

The results indicated in the last paragraph for the  $\text{Cu}^{2+}$  systems seem to hold also for those with  $\text{Zn}^{2+}$  as far as this can be judged, because the observed differences are smaller. This seems to be generally true for  $\text{Zn}^{2+}$  complexes in 50% aqueous dioxane (Figure 3), but a further possible reason for this apparently different behavior could be the weaker interaction between the  $\pi$  systems of 1,10-phenanthroline or 2,2'-bipyridyl and  $\text{Zn}^{2+}$  with its  $d^{10}$  electron configuration; in the case of  $\text{Cu}^{2+}$ , phen and bpy act as  $\pi$  acceptors.<sup>39</sup>

Overall it appears that the aryl residues of the ligands in Chart III presumably act as electron donors and 1,10-phenanthroline and 2,2'-bipyridyl are acceptors in the  $\pi/\pi$  interactions within the intramolecular stacks.

### General Conclusions

That organic molecules with two aromatic-ring systems which are linked together by an aliphatic chain may favor in solution a folded configuration is well-known and has been shown, e.g., for a series of 2-arylethyl *p*-toluenesulfonates<sup>37</sup> and many other molecules allowing an intramolecular aryl/aryl interaction.<sup>40,41</sup> It is also known that the distance between the aromatic residues has an influence on the properties of such aryl/aryl molecules: e.g., the pyrene-( $\text{CH}_2$ )<sub>*n*</sub>-pyrene systems were studied for a large number of *n* values, and it was observed that the intramolecular interaction was most pronounced for *n* = 3.<sup>42,43</sup>

The spacing of two aromatic-ring moieties by a trimethylene bridge has been well exploited.<sup>44</sup> For example, in aqueous solution interactions are observable between bridged nucleic acid bases, like 9-substituted adenine or guanine, or 1-substituted cytosine, thymine, or uracil residues.<sup>44</sup> The trimethylene bridge is probably most suitable because it is the shortest link allowing a stacked arrangement of the aromatic planes with a distance of about 3.4 Å; this distance has often been observed in the solid state.<sup>1,29,30,45</sup>

between aromatic-ring systems.

It is interesting to view the present results in connection with the above observations. The highest formation degree of the intramolecular stack is obtained in the ternary  $\text{M}(\text{phen})(\text{PAC})^+$  and (usually to a somewhat smaller extent)  $\text{M}(\text{phen})(\text{PPr})^+$  complexes (Figure 3; Tables III and IV). This means that the following atoms form the link between the aromatic moieties (Figure 2): one  $\text{M}^{2+}$ , one O, and two (or three) C. Hence, the most suitable linking chain contains in the case of ternary metal ion complexes in total four (or five) atoms, in contrast to the three C atoms observed for the alkyl link in pure organic molecules. This difference is understandable, because the metal ion coordinates to 1,10-phenanthroline in the plane of the aromatic-ring system (Figure 2) and contributes little ( $\text{Zn}^{2+}$ ) or nothing ( $\text{Cu}^{2+}$ ) to shorten the link of the aryl residue that forms the stack. Thus, overall the situation is comparable in metal ion bridged and purely alkyl-linked stacking adducts.

A remarkable property that seems to be connected with the participation of a metal ion in the formation of the stack is indicated by the results of Tables III and IV: addition of ethanol or dioxane to an aqueous solution may promote the formation degree of an intramolecular stack. This observation is interesting and warrants further studies,<sup>25</sup> because the experience<sup>15</sup> with (purely organic) unbridged binary stacks is that addition of ethanol or dioxane inhibits stacking.

Another point of general interest is the influence of the geometry of the coordination sphere of the bridging metal ion on the extent of stacking. The metal ion may impose certain steric restrictions and influence thus the orientation of the coordinated ligating groups that carry the aromatic moieties forming the intramolecular stack. This type of orientation could be important, e.g., in metalloenzyme/substrate interactions.

**Acknowledgment.** The elemental analyses were kindly performed in the microanalytical laboratories of Ciba-Geigy AG, Basel, Switzerland. The computer was made available by the Rechenzentrum der Universität Basel (Univac 1100/81). These supports, a research grant from the Swiss National Science Foundation, and fellowships to U.K.H. and K.H.S. from the Stipendienfonds der Basler Chemischen Industrie are gratefully acknowledged.

**Registry No.** Ethanol, 64-17-5; dioxane, 123-91-1.

- (39) Huber, P. R.; Griesser, R.; Sigel, H. *Inorg. Chem.* **1971**, *10*, 945-947. See also ref 4, 26, and 27.  
 (40) (a) Kobayashi, K.; Kodama, Y.; Nishio, M.; Sugawara, T.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3560-3564. (b) Kunieda, N.; Endo, H.; Hirota, M.; Kodama, Y.; Nishio, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3110-3117.  
 (41) Ōki, M.; Mutai, K. *Tetrahedron* **1970**, *26*, 1181-1189. Mutai, K. *Tetrahedron Lett.* **1971**, 1125-1128.  
 (42) Zachariasse, K.; Kühnle, W. *Z. Phys. Chem. (Munich)* **1976**, *101*, 267-276.  
 (43) Winnik, M. A. *Chem. Rev.* **1981**, *81*, 491-524.  
 (44) Leonard, N. J. *Acc. Chem. Res.* **1979**, *12*, 423-429.

- (45) Gellert, R. W.; Bau, R. *Met. Ions Biol. Syst.* **1979**, *8*, 1-55.

Contribution from the Department of Chemistry,  
University of New Orleans, New Orleans, Louisiana 70148

## <sup>13</sup>C NMR Study of Nickel(II) Amino Carboxylate Binding†

R. F. EVILIA

Received September 27, 1984

The <sup>13</sup>C NMR spectra of a variety of nickel(II) amino carboxylate complexes are reported and analyzed. The spectra are interpreted to indicate that the solution structure of  $\text{Ni}(\text{EDTA})^{2-}$  is approximately 32% pentadentate at probe ambient temperature (~28 °C) with rapid (lifetime < 3 μs) pentadentate ⇌ hexadentate equilibrium. The solution structure of  $\text{Ni}(\text{PDTA})^{2-}$  is found to be 17% pentadentate, with only the in-plane acetate on the side opposite the methyl involved in the equilibrium. No evidence for any pentadentate CYDTA is found. The thermodynamic properties of the hexadentate ⇌ pentadentate equilibria of EDTA and PDTA are found to be  $\Delta H = -14.2 \text{ kJ mol}^{-1}$ ,  $\Delta S = -58.5 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $\Delta H = -9.2 \text{ kJ mol}^{-1}$ ,  $\Delta S = -43 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. These values lead to the conclusion that the mole fraction of either form of the complex is a sensitive function of temperature when the temperature is close to normal ambient conditions. At low temperature, the pentadentate form predominates, and at high temperature, the hexadentate form predominates. The temperature and ionic strength dependence of the equilibrium are believed to be responsible for the large number of contradictory conclusions regarding the coordination of EDTA.

### Introduction

The question of whether EDTA functions as a hexadentate or pentadentate ligand has been studied by a wide variety of in-

vestigators utilizing an equally wide variety of techniques.<sup>1-13</sup> The conclusions of many of these studies have, however, been con-

† Presented in part at the 187th National Meeting of the American Chemical Society, St. Louis, MO, April 8-13, 1984.

- (1) Higginson, W. E. *C. J. Chem. Soc.* **1962**, 2761-2763.  
 (2) Jorgensen, C. K. *Acta Chem. Scand.* **1955**, *9*, 1362-1377.  
 (3) Margerum, D. W.; Rosen, H. M. *J. Am. Chem. Soc.* **1967**, *89*, 1088-1092.

tradictory. Despite some reports that EDTA functions as a hexadentate ligand,<sup>6,7,12</sup> most studies point to at least some pentadentate coordination. No one has to date, however, determined the thermodynamic properties  $\Delta H$  and  $\Delta S$  for the hexadentate  $\rightleftharpoons$  pentadentate equilibrium.

This paper reports the results of a  $^{13}\text{C}$  NMR study of the paramagnetic nickel(II) complexes of EDTA and several related ligands. From the temperature dependence of the chemical shifts the  $\Delta H$  and  $\Delta S$  of removal of the sixth arm are determined. The results for EDTA agree with previous estimates of the degree of pentadentate coordination in nickel complexes of EDTA.

### Experimental Section

Most of the  $^{13}\text{C}$  NMR spectra were recorded on a JEOL FX90Q Fourier transform spectrometer. The 125 MHz  $^{13}\text{C}$  NMR spectrum was provided by the high-field NMR center at Yale University. Temperature was controlled by the JEOL NMVTS temperature control unit. The control unit temperature setting was calibrated against methyl alcohol for low temperatures and ethylene glycol for high temperatures.

All ligands were purchased commercially in the highest possible purity and were used without further purification except for *N*-ethylethylenediaminetriacetate (*N*-EtED3A), which was synthesized by reaction of *N*-ethylethylenediamine with chloroacetic acid as described in ref 14 except that the free acid did not precipitate upon acidification and standing. The complex for spectral investigation was obtained by addition of excess nickel(II) chloride solution to the reaction mixture and adjustment of the pH to approximately 6. This mixture was then passed through an anion-exchange column (Dowex-1) and washed repeatedly with distilled water.  $\text{Ni}(\text{N-EtED3A})^-$  was eluted off the column with lithium chloride solution ( $\sim 4\text{ M}$ ), the elutant evaporated to dryness on a rotary evaporator, and the resulting solid dissolved in deuterium oxide. Because of the small quantity of the complex obtained by this method, a 5-mm sample tube was used to acquire the spectrum of this complex while 10-mm tubes were used for all the other complexes. Except for that of *N*-EtED3A, all complexes were made in the same way: Two millimoles of anhydrous nickel chloride was weighed and dissolved in 5 mL of deuterium oxide. Two millimoles of ligand was weighed and dissolved in 5 mL of water with addition of sodium hydroxide to neutralize the acid groups. The two solutions were mixed, and the pH was measured and adjusted with hydrochloric acid or sodium hydroxide as needed. The approximately 50% deuterium oxide solvent served as the lock signal for the spectrometer. No concentration-dependent shifts were observed that could be attributed to shifts in the lock signal from the paramagnetic complexes. Because of the broadness of the peaks, peak positions are probably good to only  $\pm 4$  ppm. The position and broadness of the carboxylate peak undergoing uncoordinated  $\rightleftharpoons$  coordinated equilibrium is a function of ionic strength, pH, and temperature (in excess of the expected Curie law dependence) while the other peak positions virtually are unaffected by these factors.

The pHs of the solutions were measured with a Corning Model 110 digital pH meter equipped with a Graphic Controls pH electrode standardized against commercial buffers. No attempt was made to correct the measured pH for the partially deuterated nature of the solvent.

### Results and Discussion

Figure 1 shows the  $^{13}\text{C}$  NMR spectra of the EDTA, 1,2-PDТА, CYDTA, and *N*-EtED3A complexes. The assignments of these spectra as a function of pH, of  $\text{Ni}(\text{EDTA})^{2-}$   $^{13}\text{C}$  enriched at the carboxylates have previously been published and have been interpreted to indicate

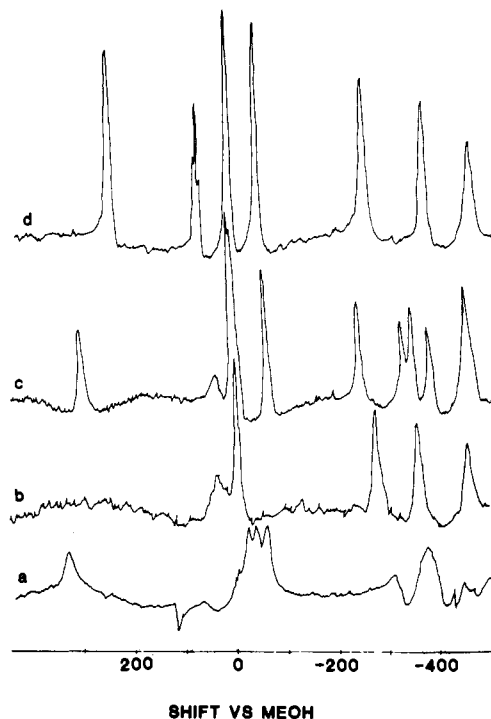


Figure 1.  $^{13}\text{C}$  NMR spectra of nickel(II) complexes (all shifts in ppm from methyl alcohol): (a) *N*-EtED3A, pH  $\sim 7$ ; (b) EDTA, pH  $\sim 8$ ; (c) 1,2-PDТА, pH  $\sim 8$ ; (d) CYDTA, pH  $\sim 8$ .

Table I. Assignment of  $^{13}\text{C}$  NMR Spectra of Nickel Complexes

peak location <sup>a</sup>	assignt	peak location <sup>a</sup>	assignt
<b>Ni(<i>N</i>-EtED3A)<sup>-</sup></b>			
+348	CH <sub>2</sub> CH <sub>2</sub>	-313 <sup>b</sup>	CH <sub>2</sub> CH <sub>2</sub>
-27	out-of-plane CO <sub>2</sub> <sup>-</sup>	-382 <sup>b</sup>	CH <sub>2</sub> CH <sub>2</sub>
-40	out-of-plane CO <sub>2</sub> <sup>-</sup>	-456 <sup>b</sup>	CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
-64	in-plane CO <sub>2</sub> <sup>-</sup>	-498 <sup>b</sup>	CH <sub>2</sub> CO <sub>2</sub>
<b>Ni(EDTA)<sup>2-</sup></b>			
+22	equilibrating CO <sub>2</sub> <sup>-</sup>	-376	in-plane + equilibrating CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
-16	out-of-plane CO <sub>2</sub> <sup>-</sup>	-476	out-of-plane CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
-294	-CH <sub>2</sub> CH <sub>2</sub>		
<b>Ni(PDТА)<sup>2-</sup></b>			
+296	CH <sub>3</sub>	-264	CH <sub>3</sub> CH
+22	equilibrating CO <sub>2</sub> <sup>-</sup>	-348	CHCH <sub>2</sub>
-8	out-of-plane CO <sub>2</sub> <sup>-</sup>	-369	equilibrating CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
-12	out-of-plane CO <sub>2</sub> <sup>-</sup>	-403	in-plane CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
-78	in-plane CO <sub>2</sub> <sup>-</sup>	-480	out-of-plane CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
<b>CydTA</b>			
-216	ring carbons $\beta$ to nitrogen	-290	ring carbons $\alpha$ to nitrogens
+39	ring carbons $\gamma$ to nitrogen	-413	(2) in-plane CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
-17	(2) out-of-plane CO <sub>2</sub> <sup>-</sup>	-493	(2) out-of-plane CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>
-65	(2) in-plane CO <sub>2</sub> <sup>-</sup>		
<b>Zn(PDТА)<sup>2-</sup></b>			
+124	coordinated CO <sub>2</sub> <sup>-</sup>	+6 <sup>b</sup>	CHCH <sub>2</sub>
+123	coordinated CO <sub>2</sub> <sup>-</sup>	+4 <sup>b</sup>	CHCH <sub>2</sub>
+9	CH <sub>2</sub> CO <sub>2</sub> <sup>-b</sup>	-38	CH <sub>3</sub>
+7	CH <sub>2</sub> CO <sub>2</sub> <sup>-b</sup>		

<sup>a</sup>In ppm from MeOH. <sup>b</sup>These assignments are uncertain but do not affect the interpretation of the carboxylate data.

hexadentate coordination at high pH and protonation of a carboxylate, making EDTA behave as a pentadentate ligand, at pH

- Grant, M. W.; Dodgen, H. W.; Hunt, S. P. *J. Am. Chem. Soc.* **1971**, *93*, 6828-6831.
- Everhart, D. S.; Evilia, R. F. *Inorg. Chem.* **1975**, *14*, 2755-2759.
- Matwiyoff, N. A.; Strouse, N. A.; Morgan, L. O. *J. Am. Chem. Soc.* **1970**, *92*, 5222-5224.
- Krishman, K.; Plane, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3195-3200.
- Bhat, T. R.; Krishnamurthy, M. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1147-1154.
- Brunetti, A. P.; Nancollas, G. H.; Smith, P. N. *J. Am. Chem. Soc.* **1969**, *91*, 4680-4683.
- Wilkins, R. G.; Yelin, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 1191-1194.
- Harada, S.; Funaki, Y.; Yasunaga, T. *J. Am. Chem. Soc.* **1980**, *102*, 136-139.
- Erickson, L. E.; Young, D. C.; Ho, F. F.-L.; Watkins, S. R.; Terrill, J. B.; Reilly, C. N. *Inorg. Chem.* **1971**, *10*, 441-453.
- Everhart, D. S.; Evilia, R. F. *Inorg. Chem.* **1977**, *16*, 120-125.
- Dwyer, F. P.; Garvin, F. L. *J. Am. Chem. Soc.* **1959**, *81*, 2955-2957.

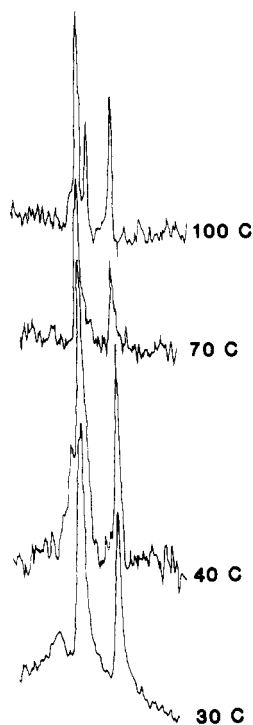


Figure 2. Temperature dependence of 1,2-PDTA carboxylate peaks at pH  $\sim$ 8.

<4.<sup>6</sup> As previously reported, we have also observed a large downfield shift of a resonance of EDTA at pH <4, consistent with carboxylate protonation. Examination of these spectra and temperature studies, however, has led to the conclusion that, even at high pH, EDTA is pentadentate a significant fraction ( $\sim$ 32%) of the time at ambient temperature. The reasons for this conclusion are explained below. A similar conclusion based on  $^{17}\text{O}$  NMR studies has also been reported.<sup>4</sup>

On the basis of the spectrum of the  $^{13}\text{C}$ -enriched study, the EDTA peaks at approximately +22 and -16 ppm (vs. MeOH) are known to be the carboxylates. It is obvious from Figure 1 that the peak at +22 ppm is considerably broader than the other. Integration of the peaks and the earlier work indicate that they are of equal areas within experimental error. Furthermore, by variable-temperature studies, it is easily shown that the broad peak arises from a carbon undergoing a rapid chemical exchange between two quite different chemical environments while the other peak does not. Before the variable-temperature study shown in Figure 3 is discussed, the spectra shown in Figure 1 should be considered. If one compares the carboxylate regions of CYDTA, PDTA, EDTA, and *N*-EtED3A, it is apparent that the broad carboxylate peak is only observed in the EDTA and PDTA cases and, furthermore, that this peak corresponds in area to about one carbon in the PDTA case and to two carbons in the EDTA case. On the basis of the variation of this peak position with pH and temperature (see below), it is assigned to a carboxylate undergoing rapid coordinated  $\rightleftharpoons$  uncoordinated equilibrium. Because this peak has the same shift in PDTA as in EDTA, it is concluded that the position of the equilibrium is essentially the same for that carboxylate in each complex. The absence of such a peak in either the CYDTA or *N*-EtED3A case and the lack of similar pH or temperature dependence of any of the CYDTA peaks indicate that the carboxylates are coordinated virtually 100% of the time in these two complexes. Because the difference between PDTA and EDTA is only one methyl group and peaks due to in-plane, out-of-plane, and equilibrating carboxylates are observed for PDTA, it is clear that one side of the complex is undergoing the equilibrium while the other side is not. On the basis of the observation that both sides of EDTA are equally involved in this equilibrium, it is concluded that the uncoordinated arm in PDTA is on the opposite side from the methyl group. This conclusion is supported by the lack of any uncoordinated carboxylate in

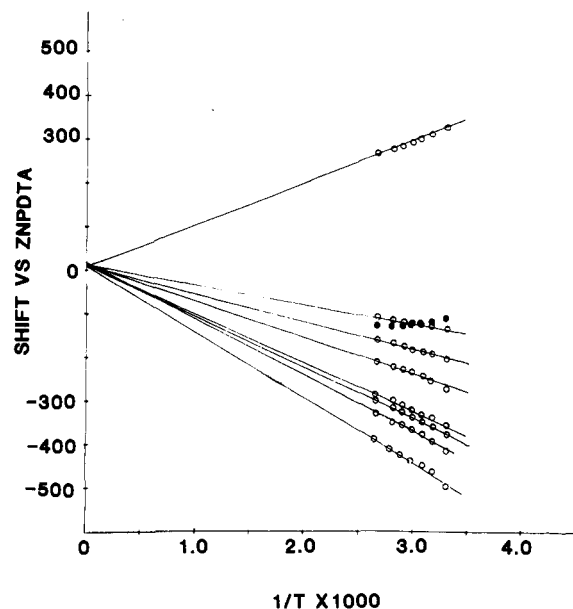


Figure 3. Curie law plot of 1,2-PDTA resonances. Solid dots are data for the carboxylate undergoing equilibration.

Table II. Shift of Equilibrating Carboxylate vs. Temperature for PDTA and EDTA

temp <sup>a</sup>	shift <sup>b</sup>	temp <sup>a</sup>	shift <sup>b</sup>
Ni(PDTA) <sup>2-</sup>			
304	-102	346	-115
316	-107	356	-116
326	-113	376	-120
336	-115		
Ni(EDTA) <sup>2-</sup>			
256	-30	296	-101
266	-65	304	-102
276	-55	316	-107
286	-86		

<sup>a</sup> In K. <sup>b</sup> In ppm vs. Zn(PDTA)<sup>2-</sup>.

CYDTA. This interpretation is confirmed by the temperature study shown in Figure 2. In this figure one can see that the broad peak of PDTA sharpens at high temperature and moves toward the upfield carboxylate peak. Clearly, the reaction is more rapid and the equilibrium is shifted toward 6-coordinate at high temperature. The shift vs. temperature data for this carboxylate in EDTA and PDTA are tabulated in Table II.

Examination of the CYDTA spectrum shows that shifts of in-plane, where in-plane refers to the nitrogen-metal-nitrogen plane, coordinated carboxylates give rise to peaks approximately 48 ppm different from those for out-of-plane carboxylates. Although it is not obvious a priori, the more upfield peak is assigned to the in-plane carboxylates since that is the peak which is missing in the EDTA spectrum and has reduced intensity in the PDTA spectrum. Previous studies have shown that the in-plane acetate is most likely to be uncoordinated.<sup>15,16</sup> These data can be used to quantitatively establish the amount of 5-coordinate EDTA species if the shift of fully coordinated and fully uncoordinated carboxylates can be determined. The fraction of 5-coordinated EDTA will be twice that of PDTA since it contains two equivalent sides, and on the basis of the similar shifts of the partially uncoordinated groups in these two complexes, both of these acetates are uncoordinated for equal fractions of time. A similar order of percentage pentadentate structures has been reported for the Co(II) EDTA, PDTA, and CYDTA complexes. In fact the PDTA complex has been reported to have only half as much

(15) Smith, G. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 556-560.

(16) Weakliem, H. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 549-555.

Table III. Parameters for Acetate Arm Coordination

compd	arm <sup>a</sup>	lifetime <sup>g</sup>	$\Delta H^b$	$\Delta S^c$	fraction uncoordinated at 28 °C
EDTA	either	$\sim 3 \times 10^{-6}$	-14.2	-58.5	0.16 <sup>d</sup>
PDTA	CH <sub>2</sub> side	$\sim 3 \times 10^{-6}$ <sup>e</sup>	-9.2	-43.0	0.17
PDTA	methyl side		$\geq -2^f$	$\leq -15^f$	$\sim 0$

<sup>a</sup>It is assumed that only the in-plane arms are involved. <sup>b</sup>In kJ Mol<sup>-1</sup> for the reaction hexadentate  $\rightleftharpoons$  pentadentate. <sup>c</sup>In J mol<sup>-1</sup> K<sup>-1</sup>. <sup>d</sup>Total fraction of pentadentate species is  $2 \times 0.16 = 0.32$ . <sup>e</sup>It is assumed that the rate of the PDTA reaction is approximately equal to the rate of the EDTA reaction because of the similarity in peak width as a function of temperature between them. <sup>f</sup>The data are explained by  $\Delta H$  of this value or less or by  $\Delta S$  of this value or less. <sup>g</sup>In seconds.

5-coordinate species as the EDTA complex, as predicted here.<sup>17</sup> Thus, these spectra indicate that the presence of an alkyl group on the carbon adjacent to the nitrogen coordination site represses removal of that carboxylate from the primary coordination sphere. The effect of the alkyl substitution on the opposite side of the molecule increases both the  $\Delta H$  and  $\Delta S$  of coordination. The combined effect, in this case, results in virtually no change in the degree of coordination of that carboxylate.

This rather unexpected phenomenon can be rationalized on the basis of the X-ray crystallographic study of the pentacoordinated nickel EDTA complex. Examination of this structure shows that the dihedral angle (relative to the N-Ni-N plane) is about 5° less on the side containing the uncoordinated carboxylate.<sup>15,16</sup> Thus, if the carboxylate on the methyl side of 1,2-PDTA becomes uncoordinated, the methyl will experience an increase in its axial character. The great steric preference of alkyl groups for an equatorial environment opposes such a change. These data indicate, therefore, that this equatorial preference is sufficient to shift the equilibrium to complete, within experimental error, coordination. Such a dramatic effect at a site so far removed from the point of substitution appears somewhat surprising but is the result of two factors: the large preference by the methyl group for an equatorial environment and the only slight preference, at room temperature, for coordination in the absence of the alkyl group. Because the equilibrium constant is nearly unity when a hydrogen is present, the slight equilibrium shift caused by the methyl substitution causes a dramatic change in the concentration of pentadentate ligand.

Figure 3 shows the observed temperature dependence of PDTA as a Curie law plot. Table II summarizes the temperature dependence of the equilibrating carboxylate for EDTA and PDTA. Figure 4 shows a blowup of the carboxylate peaks and theoretically generated curves for the equilibrating carboxylate of EDTA and PDTA using the values of  $\Delta H$  and  $\Delta S$  reported below. The procedure used to generate the theoretical curves will be explained below. The best fit curves correspond to the  $\Delta H$  and  $\Delta S$  values in Table III.

The data for the methyl-side carboxylate of PDTA are reproduced within experimental error ( $\pm 4$  ppm) if it is assumed that the methyl destabilizes the pentadentate form by 6.3 kJ mol<sup>-1</sup> in  $\Delta H$  or by 25 J mol<sup>-1</sup> K<sup>-1</sup> in  $\Delta S$ . This fit is also within experimental error of the ideal Curie law line for 100% coordination of this arm. Thus, even a slight destabilization of the 5-coordinate form by the increased axial nature of the methyl is sufficient to shift the equilibrium to complete coordination, within experimental error, at room temperature. Because the equilibrium constant is so close to unity, the spectral appearance is also greatly affected by any conditions that shift the equilibrium even slightly. For this reason, the position of the equilibrating peak is very sensitive to ionic strength and the presence of other ions that compete for water. The data discussed in this paper were obtained on dilute ( $\sim 0.2$  M) solutions with no added salts. The addition of lithium chloride to the solution favors hexacoordination presumably by decreasing the effective water concentration. This phenomenon was not studied quantitatively, however.

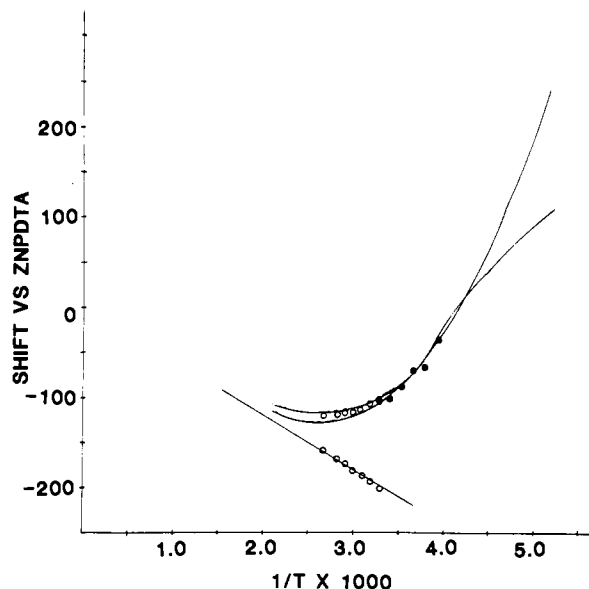


Figure 4. Expansion of the Curie law plot of in-plane carboxylates of EDTA and 1,2-PDTA: lower curve, theoretical curve calculated as described in text for EDTA by using best fit  $\Delta H$  and  $\Delta S$ ; upper curve, theoretical curve for 1,2-PDTA. Solid dots are data for EDTA.

In order to quantitatively assess the fraction of time that the ligand is 5-coordinate, it is necessary to determine the "frozen" resonance positions in the two environments being averaged. Then, from the position of the observed average resonance, the fraction of each form is calculated. The shift of a coordinated in-plane carboxylate is obtained directly from the shift position of the in-plane carboxylate on the methyl side of the PDTA molecule as -202 ppm at 28 °C (vs. the diamagnetic zinc complex). As an estimate of the position of an uncoordinated carboxylate, the methyl position of *N*-ethylethylenediaminetriacetate, +386 ppm at 28 °C (vs. the methyl resonance of Zn(1,2-PDTA)<sup>2-</sup>), is used. This leads to the conclusion that the coordinated carboxylate shift is 588 ppm upfield of the uncoordinated shift.

A computer program for calculating the contact shift temperature dependence of the equilibrating carboxylate in EDTA and PDTA was written. The program iterates  $\Delta H$  and  $\Delta S$  values until a minimum deviation between the predicted and observed temperature dependences is obtained. These values of  $\Delta H$  and  $\Delta S$  were then used to calculate the predicted shift vs. temperature curves shown in Figure 4. Because EDTA has two equally probable carboxylates while PDTA has only one, the EDTA program differed slightly to account for the statistical factor. The program is available on request.

It should be noted that the shift positions shown in Figure 1 are relative to methyl alcohol. Because the diamagnetic reference for carboxylates is significantly different from the reference for non-carboxylates, shift values in Figure 1 are not equally displaced from the shifts shown in the Curie law plot of Figure 3. The Zn(PDTA)<sup>2-</sup> reference used to calculate the shifts for the Curie law plot gave +124 ppm for coordinated CO<sub>2</sub><sup>-</sup>, -38 ppm for uncoordinated -CH<sub>3</sub>, +9 ppm for the methylene backbone, and +9 ppm for coordinated acetate methylene. Thus the contact shift of the uncoordinated carboxylate is calculated from the *N*-EtED3A spectrum as the observed resonance (+348 ppm) minus the Zn(PDTA)<sup>2-</sup> diamagnetic shift of CH<sub>3</sub> (-38 ppm) for a contact shift of +386 ppm at probe ambient temperature. The contact shift of a coordinated in-plane carboxylate is calculated in a similar manner as the difference between the observed shift of the Ni(PDTA)<sup>2-</sup> carboxylate (-78 ppm) minus the Zn(PDTA)<sup>2-</sup> diamagnetic carboxylate shift (+124 ppm) for a shift of -202 ppm. All the other shifts in Figure 3 were calculated in a similar fashion.

Because of racemization of the EDTA complex, EDTA data above 40 °C were not used. PDTA data at low temperatures were not used because of phasing difficulties associated with the downfield methyl peak and base line roll, which causes the car-

boxylate peak location to be greatly influenced by the phasing of the spectrum when the uncoordinated peak moves downfield. In view of the fact that the calculations show very little difference between the EDTA and PDTA peaks over the accessible temperature range, no attempt was made to overcome this problem. The values of  $\Delta H$  and  $\Delta S$  for the coordinated  $\rightleftharpoons$  uncoordinated equilibria are summarized in Table III. The value of  $\Delta H$  for EDTA found in this work,  $-14.2 \text{ kJ mol}^{-1}$ , is in reasonable agreement with the previous estimate of  $-12.2 \text{ kJ mol}^{-1}$  (25% uncoordinated).<sup>4</sup>

Examination of Figure 3 indicates that only the equilibrating carboxylate resonance appears to violate the Curie law. One would expect, however, that all resonances would be affected by the equilibration of the carboxylate and, hence, that all the resonances should violate the Curie law. That this is not observed is explained by reference to the *N*-EtED3A spectrum. The spectrum of this 100% pentadentate ligand corresponds quite well to the spectra of the other ligands, indicating that the shift differences between pentadentate and hexadentate forms are very small except for the carboxylates. This is consistent with the fact that contact shifts transmitted through oxygen are much smaller than those transmitted through nitrogen.<sup>18</sup> Thus, the deviations from the Curie

law of these resonances are small and, hence, not observable over experimental error.

All attempts to slow the exchange rate so that the coordinated and uncoordinated peaks could be observed directly were unsuccessful. This failure is not surprising since the percentage of 5-coordinate species shifts dramatically in the available low-temperature region toward more pentadentate. A <sup>13</sup>C NMR spectrum of Ni(EDTA)<sup>2-</sup> obtained at 125 MHz did not contain the broad carboxylate peak or new peaks at the "frozen" positions. Assuming that the peak was not observed because of kinetic broadening, the rate constant for the reaction is estimated to be approximately  $3 \times 10^5 \text{ s}^{-1}$  in reasonable agreement with the water-exchange rate for Ni(H<sub>2</sub>O)Y<sup>2-</sup> of  $7 \times 10^5 \text{ s}^{-1}$  estimated by <sup>17</sup>O NMR.<sup>4</sup>

This work shows that the enthalpy of coordination of the sixth EDTA site is endothermic and very small, and therefore, the position of the equilibrium is easily changed by slight changes in solution conditions, temperature, or structure. The disagreement in the literature can be explained at least in part by this sensitivity.

**Acknowledgment.** The 125-MHz <sup>13</sup>C NMR spectrum was provided by the Southern New England High-Field NMR Facility at Yale University. A Merck Foundation faculty development grant is acknowledged.

(18) Evilia, R. F.; Reilley, C. N. *J. Coord. Chem.* **1973**, *3*, 7-16.

Contribution from the Department of Chemistry,  
Faculty of Science, Nara Women's University, Nara 630, Japan

## Circular Dichroism of Chromium(III) Complexes. 10. Circular Dichroism Spectra in the Spin-Forbidden Transitions of Cr<sup>III</sup>(N)<sub>6</sub> Type Complexes with Chiral Diamines

SUMIO KAIZAKI,\* MIEKO ITO, NORIKO NISHIMURA, and YUKIE MATSUSHITA

Received October 18, 1984

Room-temperature solution circular dichroism (CD) spectra were measured in the spin-forbidden <sup>2</sup>E<sub>g</sub>, <sup>2</sup>T<sub>1g</sub> ← <sup>4</sup>A<sub>2g</sub> d-d transitions of the diastereomers of [Cr(en)<sub>x</sub>(diamine)<sub>3-x</sub>]<sup>3+</sup> (*x* = 0, 2), *cis*-[Cr(NH<sub>2</sub>)<sub>2</sub>(diamine)<sub>2</sub>]<sup>3+</sup>, and [Cr(NH<sub>2</sub>)<sub>4</sub>(diamine)]<sup>3+</sup>, where the diamines used were (*R*)- or (*S*)-propylenediamine and (1*R*,2*R*)- or (1*S*,2*S*)-1,2-*trans*-cyclohexanediamine. The differences in observed CD spectra between each pair of the diastereomers were accounted for by separability and additivity of the configurational and vicinal CD effects. Consistent assignments for these configurational and vicinal CD peaks to the doublet ← quartet electronic transitions were made in connection with the CD in the spin-allowed <sup>4</sup>T<sub>2g</sub> ← <sup>4</sup>A<sub>2g</sub> transitions on the basis of the theoretical approaches for the energy ordering and the rotational strengths between the spin-forbidden and the spin-allowed transitions; e.g., four vicinal CD peaks in the spin-forbidden transitions of the tris(diamine) complexes were assigned to the 2 $\bar{A}$ (<sup>2</sup>E<sub>g</sub>), E(<sup>2</sup>E<sub>g</sub>), <sup>2</sup>A<sub>2</sub>(<sup>2</sup>T<sub>1g</sub>), and <sup>2</sup>E(<sup>2</sup>T<sub>1g</sub>) from the lower frequency side. This is the first demonstration by the room-temperature solution CD measurements for the <sup>2</sup>E<sub>g</sub> split components due to the electronic transitions to the Kramers doublets (2 $\bar{A}$  and E) with a small spacing of less than 100 cm<sup>-1</sup>.

### Introduction

In our previous papers of this series,<sup>1-4</sup> room-temperature solution circular dichroism (CD) spectra in the spin-forbidden <sup>2</sup>E<sub>g</sub>, <sup>2</sup>T<sub>1g</sub> ← <sup>4</sup>A<sub>2g</sub> transitions of trigonal and tetragonal Cr(III) complexes have been examined in comparison with those in the first spin-allowed <sup>4</sup>T<sub>2g</sub> ← <sup>4</sup>A<sub>2g</sub> transitions. As a result, it has been demonstrated that weak but sharp well-resolved CD peaks in the spin-forbidden transitions can be elucidated by the close correlation (spin-orbit coupling) between the quartet (<sup>4</sup>T<sub>2g</sub>) and doublet (<sup>2</sup>E<sub>g</sub> and <sup>2</sup>T<sub>1g</sub>) excited states. Still, there have remained some ambiguous elucidations of the spin-forbidden transitions even for one of the most popular complexes, [Cr(en)<sub>3</sub>]<sup>3+</sup>, though the understanding of chiroptical spectra of this complex in both the spin-forbidden and the first spin-allowed transitions has much advanced in experiments and theories for the last decade.<sup>1,5-14</sup> The low-

temperature single-crystal spectroscopic studies<sup>5-8</sup> have confirmed our previous assignments<sup>1</sup> of the lowest frequency CD peak to the spin-forbidden <sup>2</sup>E<sub>g</sub> ← <sup>4</sup>A<sub>2g</sub> transition and have substantiated the splitting of the <sup>2</sup>E<sub>g</sub> state with a spacing of 18 cm<sup>-1</sup> and the overlapping of the <sup>2</sup>T<sub>1g</sub> split components with the vibronic progression of the <sup>2</sup>E<sub>g</sub> origins. However, they are in some disagreement with theoretical treatments.<sup>1,6a,9</sup> Thus, it is important to reexamine whether room-temperature solution CD peaks in this region from the electronic or vibronic origins. For this

- (1) Kaizaki, S.; Hidaka, J.; Shimura, Y. *Inorg. Chem.* **1973**, *12*, 142.
- (2) Kaizaki, S.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3611.
- (3) Kaizaki, S.; Ito, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2499.
- (4) Kaizaki, S.; Mori, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3562.
- (5) Güdel, H. U.; Trabjerg, I.; Vala, M.; Ballhausen, C. J. *Mol. Phys.* **1972**, *24*, 1227.

- (6) (a) McCarthy, P.; Vala, M. T. *Mol. Phys.* **1973**, *25*, 17. (b) Flint, C. D.; Matthews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 576.
- (7) Geiser, U.; Güdel, H. U. *Inorg. Chem.* **1981**, *20*, 3013.
- (8) Peacock, R. D.; Stewart, B. J. *J. Chem. Soc., Chem. Commun.* **1982**, 295.
- (9) Hilmes, G. L.; Brittain, H. G.; Richardson, F. S. *Inorg. Chem.* **1977**, *16*, 528.
- (10) Jensen, H. P. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 127.
- (11) Harnung, S.; Laier, T. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 41.
- (12) Evans, R. S.; Schreiner, A. F.; Hauser, P. J. *Inorg. Chem.* **1974**, *13*, 2185.
- (13) Mason, S. F. In "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism"; Ciardelli, F., Salvadori, P., Eds.; Heyden and Son Ltd.: New York, 1973; p 196.
- (14) Jensen, H. P. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 355.