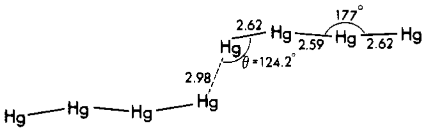
Table II

atom	orbital	H_{ii}, eV	ξ_i	ref
C	2p	−11.4	1.625	6
K	4s	−4.34	0.87	8b,c
Hg	6s	−13.68	2.649	23
	6p	−8.47	2.631	
	5d[a]	−17.50	6.436 (3.032)	

[a] Exponents: ξ_1 = 6.436; ξ_2 = 3.032. Double-ζ expansion coefficients: C_1 = 0.6438; C_2 = 0.5215.

Analogously, polyiodides with a charge of $-^1/_3$ per iodine lead to the formation of I_3^- units as has been analyzed by Vonderviszt and one of us[22] (unit cell trebling). The energy gain associated with this Peierls distortion is calculated by our EHT scheme to be 0.09 eV/Hg. This compares well[22] with the energy gain calculated for the trimerization of the $(I^{1/3-})_\infty$ chain (0.07 eV/iodine atom).

The angular deformation due to variations in θ (see **3**) costs some energy: according to band calculations we have performed for $(Hg_4^{2+})_\infty$ chains the most stable configuration occurs at θ = 180°. However, the potential energy curve as a function of θ is soft (see Figure 8). The energy cost to deform the chain from θ = 180° to the experimentally observed value[5] (124.2°) in $Hg_4(AsF_6)_2$, as indicated by an arrow in Figure 8, is only 0.03 eV/Hg. The potential energy curve in Figure 8 can be rationalized as follows. Due to $sp^{1-\delta}$ hybridization, a linear configuration is favored. Furthermore, if the p orbitals would not be involved at all, the electronic energy would depend on θ only very weakly. Due to the small s–p mixing, the calculated energy surface is still flat around θ = 180°, as shown in Figure 8. Consequently, in further experimental studies of new Hg chains, a broad scatter of θ values is expected.



3

Acknowledgment. The financial support of the Camille and Henry Dreyfus Foundation is gratefully acknowledged. We are indebted to Ann Pope for the expert drawings and Kay Bayne for the typing.

Appendix

An extended Hückel crystal orbital method was used with the parameters given in Table II. The k-space integrations were performed with a 55-k-point set for the 2D calculations and a 165-k-point set for the 3D calculations.

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^{13}C NMR Study of (*meso*-2,3-Butanediaminetetraacetato)nickelate(II)

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The temperature and pH dependences of the ^{13}C NMR spectrum of the paramagnetic nickel(II) complex with *meso*-2,3-butanediaminetetraacetic acid are reported and interpreted to indicate that the ligand acts as a hexadentate coordinator at all temperatures accessible in deuteriated water and over the pH range from 1 to 13. Less than 1% of the ligands act as pentadentate coordinators. The incomplete coalescence of acetate resonances coupled with concurrent complete coalescence of backbone resonances is interpreted to indicate that $\Delta \rightleftarrows \Lambda$ conversion proceeds rapidly at moderate (ca. 70 °C) temperatures through a symmetrical intermediate formed without bond breaking, while nitrogen inversion, which requires nickel–nitrogen bond rupture, is slow over the accessible temperature range (<109 °C). The previously proposed mechanism for the racemization of $Ni(EDTA)^{2-}$, which required the presence of an uncoordinated ligand arm, is probably incorrect. A mechanism is proposed that explains the previous and current data without invoking action by a free acetate arm. The *meso*-BDTA chelate ring is found to be more puckered than the chelate ring of EDTA. The pentadentate form of *meso*-BDTA is destabilized by at least 8 kJ mol^{-1} relative to the pentadentate form of EDTA because of steric interaction between a free carboxylate and the axial methyl substituent.

Introduction

Many workers have studied the coordination details of polydentate ligands. The amino carboxylate ligands have received considerable attention from many researchers using a variety of different techniques.[1-16] Although there has been some disagreement in the past, it appears that for ethylenediaminetetraacetic acid (H_4EDTA) coordinated to nickel(II) and other dipositive metal ions, the chelation involves hexadentate coordination by approximately two-thirds of the EDTA molecules and pentadentate coordination by the remaining one-third of the EDTA molecules.[11,16] The thermodynamic values ΔH and ΔS for the pentadentate $\rightleftarrows$ hexadentate equilibrium have been measured for the complexes $Ni(EDTA)^{2-}$ and $Ni(1,2\text{-}PDTA)^{2-}$.[16]

A recent report has confirmed an earlier study which concluded that when a methyl group is substituted onto the EDTA backbone to produce the ligand 1,2-propylenediaminetetraacetic acid (H_4-1,2-PDTA), the percentage of pentadentate coordination is reduced to half that of the EDTA complex. When a cyclohexane ring composes the backbone as in the ligand 1,2-cyclohexanedi-

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aminetetraacetic acid (H_4CyDTA), no pentadentate coordination is observed, within experimental error (ca. 1%).[16,18] Furthermore, for 1,2-PDTA, removal of the in-plane acetate arm on the side opposite the methyl group apparently occurs with the same ease as does removal of an in-plane carboxylate in EDTA. However, there was no measurable uncoordination of the acetate arm on the methyl side of the 1,2-PDTA molecule.[16] The greater percentage of pentadentate coordination in EDTA was, therefore, explained on statistical grounds. No evidence for any measurable fraction of noncoordinated out-of-plane carboxylates was observed for any of the amino carboxylates studied.

The 1,2-PDTA results were explained on the basis that removal of a coordinated acetate group results in a decrease in puckering of the adjacent backbone carbon and, hence, an increase in the axial character of the normally equatorial methyl group that is attached there. The increased energy of the more axial methyl group is sufficient to shift the equilibrium toward coordination to such an extent that no evidence for any uncoordinated acetate could be found for the methyl side of the complex. The inability of the cyclohexane ring to accommodate such a change on either side explained the lack of any pentadentate coordination at all for the CyDTA ligand.

The present work was undertaken to evaluate the effect of an axial methyl group on the coordination properties of EDTA type ligands. The ligand *meso*-2,3-butanediaminetetraacetic acid (H_4-*meso*-BDTA) was investigated because hexadentate coordination by this molecule dictates that one methyl group must be axial while the other methyl group is equatorial. A previous ^{1}H NMR study of the nickel(II) complex of this ligand offered no conclusions as to whether the ligand was pentadentate or hexadentate.[10]

Experimental Section

meso-2,3-Butanediaminetetraacetic acid was obtained as a gift from James Carr of the University of Nebraska. The purity of the ligand was confirmed from the ^{1}H and ^{13}C NMR spectra of the free ligand in the same manner as previously published.[17] No methyl resonances attributable to the racemic compound were observed, indicating a minimum purity of the meso species of at least 95%. The ligand was subsequently used as received. Metal complexes were prepared by mixing 1:1 mole ratios of the free ligand and anhydrous nickel chloride, dissolving in 50% water/50% deuterium oxide, and adjusting the pH to the desired value with sodium hydroxide. All solutions were approximately 0.4 M in the complex.

The pH was measured with a Corning Model 110 digital pH meter calibrated against commercial buffers. No correction to the pH was made to account for the partially deuteriated nature of the solvent. All samples were run in 10-mm thin-walled NMR tubes on a JEOL, Inc., Model FX90Q Fourier transform NMR spectrometer operating at a field strength of 22.1 kG and an operating frequency of 22.5 MHz for ^{13}C. The sample temperature was controlled by the NM-VTS temperature control unit calibrated against ethylene glycol for high temperatures and methanol for low temperatures. All spectra, except as specifically mentioned below, were run without proton decoupling. No spin–spin multiplets were observed, however, because of the large line widths caused by rapid relaxation induced by the paramagnetism of the complex. The zinc(II) complex of *meso*-BDTA was used as the diamagnetic reference for the contact shifts. The zinc complex was prepared in the same fashion as were the nickel complexes. Only an ambient-temperature (ca. 22 °C) spectrum with complete proton decoupling was acquired for the zinc complex. The zinc complex spectrum was assigned by analogy with the $Zn^{II}(1,2\text{-PDTA})^{2-}$ spectrum.[16]

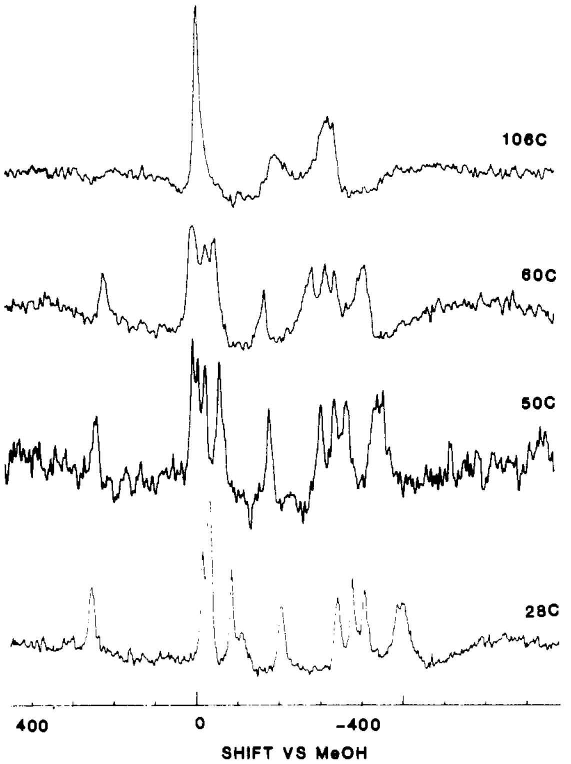

Figure 1. ^{13}C spectra of $Ni(\textit{meso}\text{-BDTA})^{2-}$ at various temperatures (pH 8.0; concentration approximately 0.4 M). Each spectrum is the result of averaging approximately 150 000 scans.

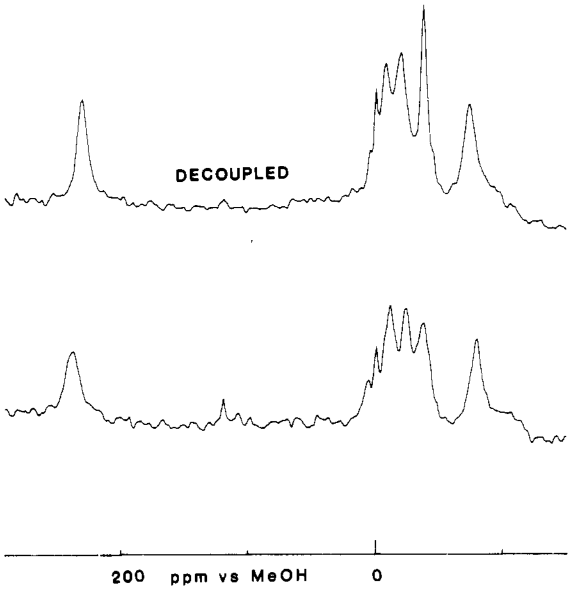

Figure 2. Effect of ^{1}H decoupling on the ^{13}C NMR spectrum. The peaks from −200 to −500 ppm are not shown. No difference between coupled and decoupled spectra was observed in that range.

Results and Discussion

Figure 1 shows the ^{13}C spectra of a pH 8 solution of $Ni^{II}(\textit{meso}\text{-BDTA})^{2-}$ at various temperatures. No significant spectral differences were observed over the pH range 1–13. This is in contrast to the pH dependence of the $Ni^{II}(EDTA)^{2-}$ complex, where a downfield shift of one carboxylate resonance occurs below pH 3, indicating uncoordination of that acetate arm a larger fraction of the time at low pH than at high pH.[8] Furthermore, below pH 2, diprotonated $Ni^{II}(H_2EDTA)$ precipitates, while no such precipitation of a $Ni^{II}(H_2BDTA)$ complex occurs. The behavior of $Ni^{II}(EDTA)^{2-}$ is readily explained on the basis of the known existence of a substantial percentage of pentacoordinated ligand. Because $Ni^{II}(\textit{meso}\text{-BDTA})^{2-}$ exhibits different behavior, it is believed to contain almost none of the five-coordinated form. The spectral assignments and variable temperature studies which follow confirm this conclusion.

In order to interpret the temperature dependence, it is necessary to first assign the ^{13}C spectrum. On the basis of previous studies of $Ni^{II}(EDTA)^{2-}$ and related complexes,[16] the ^{13}C resonances in the region of −8 to −102 ppm vs. methanol are assigned to coordinated carboxylate carbons. One problem with this assignment can be seen in Figure 2: namely, there are five peaks in this region,

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Table I. Spectral Assignments

assignt	shift vs. methanol[a]	shift vs. Zn(BDTA)[a]
equatorial Me	+256	+294
out-of-plane carboxylate	−8	−138
out-of-plane carboxylate	−21	−151
axial Me	−29	+9
in-plane carboxylate (eq side)	−77	−207
in-plane carboxylate (ax. side)	−102	−232
methine[b]	−201	−208
methine[b]	−332	−339
acetate methylene[c]	−369	−384
acetate methylene[c]	−397	−412
2 acetate methylenes[d]	−492	−507

[a] In ppm at 298 °C, with positive shifts downfield. [b] Uncertain as to which methine has the axial methyl substituent. [c] In-plane. [d] Out-of-plane.

but the ligand contains only four carboxylate carbons. A decoupling experiment has demonstrated that the peak at −29 ppm is not due to a carboxylate carbon, but rather it is the axial methyl substituent. The bottom spectrum in Figure 2 is the ^{13}C spectrum with proton coupling while the top spectrum shows the same region acquired under conditions of selective proton decoupling. The decoupler was set to a frequency band centered between the frequencies of the proton resonances for the axial and equatorial methyl groups.[10] The peaks at +256 and −29 ppm sharpen with proton decoupling, whereas the line widths of the carboxylate peaks remain unchanged due to the fact that there are no protons attached to those carbons. The peak at +256 ppm is assigned to the equatorial methyl group on the basis of the $Ni^{II}(1,2\text{-PDTA})^{2-}$ spectrum. This assignment results in the assignment of the peak at −29 ppm to the axial methyl group. The other peaks are assigned by analogy with the $Ni^{II}(EDTA)^{2-}$ spectrum. Table I summarizes the ^{13}C resonance positions and assignments for the *meso*-BDTA complex. The peak positions are reported vs. both methanol and the corresponding carbon atoms in the diamagnetic zinc(II) complex. It should be noted that there is not a constant difference between the two shift values for each resonance because the diamagnetic shifts for each carbon are significantly different from each other and, thus, the reference value is different for each type of carbon.

The spectrum of $Ni^{II}(meso\text{-BDTA})^{2-}$ shown in Figure 1 appears to be consistent with totally hexadentate coordination by this ligand.[16] This conclusion is reached from the observation that the downfield-shifted resonance of the uncoordinated carboxylate that is prominant in the spectrum of the EDTA and 1,2-PDTA complexes is absent from the BDTA spectrum. For the two in-plane carboxylates, a 25 ppm difference in resonance position (at 25 °C) is explained by the distortion of the acetate puckering angle caused by the interaction of one acetate arm with the axial methyl group. The peak at −77 ppm in the BDTA spectrum is assigned to the in-plane carboxylate on the equatorial methyl side because it is in very good agreement with the −78 ppm peak observed for that same carbon in the 1,2-PDTA spectrum. This assignment leaves the peak at −102 ppm representing the in-plane carboxylate on the axial methyl side. The fact that the shift of this carboxylate is upfield, rather than downfield, of the other in-plane resonance is significant and lends weight to the argument that the shift is not a manifestation of coordination $\rightleftarrows$ uncoordination equilibrium as is observed in EDTA and 1,2-PDTA.

The Curie law plot shown in Figure 3 adds further evidence to the case for hexadentate coordination because all of the ligand resonances appear to obey the Curie law relationship in that the contact shift is inversely proportional to temperature and the extrapolation to infinite temperature goes to zero within experimental error (±5 ppm). If a group is involved in an equilibrium reaction (such as coordination $\rightleftarrows$ uncoordination) significant deviations from Curie law behavior are observed.[16,20] Because we see no evidence for any deviations from the Curie law (until the complex becomes stereochemically nonrigid at ca. 70 °C), we conclude that there is no significant equilibrium reaction involving removal of a carboxylate. Because of the other observations, mentioned above, we conclude that the equilibrium lies completely (within experimental error) toward hexadentate coordination. It is estimated that no more than 1% of the ligand is coordinated in the pentadentate form. This estimate of experimental error assumes that the "frozen" shift positions previously measured for coordinated and uncoordinated carboxylates in EDTA and 1,2-PDTA complexes would be valid for the BDTA case and is the percentage of pentadentate form that would result in a deviation of 5 ppm from the Curie law line. Thus, it appears that *meso*-BDTA acts almost exclusively as a hexadentate ligand toward nickel(II) and, presumably, to other metals as well.

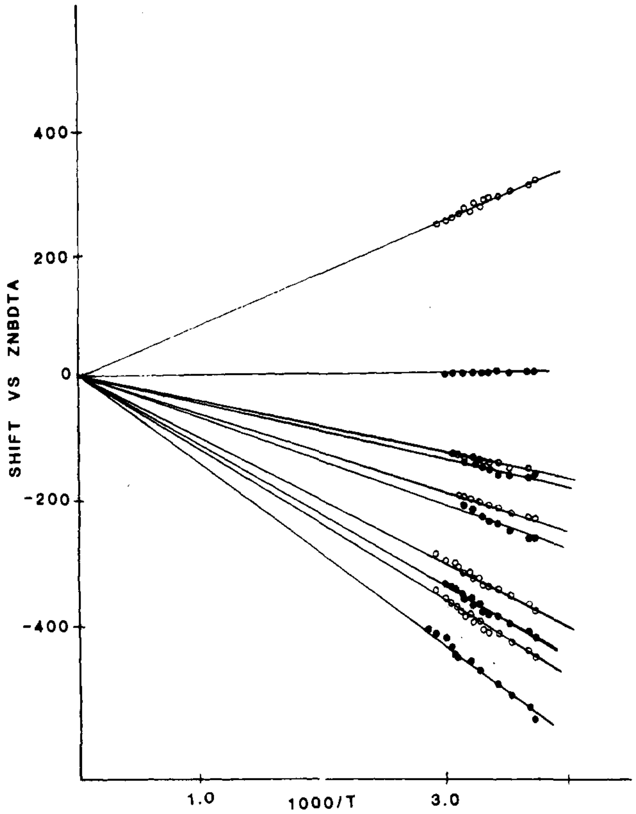

Figure 3. Curie law plot of $Ni(meso\text{-BDTA})^{2-}$. Points affected by averaging at high temperatures are not shown. Some intermediate points are omitted for clarity. Chemical shifts in this figure are not equal to the shifts in Figure 1 because they are referenced to the shifts of the diamagnetic zinc complex rather than those of methanol (see text).

The results reported in this paper and previously reported results[16] show a surprisingly large effect on the ligand coordination details caused by superficially minor changes in the ligand. For example, pentadentate coordination is only half as frequent for $Ni^{II}(1,2\text{-PDTA})^{2-}$ as it is for $Ni^{II}(EDTA)^{2-}$, even though the two ligands differ only by one methyl group and that methyl group is located several bonds away from the coordination sites and points away from the metal. Furthermore, only one of the in-plane carboxylates of 1,2-PDTA is uncoordinated for any measurable fraction of time and that is the one furthest removed from the methyl group. Thus, the effect of substitution of one of the EDTA backbone hydrogens with a methyl results in total coordination of the carboxylates on the methyl side but does not effect the carboxylates on the other side of the ligand. In these two ligands, substantial amounts of pentadentate species are formed: ca. 34% of EDTA and 17% of 1,2-PDTA.

The large effect of the far-removed methyl group on the coordination details of 1,2-PDTA is due to thermodynamic factors. Removal of an in-plane carboxylate decreases ring puckering on that side of the complex and, therefore, increases the axial nature of the equatorial substituents located on that carbon.[16,19] The energy, therefore, required to move a large substituent from a

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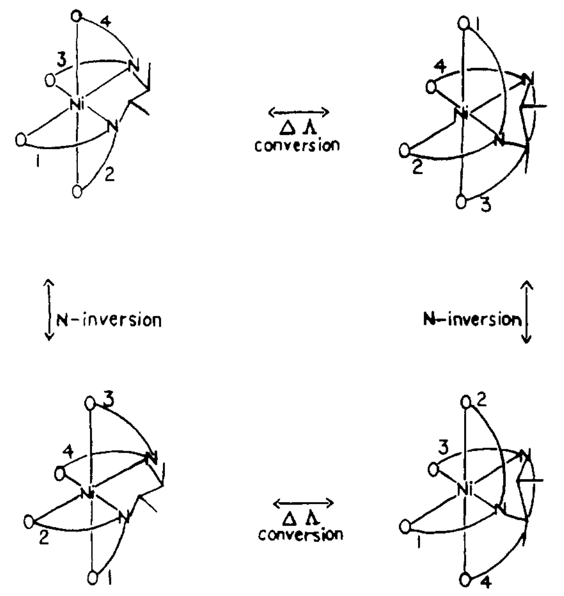
(20) Ho, F.-L.; Reilley, C. N. *Anal. Chem.* **1969**, *41*, 1835–1841.

Scheme I



stable equatorial environment to a less stable axial environment decreases the relative stability of the uncoordinated form and results in a shift of the equilibrium to favor coordination by a large extent. Because the other backbone carbon does not have an attached alkyl substituent, removal of the in-plane carboxylate on the side opposite the methyl does not cause a similar effect.

On the basis of the previous observations and reasoning discussed above, one expects that the in-plane carboxylate on the equatorial methyl side in *meso*-BDTA should be coordinated >99% of the time, and, indeed, this is observed. However, it is not predicted that a similar effect be observed on the axial methyl side. In fact one might argue that the axial methyl would favor uncoordination because an increase in planarity would decrease the unfavorable axial interactions of the methyl group. The experimental results, however, show that such is not the case, and one must look elsewhere for an explanation.

We believe that hexadentate coordination is dominant in the case of *meso*-BDTA because of intramolecular interactions of the coordinated ligand. One possible interaction is between the two methyl groups. Removal of an in-plane carboxylate results in an increase in planarity and, hence, an increased methyl–methyl interaction. This increased interaction will be partially offset by a decrease in interaction between the axial methyl and the out-of-plane carboxylate, but because of the very slight energy difference between the two coordination possibilities, even a minor interaction can result in a large change in the equilibrium constant and in the populations of the two forms. The maximum methyl–methyl interaction of *meso*-BDTA can be estimated from the activation energy for $\Delta \rightleftarrows \Lambda$ conversion. Scheme I shows the changes that occur upon $\Delta \rightleftarrows \Lambda$ conversion and nitrogen inversion of the ligand in a typical octahedral complex. It should be noted that $\Delta \rightleftarrows \Lambda$ conversion does not require metal–nitrogen bond rupture while nitrogen inversion does and that $\Delta \rightleftarrows \Lambda$ conversion interchanges the backbone methyl groups while nitrogen inversion does not. Because $\Delta \rightleftarrows \Lambda$ conversion involves the formation of a planar backbone ring in the activated complex, the activation energy for this process in BDTA is increased relative to the activation energy of EDTA by an amount equal to or greater than the methyl–methyl interaction. Previous ^{1}H studies, confirmed by the ^{13}C studies reported here, have found an increase of approximately 4 kJ mol^{-1} for the $\Delta \rightleftarrows \Lambda$ activation energy.[10,12] Reducing the stability of the pentadentate form by this total amount is not sufficient to completely eliminate pentadentate coordination. A 4 kJ mol^{-1} destabilization would result in approximately 5% pentadentate coordination. Since we are confident that there is 1% or less of the pentadentate form, we conclude that methyl–methyl interaction is not the primary cause of the observed hexadentate preference. This interaction can, obviously, be a contributing factor, however.

It is our belief that the interaction primarily responsible for the structure of this complex is the interaction that would occur in the pentadentate form between the uncoordinated carboxylate group and the axial methyl group. The single-crystal X-ray structure of the pentadentate $Ni(H_2EDTA)$ complex shows that the free acetate rotates away from the coordination sphere and forms a structure in which all of the atoms (except the hydrogens) of this free arm are in the same plane.[19] Examination of molecular models indicates that such a rotation and structure would involve considerable interaction between the free carboxylate and the axial methyl group. A similar interaction between a free carboxylate and the cyclohexane ring of CyDTA was earlier proposed as partially responsible for the hexacoordination of CyDTA observed in some inert complexes by Howarth et al.[13] In that case, the steric compression occurred between a free carboxylate and one of the hydrogens on the cyclohexane backbone and was most significant for the out-of-plane carboxylate. The greater size of the axial methyl group in the present case causes this interaction to be dominant, destabilizing the pentadentate form and favoring hexadentate coordination. Since we can see no evidence for any pentadentate coordination, we cannot quantitatively assess the magnitude of this effect. In view of the very small energy difference between the two forms in the EDTA complex, however, one can say that it does not have to be very large to lead to the observed coordination behavior. On the basis of the previous study of the 1,2-PDTA complex, a destabilization of only 8 kJ mol^{-1} would explain the data observed in this investigation. Thus, we conclude that the energy of interaction between a free in-plane carboxylate and the axial methyl of *meso*-BDTA is at least 8 kJ mol^{-1} when it is coordinated to nickel(II).

The contact shifts reported for the axial and equatorial backbone protons in EDTA and *meso*-BDTA are −10, −126 and −16, −109 ppm, respectively. By the procedure described in ref 21, dihedral angles of 74 and 68° are calculated for EDTA and *meso*-BDTA, respectively.[9,10] These calculations show that BDTA is somewhat more puckered than is EDTA presumably because of the greater interaction between the two methyl groups of BDTA compared to the interaction between the two hydrogens of EDTA.

One aspect of this study requires further discussion. In a previous report, it was proposed that the rate-determining step in the racemization of $Ni(EDTA)^{2-}$ involved attack by an uncoordinated ligand in-plane carboxylate group. Furthermore, it was also proposed that the reason rapid racemization of diacetate and triacetate ligands was not observed was the lack of uncoordinated carboxylates in the complexes of those ligands.[12] These conclusions were based upon the observation of coalescence of the ^{1}H NMR spectrum of $Ni(EDTA)^{2-}$ at 72 °C, while the Ni(EDDA) spectrum (H_2EDDA = ethylenediaminediacetic acid) did not coalesce at temperatures up to 100 °C. It was reasoned that, if a twist mechanism without bond rupture was involved, the diacetate should coalesce more easily than the tetraacetate because there are fewer bonds to stretch to reach the activated complex. The results reported here show the coalescence is rapid in a complex that is known not to have any uncoordinated carboxylates and, hence, the conclusion that such a free carboxylate is a critical factor in the mechanism of the averaging process is questionable. We, therefore, reconsider the mechanism of spectral coalescence in amino carboxylates below.

First of all, one could argue that the *meso*-BDTA coordination must involve *some* pentadentate coordination and, hence, that the previous mechanism could be correct and the slower rate of averaging, compared to that of EDTA, reported here simply reflects the lower percentage of this form. This explanation is rejected, however, because the experimental error of these measurements establishes that there is no more than 1% of the pentadentate form present, while EDTA has approximately 32% pentadentate form (at 22 °C). These values would suggest that, if the pentadentate form is required, the BDTA averaging should

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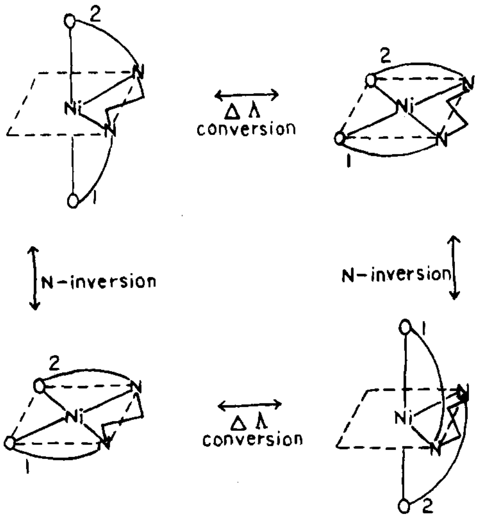
(21) Zamaraev, K. I.; Molin, Y. N.; Skubnevskaya, G. I. *J. Struct. Chem.* (*Engl. Transl.*) **1966**, *7*, 740–742.

Scheme II



be approximately $^1/_{30}$ that of EDTA. The experimentally measured rate is, however, approximately $^1/_3$ that of EDTA, 1 order of magnitude larger than expected. When one realizes that methyl–methyl interaction in the BDTA complex would lead to a further slowing down of the rate, this explanation is discarded and we conclude that the averaging process in the *meso*-BDTA and, presumably, the EDTA complexes as well does not require an uncoordinated carboxylate as previously reported.

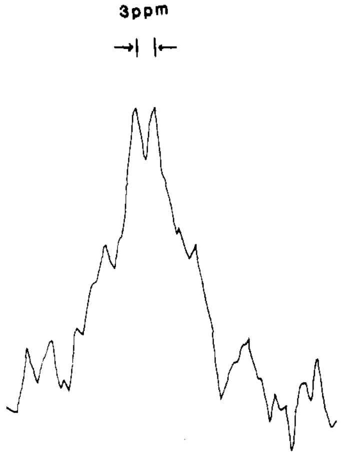


Figure 4. High-temperature ^{13}C NMR spctrum acquired under high-resolution conditions (temperature 109 °C). Only the coalesced carboxylate peaks are shown.

To bring these two studies together, we must consider the changes that result in averaging of the spectra. Two processes are possible: $\Delta \rightleftarrows \Lambda$ conversion and nitrogen inversion. The stereochemical consequences of these two processes have been considered in detail elsewhere[9] and are illustrated in Scheme I. As mentioned above, the major difference between these two processes is that $\Delta \rightleftarrows \Lambda$ conversion results in averaging of the backbone resonances, while nitrogen inversion does not. Each results in the averaging of in-plane with out-of-plane resonances. Complete racemization (i.e. complete averaging of all acetate and backbone resonances) of a complex requires that both processes occur rapidly on the NMR time scale. Since the backbone resonances are averaged in both EDTA and *meso*-BDTA complexes, it is clear that $\Delta \rightleftarrows \Lambda$ conversion is rapid in both cases. However, because structures of equal energy are being averaged and because the residual chemical shift differences are small compared to typical paramagnetic line widths, rapid $\Delta \rightleftarrows \Lambda$ conversion with slow nitrogen inversion is virtually indistinguishable from complete racemization of these two molecules. In the case of the di- and triacetate complexes, however, the structures interconverting are of unequal energy because out-of-plane arms are moved to the less stable in-plane position without the compensating opposite change that occurs in the tetraacetate complexes. Scheme II shows the effect of $\Delta \rightleftarrows \Lambda$ conversion with and without nitrogen inversion on the structure of an EDDA complex. Note that the structures interconverted by only one process have unequal energies. Hence, $\Delta \rightleftarrows \Lambda$ conversion of EDDA will not result in spectral averaging unless nitrogen inversion is also rapid. One can explain the apparent contradication between the present work and the earlier study if nitrogen inversion is slow. Evidence to that effect is found in a study of the rate of acetate deuteriation reported by Young and Reilley for the *meso*- and *rac*-BDTA complexes.[10] They found that the rate of nitrogen inversion was slow on the separation time scale (days) at 72 °C even though conversion was rapid on the NMR time scale (milliseconds) at that temperature. If this report is correct, then nitrogen inversion is also slow on the NMR time scale. Because this earlier work was based upon minor differences in rates of deuteriation, there was some uncertainty about the conclusion. If this report is correct, the average carboxylate positions are, in principle, different. To test this contention, the carboxylate region of Ni(*meso*-BDTA) was examined at high temperature (109 °C) under high-resolution data acquisition and manipulation conditions in an attempt to experimentally confirm by direct observation the prediction that the carboxylates are not truly averaged identically. Figure 4 shows the result of this experiment. Because of the higher noise level associated with the higher resolution conditions, one may question whether the observed two peaks are real or are manifestations of the noise. We believe that the two peaks do reflect true average chemical shift differences because the experiment was repeated three times, with identical results each time. Thus, we concur with the earlier work that nitrogen inversion is slow while $\Delta \rightleftarrows \Lambda$ conversion is fast.

In conclusion, this study supports a twist mechanism without bond breaking for $\Delta \rightleftarrows \Lambda$ conversion of nickel(II) EDTA type complexes. It also confirms the previous contention that nitrogen inversion is slow in these complexes at temperatures up to 100 °C. The earlier report that coalescence of the Ni(EDTA)$^{2-}$ ^{1}H spectrum occurs because of rapid racemization involving a mechanism in which a free ligand arm is required is shown not to be true. Finally, this study has given another example of a significant change in coordination detail caused by what appears to be a minor change in ligand structure at a position several bonds removed from the coordination site. The need for caution in attempting to ascertain the structure of one complex from the known structure of an analogous complex is strongly suggested by the large differences observed in this and other studies on the superficially similar ligands EDTA, 1,2-PDTA, CyDTA, and *meso*-BDTA.

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