In concluding this, they rejected early arguments of Higginson,[21] based on the similarity of pK_a values of several 1:1 complexes, that most EDTA complexes of bivalent metals are pentadentate at pH >5. Wilkins and Yelin,[22] on the basis of kinetic data for outer-sphere oxidation reactions, similarly concluded that Co(EDTA)$^{2-}$ is at least 80% in the hexadentate form. Although it is clear that EDTA is five-coordinate in its acid salts of Ni(II) and Cu(II),[5] the crystal structures of solid hydrates of 1:1 complexes isolated from high-pH aqueous solutions show no evidence for the pentadentate species which has a water molecule occupying one of the in-plane positions.[5] Of course, this does not rule out the possibility that a substantial concentration of pentadentate species exists in solution.

The comparative simplicity of the nmr spectra of these complexes could be cited as evidence for the six-coordinate species. However, the possibility of a rapid equilibrium between five-coordinate and six-coordinate species cannot be ruled out. The effects of such rapid equilibration can be predicted with some confidence.

The empirical conclusion that loss of carboxyl coordination produces a substantial downfield shift (~30 ppm) for average acetate protons[14,15] suggests that the acetate portion of the spectrum of Ni(EDTA)$^{2-}$ ought to depend on the coordination scheme as shown in Figure 10 for the four acetate protons of one end of the molecule. The hypothetical spectra are based on the assumptions that the average shift for a chelated acetate CH$_2$ proton should be about −50 to −70 ppm, that the shift of a free acetate CH$_2$ proton should be ~−80 ppm, that the difference between in-plane proton shifts should be greater than that between out-of-plane proton shifts, and that the difference between out-of-plane protons should be decreased by in-plane ring formation. Rapid equilibrium between free and chelated (in-plane) acetates, with an average ligand coordination number of 5, would then yield the weighted average spectrum shown in Figure 10c. For an average ligand coordination number nearer 6, the spectrum would approach that of Figure 10a. For none of the three ligands is the separation as great as in Ni(EDDA) (~100 ppm), which would be comparable to Ni(EDTA)$^{2-}$ with neither in-plane acetate attached. However, if the shift difference between H_e^o and H_a^o had been assigned a value of 0 for six-coordinate species, the observed shift differences (35–65 ppm) could be cited as evidence for an average coordination number close to 5. Thus, the spectra can be rationalized as consistent with a coordination number anywhere between 5 and 6. In any case, the significantly smaller shift difference of out-of-plane acetate protons of Ni(CyDTA)$^{2-}$, compared to corresponding protons of Ni(EDTA)$^{2-}$ and Ni(PDTA)$^{2-}$, suggests that the contribution from five-coordinate species may be somewhat greater for the latter pair.

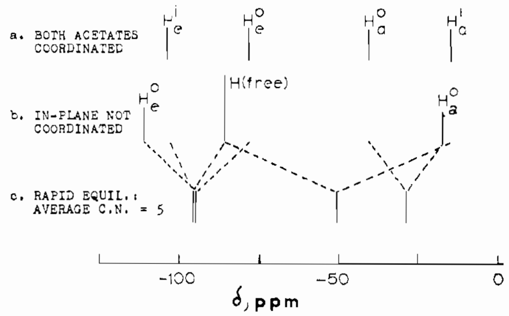

Figure 10.—Hypothetical spectra for various average ligand coordination schemes.

Rationale for Missing H_a^i Peak.—We are able to offer no completely satisfactory explanation for the failure to observe the axial in-plane acetate proton (H_a^i) in spectra of any of the three complexes. The acetate proton exchange data, especially for Ni(CyDTA)$^{2-}$ (Table III), permit no other interpretation of the spectra. The rapid equilibration scheme just described suggests one possible explanation. Unlike the other three types of protons, the H_a^i-type protons would be moving between two environments, designated H_a^i and H_{free}, characterized by very different shifts. A critical rate of interconversion could lead to extreme broadening of the peak. The same rate might be great enough to produce complete averaging of the other three types of protons, which have smaller shift differences in the two forms. The credibility of such an explanation is, however, severely undermined by the failure to observe any significant effect of temperature (up to 90°) on the spectra of Ni(EDTA)$^{2-}$ or Ni(CyDTA)$^{2-}$, aside from a general upfield shift

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[21] W. C. E. Higginson, *J. Chem. Soc.*, 2761 (1962).

[22] R. G. Wilkins and R. E. Yelin, *J. Amer. Chem. Soc.*, **92**, 1191 (1970).

of all protons with increasing temperature. Furthermore, it does not account for the failure to observe one of the expected five peaks for cyclohexane ring protons.

A second explanation may be more satisfactory, but it is not without flaws. Perhaps the close proximity of these protons to the metal ion provides a mechanism for spin relaxation and resultant line broadening which prevents their observation under the conditions employed. This could account for the observation of only four of the five expected peaks for cyclohexane ring protons, since H_1 (Figure 2) would occupy a similar position. It could also account for the excessive broadening of the reatively nearer H_a^e peak of $Ni(CyDTA)^{2-}$. The picture is further complicated by the fact that the axial en protons of $Ni(EDTA)^{2-}$ do give rise to a clear peak (at −10 ppm). It could be argued that the en ring is less rigid in $Ni(EDTA)^{2-}$ than in $Ni(CyDTA)^{2-}$, so that the axial en proton is not as near the nickel ion on the average in the former as in the latter. A greater contribution of pentadentate species for $Ni(EDTA)^{2-}$ could be invoked to permit this additional flexibility.

Conclusion and Prognosis.—We set out to employ nmr techniques to answer some questions concerning the structures and kinetic properties of nickel(II) chelates of EDTA, PDTA, and CyDTA. The nmr techniques have proven to be tremendously effective in providing some of the answers. No doubt the experiments described will provide a sound basis for obtaining other useful kinetic and structural information about these and related complexes. However, neither an unequivocal answer to the question of the coordination number of the ligand in solution nor a satisfactory rationale for the absence of certain resonances has been provided.

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.

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Spectrochemical Studies on Some Tetragonal NiL_2X_2 Complexes

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Received July 10, 1970

The electronic spectra of tetragonal nickel(II) complexes of the general formula NiL_2X_2 (L refers to NH_3, H_2O, C_5H_5N, or $C_6H_5NH_2$ and X is chloride or bromide) have been studied where L is the axial ligand. The spectra contain enough bands to permit us to calculate crystal field parameters (including all of the diagonal elements in their evaluation) and to have data left over to check our fit. Errors exist in previous reports of the parameters and in the assignments of transitions in some of these nickel(II) complexes. The crystal field parameters for the same ligand in different complexes (*e.g.*, NiL_4X_2 and NiL_2X_2) are compared and the spectrochemical parameters are compared with single-crystal X-ray results. The values for the McClure parameters $\delta\pi$ and $\delta\sigma$ are discussed.

Introduction

Continuing interest in the assignment of the electronic spectra and the evaluation of ligand field parameters, such as *Dq*, *Ds*, and *Dt*, has prompted a detailed crystal field calculation of some low-symmetry complexes.[2] In order to obtain a reliable set of parameters, the number of spectral bands should be greater than the number of parameters. The electronic spectra of tetragonally distorted nickel(II) complexes often satisfy this requirement. Consequently, it is possible to evaluate the parameters of such complexes with the inclusion of all off-diagonal matrix elements from the strong-field point of view.[3] The system reported here consists of complexes of the form NiL_2X_2, where L_2 represents two ammonia, aniline, water, or pyridine ligands and X_2 represents two chlorines or two bromides. In each of the complexes reported here, the metal ion is surrounded by four bridging halide ions forming a polymeric chain and by two other ligands giving six-coordination[4] about the nickel(II). The site symmetry is assumed to be D_{4h} and the electronic spectra fit this model. The spectra of some of these complexes were previously[2a,4c,5] observed, but a complete analysis was not attempted.

In this study, the *Dq* values for the various ligands were calculated along with the McClure $\delta\pi$ and $\delta\sigma$[6] parameters. The spectral bands have been assigned on the basis of the signs and relative magnitudes of $\delta\sigma$ and

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[1] Abstracted in part from the Ph.D. thesis of R. L. Chiang, University of Illinois, Urbana, Ill., 1971.

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[6] D. S. McClure, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 498.