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Evidence for some Pentadentate Coordination in Ethylenediamine-*N*,*N*′-diacetato-*N*,*N*′-di-3-propionatonickelate(II)

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Abstract

The ^{1}H and ^{13}C contact shifted NMR spectra of the nickel(II) complex of EDDDA are reported as a function of temperature. The data indicate that the ligand acts as a hexadentate coordinator at least 98% of the time at room temperature with the six-membered propionate rings occupying the in-plane sites and the acetates occupying the out-of-plane sites. The acetate rings are almost planar with a time averaged puckering angle of approximately 7°. Puckering of the ethylenediamine ring is approximately the same as in EDTA and the propionate ring puckering is comparable to that in 1,3-diamines. The amount of pentadentate form of the ligand increases at high temperatures, reaching 22% pentadentate at 100 °C. ΔH and ΔS for the hexadentate $\rightleftarrows$ pentadentate equilibrium are +13 ± 8 kJ mol^{-1} and +17 ± 1 J mol^{-1} K^{-1} respectively. The conversion from hexadentate to pentadentate form involves removal of one of the out-of-plane acetates. No evidence for uncoordinated propionate was observed at any temperature.

Introduction

Amino acetate ligands, especially those related to EDTA, have been investigated by many researchers over an extended period of time [1–15]. The fundamental question as to how many of the potential metal binding sites are actually used by these ligands in solution has been surprisingly difficult to answer. Recent studies of EDTA and some closely related ligands have shown that the average ligand coordination number lies between five and six with rapid pentadentate $\rightleftarrows$ hexadentate equilibrium occurring at room temperature with substitution labile metal ions [4, 9, 15]. Furthermore, the position of this equilibrium is highly sensitive to relatively minor changes in the ligand structure. For example, substitution of a methyl for one of the 'backbone' hydrogens of EDTA results in a reduction of the fraction of pentadentate form from 32% to approximately 17%, i.e. a 50% reduction at room temperature [9, 15] and replacement of two 'backbone' hydrogens by methyl in the ligand *meso*-2,3-butanediaminetetraaceticacid resulted in totally hexadentate coordination of nickel(II) within experimental error (±1%) [14].

In previous studies, it was found that the percentage of pentadentate coordination decreased as the sample temperature was increased indicating a negative ΔH for removal of the last in-plane carboxylate [9]. In this paper we report the results of an investigation of the coordination of ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate (EDDDA), a ligand that differs from EDTA in that two of the EDTA acetate groups are replaced by 3-propionate groups. The presence of the two propionate groups results in the formation of two six-membered chelate rings in place of two of the five-membered acetate rings. Other workers have studied the coordination properties of this ligand to some substitution inert metals by various experimental techniques [16–21] and have concluded that the ligand acts strongly as a hexadentate coordinator with the two propionate arms occupying in-plane positions (so called *trans* (O5) geometry) with small amounts of the unsymmetrical *trans* (O5O6) isomer found in one study [16]. Attempts to prepare a five-coordinate cobalt(III) complex at low pH were unsuccessful [19]. This work was undertaken to utilize the power of NMR contact shift measurements to probe the ligand coordination number in a labile metal complex and to compare the microscopic and dynamic behavior of this ligand to EDTA as part of a continuing study of the effects of ligand structure on coordination properties.

Experimental

EDDDA was purchased from Sigma Chemical Company as the tetraacid and was used as received. The metal complexes were prepared by combining aqueous solutions containing equal molar amounts of nickel(II) (from anhydrous nickel(II) chloride (alfa))

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and partially neutralized (potassium hydroxide) ligand. The pH was adjusted by addition of potassium hydroxide or hydrochloric acid, as needed, while monitoring the solution pH with a Corning model 110 pH meter calibrated against commercial buffers. For ^1H spectra, the water was removed by rotary evaporation and the complex redissolved in deuterium oxide several times to reduce the residual water peak to acceptable levels. Samples used for ^{13}C spectra were made up in approximately 50% deuterium oxide. The final concentration of complex was approximately 0.5 M, but was not accurately determined. No concentration dependence to the chemical shifts was observed. No correction to the measured pH was made to account for the whole or partially deuterated nature of the solvent [22, 23].

Spectra were acquired on a JEOL, Inc. FX90Q Fourier transform spectrometer or on a Hitachi R20B cw instrument modified as previously described [5]. All variable temperature experiments were performed on the JEOL instrument with the temperature controlled by the FX90Q variable temperature accessory calibrated against ethylene glycol for high temperatures and methyl alcohol for low temperatures. Temperature accurary of ±2 °C is assumed.

Results and Discussion

^1H *Spectra*

Figure 1 shows the ^1H spectrum of the nickel(II) complex. The spectrum was pH independent over the range studied (2–12) and no dramatic spectral changes occurred with temperature variation from –10 to 100 °C. All of the resonances appeared to obey Curie law within experimental error except for the peak at –18 ppm and the peak near 0 ppm. These deviations are small and probably not significant because they occur in resonances with very small shifts and, hence, the largest experimental uncertainties. The small deviation of the –18 ppm peak may indicate a slight shift in the chair $\rightleftarrows$ skew boat conformational equilibrium of the six-membered propionate ring [24]. The ^{13}C spectrum discussed below shows that one of the resonances does not obey Curie law by a significant amount. The difference between the ^{13}C and ^1H Curie dependence arises because the chemical shift differences of the ^{13}C spectrum are so much larger than the ^1H differences and, thus, a small shift in equilibrium is observable in the carbon temperature dependence, but not in the proton temperature dependence.

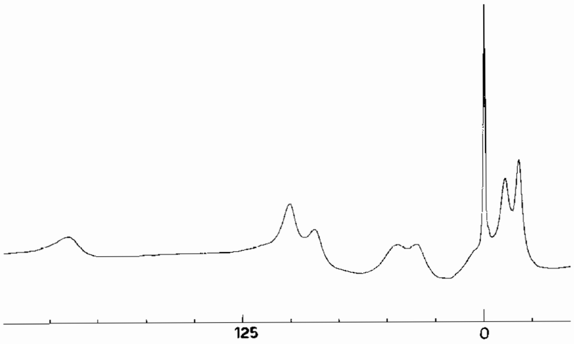

Fig. 1. Room temperature (28 °C) ^1H spectrum of Ni(EDDDA)$^{2-}$. pH approximately 7. Scale in ppm from H_2O. The large peak at 0 ppm is residual HOD in the solvent.

The ^1H spectrum shown in Fig. 1 is assigned by comparison with other spectra reported for similar complexes and by noting that the resonances at +36 and +88 ppm undergo base catalyzed deuteration and, therefore, are the acetate protons. The spectral assignments and shifts of the corresponding protons in the model compounds used to assign the spectrum are summarized in Table 1.

Figure 2 shows a drawing of one half of the complex with the various protons labeled to correspond to the assignment in Table 1. It is clear from the number of peaks in both the ^1H and ^{13}C spectra that the complex is symmetrical and, therefore, only one half of the complex is shown. The six-membered propionate ring is drawn in the nitrogen–nitrogen plane because studies of various substitution inert

TABLE 1. ^1H spectral assignments

Ligand proton	Contact shift^a	Model shift	Model compound	Literature reference
H_g	–18	-17^b	1,3-propanediamine	24
H_h	–11	-8^b	1,3-propanediamine	24
H_b	*c.* 0	$+5^a$	EDTA	5
H_d	+36	$+25^a$	EDTA	5
H_f	+45	$+51^{b,c}$	*N*-Me-1,3-propanediamine	24
H_c	+88	$+88^a$	EDTA	5
H_a	+100	$+117^a$	EDTA	5
H_e	+213	$+285^b$	*N*-Me-1,3-propanediamine	24

[a] ppm from residual HOD downfield shifts positive. [b] ppm from diamagnetic Pt(II) complex. [c] Average of two non-equivalent sites (+46, +57).

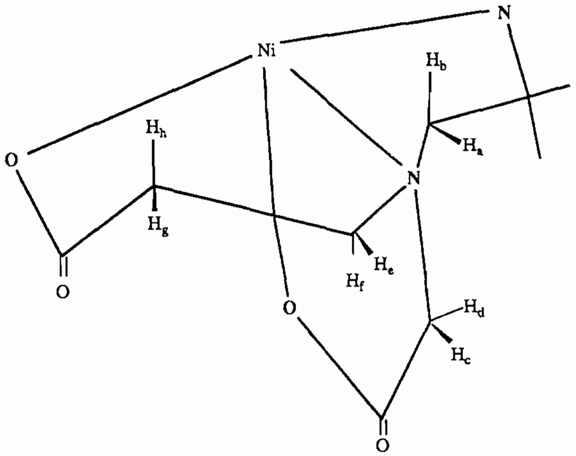

Fig. 2. Structure of Ni(EDDDA)$^{2-}$. Only one half of molecule shown for clarity.

complexes have shown that to be the case [16, 19] and the ^{13}C spectrum reported below indicates that the acetate carboxylate is in the out-of-plane position. Furthermore, deuteration of in-plane acetates does not occur under normal base catalyzed conditions [7].

Unlike EDTA which becomes stereochemically non-rigid, on the NMR time scale, at approximately 70 °C [5] the EDDDA complex retains its stereochemical integrity up to at least 100 °C. This rigidity is consistent with a strong preference of the six-membered ring for an in-plane coordination site which precludes either nitrogen inversion or $\Delta \leftrightarrows \Lambda$ conversion since both of those processes result in the exchange of in-plane substituents for out-of-plane substituents. Similar stereochemical rigidity was previously observed in the nickel(II) complex of ethylenediamine-*N,N'*-diaceticacid (EDDA) and the difference between EDTA and EDDA was explained on the basis that either of the above processes performed on the EDDA complex produces a higher energy structure than the equilibrium one because at least one of the acetate arms is moved from the preferred out-of-plane position to the less favorable in-plane position while the same processes in the EDTA complex simply result in one acetate group replacing another in both the unfavorable in-plane and more stable out-of-plane positions [14]. Hence, the two processes interchange forms that are equally energetic in EDTA but not EDDA [14]. Since rapid interconversion between two forms results in spectral coalescence only if they are equally stable, the differences in temperature dependencies are explained. This principle also explains the lack of high temperature coalescence of the EDDDA spectrum without invoking any unusual bond lifetimes. Because both $\Delta \rightleftarrows \Lambda$ conversion and nitrogen inversion result in an exchange of coordination positions by propionate and acetate the product of either process is a structure with neither group in its preferred, low energy position and, hence, any spectral averaging occurs between states of unequal energy.

TABLE 2. Calculated puckering angles for chelate rings

Chelate ring	Equatorial shift	Axial shift	Calculated dihedral angles[a]
Ethylenediamine	+100	*c.* +0	*c.* 90[b]
Propionate	+213	+45	63, 108
Acetate	+88	+36	51, 113

[a]Dihedral angle as defined in ref. 25 in degrees. [b]Because the axial shift is so small, only an angle close to 90° is reasonable. Dihedral angles calculated from the Heller and McConnell equation [27]: $A_i = B_0 + B_2 \cos^2(\theta)$ with the usual assumption that $B_0 \ll B_2$.

The degree of chelate ring puckering in the complex can be estimated by the three-bond contact shifts of the axial and equatorial protons via the $\cos^2$ dependence of contact shift on the dihedral angle [25, 26]. Because of the squared dependence, two mathematically valid answers are obtained for any axial–equatorial pair. This is not a serious failing of the method because it is usually possible to discard one of these answers as being chemically unreasonable. The dihedral angles calculated for the various chelate rings of this complex are summarized in Table 2. These values were calculated under the usual assumption that B_0 is negligible [25]. From the results of these calculations we conclude that the ethylenediamine ring is substantially puckered with a dihedral angle of approximately 90 ± 10° (see ref. 25 for a definition of the puckering angle). The large experimental uncertainty in this calculation is caused by the extreme sensitivity of the $\cos^2$ function to slight errors in the measured axial contact shift when it is near zero. The ±10° error limit corresponds roughly to a ±3 ppm uncertainty in the axial contact shift position. This degree of puckering is equal to the 'backbone' puckering of the EDTA complex, within experimental error [7]. It is assumed in this analysis that the dipolar shifts of octahedral nickel(II) complexes are negligible. Such an assumption is routine.

Of the two mathematically valid propionate puckering angles, the 63° value is assumed to be the correct one because it is close to that measured for 1,3-diamine chelates [24] and X-ray structures of complexes of this ligand with rhodium(III) and cobalt(III) have shown substantial puckering in this ring [20]. The definition of angles used in analyzing contact shifts defines a planar ring as having a 120° dihedral angle. Because of the much lower sensitivity of the $\cos^2$ function to experimental errors when neither of the shifts is near zero, a ±3 ppm error in both the equatorial and axial contact shift measurements, results in only a ±1° uncertainty in the dihedral angle. Therefore, one can be more certain in the value of the puckering of the propionate ring than the ethylenediamine ring, so long as the 108° result can be disregarded.

The acetate ring puckering value of 51° can be disregarded because such a large degree of puckering is inconsistent with X-ray studies of complexes of this ligand and EDTA in which the out-of-plane acetate groups have been consistently shown to be nearly planar and the in-plane groups are puckered considerably less than the calculated 51° value [20, 28]. Furthermore, a puckering of this magnitude is greater than that of the *gauche* form and should be less stable [25]. Thus, the puckering angle of 113 ± 1°, only 7° from planarity, is assumed to be correct and provides additional evidence for the out-of-plane coordination of the acetate groups. X-ray studies of the rhodium(III) and cobalt(III) complexes of this ligand have concluded that one of the acetate groups is essentially planar while the other is somewhat puckered [20]. The unsymmetrical nature of the solid-state structure may indicate that the acetate puckering is caused by some crystal packing or other intermolecular force not present in solution. Thus, the solution structure may contain two nearly planar acetates despite the solid-state result. Because the NMR puckering value is a time average of the two sides, the solution structure consists either of two nearly planar acetate rings, or one planar ring and one slightly puckered ring in rapid equilibrium. The maximum puckering of either side that is consistent with the average is 106 ± 2° which is close to the 110 ± 1° calculated for the out-of-plane acetates in the nickel EDTA complex [7].

^{13}*C Spectra*

Figure 3 shows the room temperature ^{13}C spectrum of the nickel complex. The spectrum is assigned by analogy with the corresponding spectra for the nickel complexes of EDTA and related ligands [9]. The ^{13}C spectral assignments are summarized in Table 3. Cursory inspection of the room temperature carbon spectrum does not indicate any unusual coordination behavior and spectra acquired at other temperatures do not show any dramatic spectral changes. Careful measurement of the contact shifts, however, reveals that the propionate carboxylate shift is virtually identical to the acetate carboxylate shift which is, in turn, nearly equal to that of the out-of-plane acetate value in EDTA type complexes [9]. The resonance at −138 ppm is assigned to the propionate carboxylate, rather than the acetate because the temperature dependence of the −144 ppm peak (assigned to acetate) indicates that it is in rapid equilibrium with a site that has a large positive shift (the equilibrium is between hexadentate and pentadentate ligand structures). Because the predicted shift of uncoordinated propionate is only slightly different to coordinated propionate (*c.* 55 ppm downfield, based upon the shift of the γ carbon of cyclohexane in CYDTA [9]) while the shift of uncoordinated acetate is more than 500 ppm downfield of the coordinated value, it is concluded that the −144 ppm peak is acetate and, therefore, that the −138 ppm peak is propionate. The similarity of shifts for propionate and acetate indicates that the reason for the difference in shift noted between in-plane and out-of-plane acetates in EDTA type complexes is somehow related to ring strain or the geometry of the in-plane acetate rather than any fundamental difference in the magnitude of the contact shifts induced through the in-plane position and that the contact interaction is dominated by delocalization througn the carboxylate oxygen with relatively little unpaired spin reaching the carboxylate from the nitrogen side. It is also clear that the propionate coordination is not significantly different from acetate coordination in its interaction with nickel(II). The values of the shifts discussed above are found by subtracting the shift for the corresponding carbon of the diamagnetic zinc complex from the spectrum shown in Fig. 3. The shifts in Fig. 3 are recorded relative to methyl alcohol.

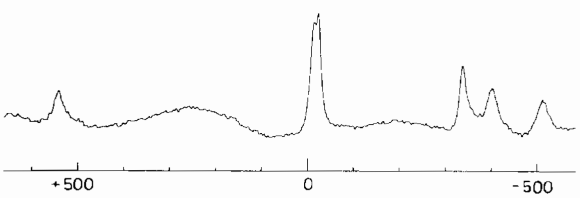

Fig. 3. Room temperature (28 °C) ^{13}C spectrum of Ni(EDDDA)$^{2-}$. pH approximately 7. Scale in ppm from methyl alcohol.

TABLE 3. ^{13}C spectral assignments

Assignment	Room temperature shift[a]	EDTA type shift[b]
Propionate alpha-methylene	+568	
Propionate carboxylate	−138	
Acetate carboxylate	−144	−133[c]
Ethylene diamine methylenes	−327	−300
Propionate beta-methylene	−396	
Acetate methylene	−513	−488[d]

[a] ppm vs. Zn(EDDDA)$^{2-}$. [b] Shift of corresponding resonance in EDTA or 1,2-PDTA complex from ref. 9. [c] Average of out-of-plane positions for 1,2-PDTA, in-plane acetate is at −202 ppm. [d] Out-of-plane acetate methylene in 1,2-PDTA, in-plane is at −413 ppm.

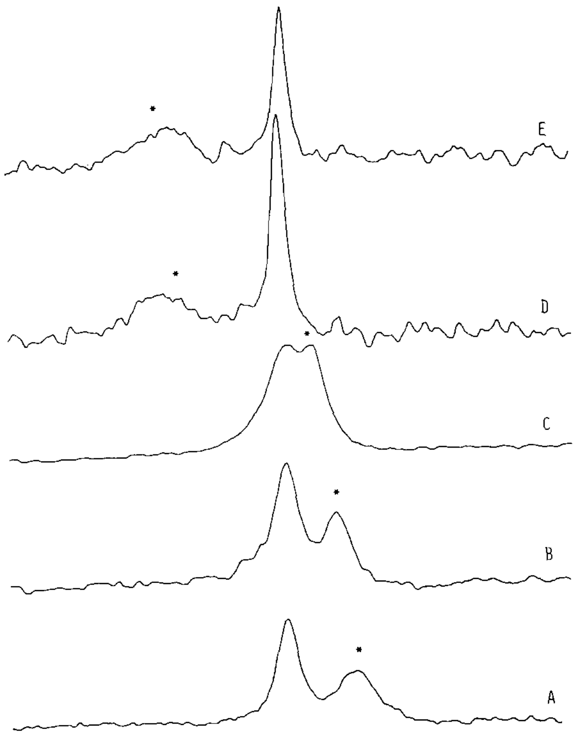

Fig. 4. Expansion of carboxylate region of ^{13}C spectrum at various temperatures. Acetate peak marked by *. A, −10 °C; B, −2 °C; C, 28 °C; D, 83 °C; E, 100 °C.

A second observation apparent upon close inspection of the temperature dependence is that the acetate peak position changes relative to the propionate peak as the temperature is varied. Figure 4 shows an expansion of the carboxylate spectral region at various temperatures to illustrate that the acetate peak is upfield of the propionate peak at low temperature and downfield of that peak at high temperature. It should be noted that the linewidth of the equilibrating acetate goes through a minimum near room temperature. This phenomenon can be explained in the following way: at low temperatures the linewidth is increased because of increases in the solution viscosity while at high temperatures the linewidth is increased because of equilibration with a site that has a much larger contact shift. It is well known that larger contact shifts lead to larger linewidths [29]. The high temperature linewidth is an average over the relatively sharp coordinated peak and the broad uncoordinated peak. The contact shift versus temperature data are summarized as a Curie law plot in Fig. 5.

Figure 5 shows that all of the ligand resonances obey Curie law within experimental error except for the acetate resonance which significantly deviates. The direction of the deviation, to more positive shift values at high temperatures, indicates that it is caused by a shift of the coordinated ⇄ uncoordinated equilibrium toward the uncoordinated form at high temperature. Because of this rapid equilibration only an averaged acetate resonance is observed whose contact shift is determined by the value of the equilibrium constant and the contact shifts of the two forms involved. The room temperature contact shift of an uncoordinated acetate has been shown to be approximately +386 ppm, or 530 ppm downfield of the coordinated value. Therefore, the deviation from Curie law arises from a shift toward uncoordination of the acetate at high temperature. The dashed line through the acetate points in Fig. 5 is calculated from the thermodynamic properties of the hexadentate ⇄ pentadentate equilibrium and the 'frozen' coordinated and uncoordinated resonance values as described below.

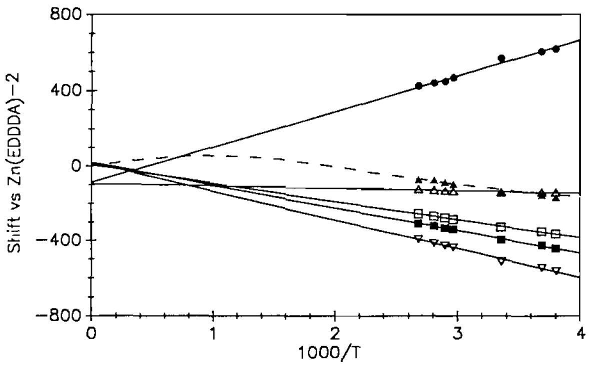

Fig. 5. Curie law plot of ^{13}C contact shifts. Note: chemical shifts in ppm vs. Zn(EDDDA)$^{2-}$ not methyl alcohol. To convert the data in Fig. 3 to the same scale, the chemical shifts of Zn(EDDDA)$^{2-}$ must be subtracted. The solid extrapolated lines are the least-squares best fit of the data. The dashed line is the predicted shift vs. temperature plot for an acetate equilibrating between coordinated and uncoordinated sites with the thermodynamic and shift values given in the text. Solid circles, propionate alpha-methylene; solid triangles, equilibrating acetate; open upward triangles, propionate carboxylate; open squares, ethylene diamine 'backbone'; solid squares, propionate beta-methylene; inverted open triangles, acetate methylene.

There are two reasonable explanations for the apparent non-zero intercept of the Curie law plot of the propionate carboxylate and alpha methylene carbons. One possibility is simply that they reflect the experimental error of the long extrapolation and, therefore, are not actually significantly different from zero. Indeed, only a very modest difference in slope is required to achieve a zero intercept. The second possibility is that the zinc(II) diamagnetic resonance position is not a suitable reference for the propionates. This latter possibility seems unlikely in view of the near equality of shifts for acetate and propionate in the zinc complex. Therefore, we conclude that the non-zero intercept is statistically insignificant.

Since the so called 'frozen' resonance positions for coordinated and uncoordinated acetate are known, the observed averaged shift value can be used to calculate the percentage of pentadentate ligand as a function of temperature and, hence, the thermodynamics of the coordination process. Analysis of the temperature dependence indicates that the amount of pentadentate form present at room temperature and below is no more than approximately 2%, roughly comparable to experimental error, but the fraction of pentadentate form increases to approximately 22% at 100 °C. From a plot of $\ln(K)$ versus $1/T$ for those temperatures where sufficient pentadentate form exists to allow reasonable estimation of its percentage (64–100 °C) the ΔH and ΔS of the hexadentate $\rightleftarrows$ pentadentate equilibrium were determined to be $+13 \pm 8$ kJ mol^{-1} and $+17 \pm 1$ J mol^{-1} K^{-1}, respectively. The error limits correspond to the 95% confidence intervals of the slope and intercept of the plot, respectively. At first it may seem surprising that the uncertainty in the entropy could be only ±1 J mol^{-1} K^{-1} while the uncertainty in the enthalpy corresponds to 27 J mol^{-1} K^{-1} at 300 K but one must realize that the enthalpy value comes from the intercept and, with a small slope, the intercept is relatively insensitive to error in the slope. The relatively high uncertainty in these values reflects the significant experimental error associated with measurements of small deviations from Curie behavior and the modest temperature range available. However, despite the somewhat large error limits on the values, it is clear that both ΔH and ΔS are positive and it is interesting to note that a similar study of EDTA yielded negative values for both of these quantities when an in-plane acetate was involved [9].

When the results of this study and the previous EDTA results are considered together one is led to conclude that acetate coordination to an in-plane site is an endothermic process while coordination to an out-of-plane site is exothermic. It is interesting to note that the propionate group coordinates 100% of the time, within experimental error, even though it is in the less favorable in-plane position and that the most stable pentadentate form contains an uncoordinated out-of-plane acetate not an in-plane propionate. This suggests that the reason for the instability of in-plane acetates is ring strain rather than an inherently weaker interaction. In fact, it appears that the out-of-plane interaction is weaker if the in-plane ring strain is eliminated by expansion of the ring. Because no uncoordinated propionate was observed at any temperature the thermodynamics of propionate coordination are not revealed in this study.

The results reported here show that EDTA type ligands function as pentadentate coordinators for a measurable fraction of time even when ring strain is reduced by increasing the chelate ring size. The percentage of pentadentate form increases at high temperature in the dipropionate containing ligand studied here and *decreases* at high temperature in EDTA. The percentage of pentadentate form found at 100 °C in this study (*c.* 22%) is comparable to the percentage of pentadentate form of EDTA at room temperature (*c.* 32%) despite the greatly reduced ring strain of the six-membered ring.

This investigation does not, however, provide a clear rationale for the two to three orders of magnitude decrease in stability constant noted for EDDDA compared to EDTA for a variety of metal ions [21]. This difference is obviously a complex net effect of differences in ring strain, energies of bond formation for in-plane and out-of-plane carboxylates and possible differences in the nitrogen donor strengths caused by the reduced inductive effect on the nitrogen lone pair of the propionate carboxylate relative to acetate carboxylate. It is apparent, however, that these results do not support the contention that acetate coordination is stronger than propionate, at least for coordination to nickel(II) [21].

This study demonstrates another example of significant differences in metal complex properties and reactions caused by relatively modest changes in ligand structure and emphasizes the need for caution when trying to explain one complex's behavior from studies of a model complex of even slightly different structure. It should also be noted that, while the coordination properties of this ligand are significantly different than EDTA, the puckering of both the ethylenediamine and acetate rings are virtually identical to those of EDTA. This suggests that the ring strain involved in completion of the final chelate ring of these hexadentate ligands remains localized at that final ring and is not greatly relieved by averaging through ligand distortion over the molecule as a whole.

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