what confused. Part of this confusion is believed to be attributable to the existence of two or more isomeric or trimeric complexes for these compounds as described earlier.[3]

Equilibrium constants of the benzodioxin and benzodithiin indicate that the sulfur analog forms a stronger complex than the oxygen analog. It is further observed that the strength of neither the oxygen complex nor the sulfur analog is affected by the addition of a second benzo group onto the hetero ring as in the case of thianthrene and diphenyldioxane.[3] Values of about 5.0 and 13.0 for oxygen and sulfur analogs, respectively, are obtained for both the benzo and dibenzo derivatives. Again it must be concluded that the silver ion interacts at the heteroatom lone-pair electrons rather than the double bond of the benzodioxin or benzodithiin. The interaction of the silver ion at the lone pair and also the stronger interaction of the silver ion with the sulfur atom lone pair again suggest strong interaction of the oxygen lone pair with the delocalized system.

In both benzodioxin and dithiin the vinyl protons have larger chemical shift changes than the aromatic protons when the complex forms. This is expected if the silver ion is complexed predominantly in the hetero ring. The resonance of the aromatic protons of the sulfur analogs which are α to the sulfur atom is changed about 27.0 Hz while the protons β to the sulfur atom are shifted only 21 Hz on complexation. The shift of the aromatic protons of benzodioxin are very small on complexing and show no significant difference between α- and β-proton shifts. Thus, for both the benzo- and dibenzo-derivative complexes the protons on the sulfur analogs have much higher shifts than the corresponding protons on the oxygen analogs. This may be a reflection of the higher equilibrium contants for the sulfur analogs, which in turn are due to a stronger interaction between the sulfur filled orbitals and silver ion vacant orbitals.

The formation constant of 1,4-dioxin–silver ion complex is about the same as that shown by 1,4-benzodioxin (Table IIA). Also chemical shifts of 1,4-dioxin complex protons are about the same as those of the vinyl protons in complexed 1,4-benzodioxin. Unfortunately, 1,4-dithiin reacts immediately when added to silver nitrate solution.

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Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. IV. Kinetics of Partial Dissociation of the Cadmium and Zinc Complexes of 1,3-Propylenediaminetetraacetic Acid[1]

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Received March 22, 1972

Dynamic nuclear magnetic resonance methods have been used to determine the average lifetimes of the magnetically nonequivalent acetate methylenic protons before interchange in the cadmium and zinc complexes of 1,3-propylenediaminetetraacetic acid (1,3-PDTA). Magnetic nonequivalence is indicated by AB multiplet patterns for the methylenic protons. The lifetimes were determined over a range of temperatures from the extent of collapse of the AB multiplet patterns by matching experimental nmr spectra with theoretical nmr spectra which were calculated as a function of the average lifetime before interchange using the density matrix formulation. It is proposed that these lifetimes are a measure of the rates of partial dissociation of the cadmium and zinc complexes of 1,3-PDTA.

Introduction

Nuclear magnetic resonance (nmr) studies have revealed through AB splitting patterns that the two protons of a given acetate methylenic group of ethylenediaminetetraacetic acid (EDTA)[2–10] and of several analogs of EDTA[3,6,8–16] are magnetically nonequivalent on the nmr time scale in a number of metal complexes of these ligands. The nonequivalence has been interpreted as indicating the inertness on this time scale of at least some if not all of the metal–ligand bonds. Day and Reilley[2] proposed, for example, that the cadmium–nitrogen bonds in $Cd(EDTA)^{2-}$ are inert on the nmr time scale on the basis of the nonequivalence of the methylenic protons of the complexed EDTA; the two protons of a given methylenic group can interchange environments and thus collapse the AB pattern to a single resonance, only by inversion of the nitrogen atom, which presumably is possible only when the nitrogen atom is not metal coordinated. Inherent in this interpretation is the assumption that, once the metal–nitrogen bond dissociates, inversion occurs at least once before the metal–nitrogen bond re-forms.

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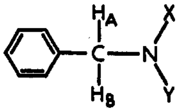
Similar AB patterns have been observed for acidic solutions of tertiary amines of the structure



where X and Y are different groups.[17–20] Studies on the AB interchange rates of the methylenic protons of several amines of this type have shown that, in acidic solutions, the rates of interchange are governed by the rates of proton exchange and/or the rates of inversion of the nonprotonated nitrogen atom.[19,20] By analogy, collapse of AB patterns by inversion of nitrogen atoms in complexed multidentate ligands is predicted to be governed by the rate of metal–nitrogen bond dissociation and/or the rate of inversion of the noncoordinated atom. If dissociation of the metal–nitrogen bond governs the rate of collapse, the AB pattern is an indication of inert metal–nitrogen bonding as has been assumed[2] and potentially can provide information about the partial dissociation kinetics of the complex.[21] Complexation reactions of multidentate ligands are known to proceed *via* stepwise formation and dissociation of the bonds to the individual dentates of the ligand;[22–24] however, in only a few systems has it been possible to obtain the rates of some of the individual steps.

In the present work, the AB patterns for the methylenic protons of the divalent cadmium and zinc complexes of 1,3-propylenediaminetetraacetic acid (1,3-PDTA) have been studied over a range of temperatures. Average lifetimes before AB interchange have been obtained by line-shape analysis of experimental spectra in the temperature ranges where the AB patterns are partially collapsed. A central purpose of this work has been to ascertain what kinetic information can be obtained from the nonequivalence of the methylenic protons in complexes of this type.

Experimental Section

Chemicals.—1,3-PDTA was synthesized by the method of Weyh and Hamm.[25] Cadmium nitrate, lead nitrate (Fisher Scientific Co.), and zinc nitrate (Baker Chemical Co.) were used as received.

pH Measurements.—All pH measurements were made with an Orion Model 801 pH meter equipped with a micro combination electrode. Saturated potassium acid tartrate and 0.01 *M* sodium tetraborate buffers, pH 3.56 and 9.18, were used to standardize the meter.

Nmr Measurements.—Nmr spectra were obtained on either a Varian A-60D high-resolution spectrometer or a Varian HA-100 spectrometer operated in the frequency sweep mode. Peak positions on the 100-MHz spectra were measured relative to the *tert*-butyl alcohol lock signal. Spectra were recorded at sweep rates of 0.1 Hz/sec for both chemical shift and line-shape measurements; sweep widths of 50 Hz were used. At each temperature, the spectrum was recorded four times and the individual spectra were averaged. The sample temperature was determined by the standard methods using methanol and ethylene glycol. This gave temperatures considered to be accurate to ±1°.

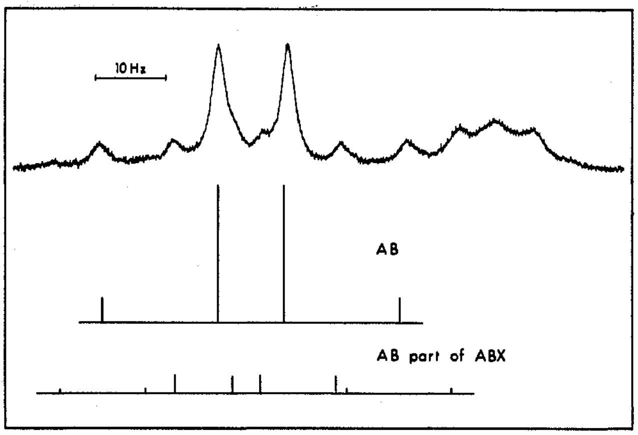


Figure 1.—The 100-MHz proton nmr spectrum of the acetate methylenic protons of Cd(1,3-PDTA)$^{2-}$ in D_2O at 10°. The pD of the solution was 7.5 at 25°.

The solutions were prepared in either triply distilled water or D_2O from the appropriate amounts of metal salt and 1,3-PDTA. KOH, KOD, or HNO_3 were used to bring the solutions to the desired pH or pD. All solutions were about 0.2 *M* in both 1,3-PDTA and metal salt.

Results

Cadmium–1,3-PDTA.—The 100-MHz nmr spectrum of the acetate methylenic protons of Cd(1,3-PDTA)$^{2-}$ in D_2O solution at 10° is shown in Figure 1. The pD of the solution was 7.5 at 25°. The multiplet pattern consists of the AB part of an ABX pattern superimposed on an AB pattern. The AB pattern arises from the complexes of cadmium isotopes whose nuclear spin quantum number is zero while the AB part of an ABX pattern is due to the cadmium-111 and cadmium-113 complexes; these isotopes have a nuclear spin quantum number of $^1/_2$ and are present at 25.0% natural abundance. The AB pattern and the AB part of an ABX pattern comprising the experimental spectrum are presented in the bottom part of Figure 1. These spectra were calculated from chemical shifts and coupling constants obtained by analyzing the multiplet pattern.[26] The 100-MHz spectra were analyzed because the two low-intensity peaks of the AB pattern were almost unobservable at 60 MHz. The broad triplet just upfield from the multiplet pattern for the methylenic protons is due to the two methylene groups bonded to the nitrogen atoms in the propylene part of the ligand.

Analysis of the AB pattern from slow-exchange spectra taken at several temperatures in the range 3–26° yielded a value of 16.3 ± 0.1 Hz for $|J_{AB}|$. The chemical shift difference, $\Delta\delta_{AB}$, was found to decrease linearly as the temperature was increased, and a least-squares analysis of the data yielded

$$\Delta\delta_{AB}(\text{ppm}) = -5.00 \times 10^{-4}T + 0.205 \qquad (1)$$

where T is the temperature in degrees centigrade. Analysis of the AB part of the ABX pattern using the value given above for J_{AB} yielded a value of 3.2 Hz for $|J_{AX} - J_{BX}|$. $|J_{AX}|$ and $|J_{BX}|$ were determined by varying them and calculating spectra until the best fit was obtained.[26] The "best fit" values were $|J_{AX}|$ =

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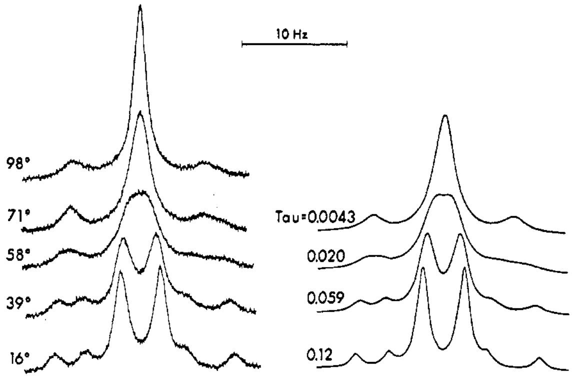

Figure 2.—Representative experimental and theoretical 60-MHz proton nmr spectra of the acetate methylenic protons of Cd(1,3-PDTA)$^{2-}$ in H_2O. The pH of the solution was 8.0 at 25°. The theoretical spectra were computer simulated using the spectral parameters given in the text and the lifetimes indicated.

11.8 and $|J_{AX}| = 15.0$ Hz, assuming the signs of J_{AX} and J_{BX} to be the same. No significant variation of these coupling constants with temperature was found.

The line shape of the multiplet pattern is temperature dependent, as shown by the 60-MHz spectra in Figure 2. The pH of the solution was 8.0 at 25°. The two low-intensity lines of the AB pattern were barely visible at 16° and are not shown in Figure 2. As the temperature is increased, the AB pattern collapses to a single, averaged resonance at a position intermediate between ν_A and ν_B while the AB part of an ABX pattern collapses to the A part of an A_2X pattern. The 98° spectrum clearly illustrates the limit of rapid interchange of the A and B protons of a given methylenic group on the nmr time scale. The coupling to cadmium-111 and cadmium-113 at 98° indicates AB interchange occurs without complete dissociation; the slight broadening of the cadmium-111 and cadmium-113 satellites at 98° suggests that at this temperature the rate of complete dissociation is just becoming appreciable on the nmr time scale.[27]

Average lifetimes before AB interchange were determined by line shape analysis of spectra of which those in Figure 2 are representative. The density matrix method[28] was used to simulate spectra theoretically as a function of the lifetime τ before exchange. Other parameters used in the calculation were $\Delta\nu_{AB}$ (Hz), J_{AB}, J_{AX}, J_{BX}, and T_2, where T_2 is the spin–spin relaxation time. $\Delta\nu_{AB}$ at a given temperature was calculated with eq 1. Similar extrapolations to high temperatures have been used previously in line-shape treatments.[29] A constant T_2 calculated from an assumed natural line width of 1.0 Hz was used; the natural line width could not be measured because some exchange broadening was observed even at the lowest temperatures attainable. Typical line widths in similar complexes are 1.0 Hz. The computer program[30] was modified so that it calculated first the line shape of the AB spectrum and then the AB part of the ABX spectrum for these parameters. It then normalized the intensities of the two spectra so that the AB part of the ABX pattern represented 25% of the total. The normalized spectra were combined to give a spectrum which was compared with the experimental spectrum for the methylenic protons. For a given set of spin–spin coupling constants and chemical shifts, τ was varied until the computed and experimental spectra matched. Those in Figure 2 are typical of the fits obtained. Average lifetimes before AB interchange determined in this way over a range of temperatures are listed in Table I. The precision in the lifetime determinations was 5–10%, due mainly to difficulties in matching computed and experimental spectra.

TABLE I

AVERAGE LIFETIMES OF THE ACETATE METHYLENE PROTONS OF Cd(1,3-PDTA)$^{2-}$ BEFORE AB INTERCHANGE[a,b]

T, °C	τ, sec	T, °C	τ, sec	T, °C	τ, sec
16	0.12	39	0.059	58	0.020
23	0.085	45	0.042	64	0.011
31	0.070	51	0.029	71	0.0043

[a] pH 8.0 at 25°. [b] Determined by line-shape analysis of 60-MHz data using the parameters given in the text.

A pH of 8.0 was chosen for this study to minimize the contributions of reactions involving hydrogen or hydroxide ion to the overall rate of AB interchange. To determine the magnitude of any pH dependence, samples at pH's 7.2, 8.4, and 9.1 (at 25°) were studied over the same temperature range. The spectra obtained were identical, at the same temperatures, with those from which the results in Table I were obtained, indicating no pH dependence within this pH range.

To establish the validity of the line shape treatment, lifetimes were determined by the above procedure for the D_2O solution of Cd(1,3-PDTA)$^{2-}$ at pD 7.5 over a range of temperatures using both 60- and 100-MHz spectra. If the treatment is valid, the lifetimes should be independent of the measuring frequency. The results (Table II) indicate this to be the case. Also the results indicate that, on the average, the rates of AB interchange for the D_2O solution are 0.6 times as fast as in H_2O at pH 8.0.

TABLE II

COMPARISON OF AVERAGE LIFETIMES OF THE ACETATE METHYLENE PROTONS OF Cd(1,3-PDTA)$^{2-}$ BEFORE AB INTERCHANGE DETERMINED FROM 60-MHz AND 100-MHz SPECTRA[a]

	τ, sec			τ, sec	
T, °C	b	c	T, °C	b	c
23	0.12		47		0.056
26		0.12	51	0.043	
31	0.10		56		0.034
39		0.094	58	0.028	
45	0.065		60		0.026

[a] pD = 7.5 at 25°. [b] 60 MHz. [c] 100 MHz.

Zinc–1,3-PDTA.—The 60-MHz nmr spectra of the acetate methylenic protons of Zn(1,3-PDTA)$^{2-}$ in aqueous solution over a range of temperatures are shown in Figure 3. The pH of the solution was 8.7 at 25°. The multiplet consists of an AB pattern, of which the upfield peak is obscured by a broad triplet due to the two methylene groups bonded to the nitrogen atoms in the propylene part of the ligand. As the temperature is increased, the AB pattern begins to collapse; however, the extent of collapse and thus the

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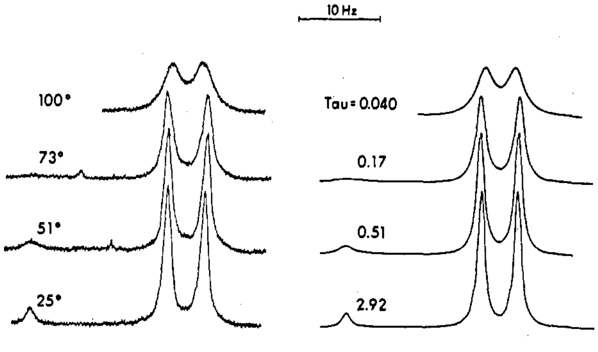


Figure 3.—Representative experimental and theoretical 60-MHz proton nmr spectra of the acetate methylenic protons of $Zn(1,3\text{-}PDTA)^{2-}$ in H_2O. The pH of the solution was 8.7 at 25°. The theoretical spectra were computer simulated using the spectral parameters given in the text and the lifetimes indicated.

rate of AB interchange are somewhat less than for $Cd(1,3\text{-}PDTA)^{2-}$. Analysis of 60-MHz slow-exchange spectra yielded 16.3 ± 0.1 Hz for $|J_{AB}|$ and 13.2 ± 0.5 Hz for $\Delta\nu_{AB}$, independent of temperature from 25 to 62°.[26] These values were used in the computer simulation of spectra.

Average lifetimes before AB interchange were determined by matching computer-simulated and experimental spectra in the same way as for $Cd(1,3\text{-}PDTA)^{2-}$. In the lower part of the temperature region studied, the line width of the low-intensity peak was the most sensitive parameter for matching experimental and simulated spectra, whereas at the higher temperatures it was the central peaks. The average lifetimes before AB interchange obtained in this way are listed in Table III; representative theoretical and experimental spectra are shown in Figure 3.

Table III

Average Lifetimes of the Acetate Methylene Protons of $Zn(1,3\text{-}PDTA)^{2-}$ before AB Interchange[a,b]

T, °C	τ, sec	T, °C	τ, sec	T, °C	τ, sec
25	2.9	62	0.25	87	0.084
39	1.2	73	0.17	93	0.060
51	0.51	80	0.12	100	0.040

[a] pH 8.7 at 25°. [b] Determined by line-shape analysis of 60-MHz data using parameters given in the text.

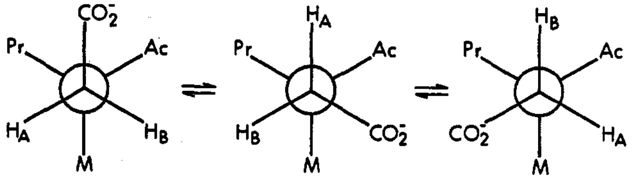
Lead–1,3-PDTA.—The 60-MHz nmr spectrum of the acetate methylenic protons of an aqueous solution of $Pb(1,3\text{-}PDTA)^{2-}$ at pH 7.9 and 25° consists of a single resonance flanked symmetrically by two satellite peaks. The width of the central resonance at half-height is 1.2 Hz. The satellites arise from the lead-207 complexes; lead-207 has a nuclear spin quantum number of $^1/_2$ and a natural abundance of 22.6%. $|J_{Pb-H}|$ was determined to be 19.6 Hz. The simplicity of the nmr spectrum for $Pb(1,3\text{-}PDTA)^{2-}$ compared to those for $Cd(1,3\text{-}PDTA)^{2-}$ and $Zn(1,3\text{-}PDTA)^{2-}$ could be due to more labile metal–nitrogen bonding resulting in averaging of the AB resonances[2] or to accidental equivalence of the methylenic proton chemical shifts.[8]

Cadmium–EDTA.—The 60-MHz nmr spectrum of the acetate methylenic protons of a neutral, aqueous solution of $Cd(EDTA)^{2-}$ consists of a complex multiplet pattern[2] similar to that of $Cd(1,3\text{-}PDTA)^{2-}$. In contrast to the $Cd(1,3\text{-}PDTA)^{2-}$ system, however, the line shape of the multiplet pattern of $Cd(EDTA)^{2-}$ is temperature invariant up to 100°.

Discussion

The multiplet patterns in Figures 1–3 for the acetate methylenic protons of $Cd(1,3\text{-}PDTA)^{2-}$ and $Zn(1,3\text{-}PDTA)^{2-}$ consist of single AB patterns indicating that, in each complex, all four methylenic groups are equivalent on the nmr time scale. If it is assumed that the coordination is octahedral and that all six dentates of 1,3-PDTA are coordinated, two acetate groups are in the plane formed by the metal and the two nitrogen atoms and two are out of the plane in the instantaneous structures of the complexes. If a given structure is long-lived on the nmr time scale, the environments experienced by the methylenic groups in the in-plane and out-of-plane sites must be equivalent to observe a single AB pattern. Nmr spectra of the nonlabile rhodium(III) complexes[31] and cobalt(III) complexes[2,9,10] of EDTA suggest it is unlikely that the environments in the in-plane and out-of-plane sites will be equivalent and rather that the single AB patterns for $Cd(1,3\text{-}PDTA)^{2-}$ and $Zn(1,3\text{-}PDTA)^{2-}$ result from rapid exchange of acetate dentates between the two sites. Exchange could be by a sequence of reactions involving dissociation of labile metal–oxygen bonds[2] or by a twist mechanism of the type proposed by Bailar.[11,32]

The AB patterns reveal that, for the given solution conditions, each nitrogen atom of $Cd(1,3\text{-}PDTA)^{2-}$ and $Zn(1,3\text{-}PDTA)^{2-}$ is permanently in one of its two possible invertomers on the nmr time scale. If the metal–oxygen bonding is labile, the environments experienced by the methylenic protons of a freely rotating acetate group when the nitrogen is metal bonded are an average of the environments in the conformations[2]



Rotation is around the nitrogen–methylenic carbon bond. Examination reveals that, regardless of the rates of interchange between these conformations, H_A and H_B do not necessarily experience equivalent environments because of the asymmetry of the nitrogen atom. The environments experienced by H_A and H_B are necessarily equivalent only when inversion of the nitrogen atom, which interchanges H_A and H_B, is rapid on the nmr time scale.

The stepwise reactions considered likely in the overall process leading to interchange of nonequivalent methylenic protons in complexes of EDTA and its homologs *via* inversion of a nitrogen atom are shown schematically in Figure 4. The ligand is shown as being hexadentate in at least some of the complex, but the conclusions from the following discussion are not dependent on this assumption. It is assumed, however, that a metal–nitrogen bond can dissociate making possible nitrogen atom inversion only after the metal bonds to the two acetate groups attached to that nitrogen atom have dissociated.

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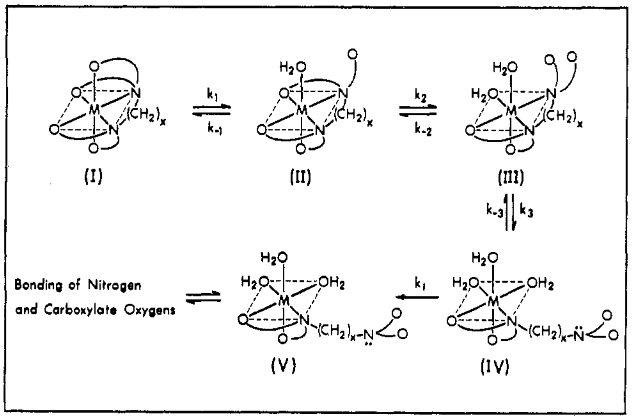

Figure 4.—Reactions that lead to the A to B interchange observed by the dynamic nmr method for the acetate methylenic protons in complexes of EDTA and its homologs.

The rate of AB interchange for a particular complex will depend on the fraction of the complex that exists in the various partially coordinated forms shown in Figure 4. The fraction of the complex in the partially coordinated forms is likely to be temperature dependent, which would give rise to nonlinear Arrhenius plots of the type obtained with the data in Tables I and II. The results in Tables I and II also indicate that the rate of AB interchange of Cd(1,3-PDTA)$^{2-}$ is different in H_2O and D_2O, suggesting that the fraction of the complex that exists in the various partially coordinated forms is different in these two solvents. This would be the case if the rate at which H_2O and D_2O dissociate from the metal complex is different. For example, K_1 $(=k_1/k_{-1})$ would be different in H_2O and D_2O if the rate of dissociation of H_2O from II is different from the rate of dissociation of D_2O.

The rate-determining step for AB interchange *via* the reaction sequence in Figure 4 is either nitrogen atom inversion or metal–nitrogen bond dissociation if K_1 $(=k_1/k_{-1})$ and K_2 $(=k_2/k_{-2})$ are rapid preequilibria on the nmr time scale. Qualitatively, if $k_{-3} \gg k_i$, the metal–nitrogen bond dissociates and re-forms many times on the average before the noncoordinated nitrogen atom inverts so that the rate-determining step is nitrogen inversion, whereas, if $k_i \gg k_{-3}$, once the metal–nitrogen bond has broken, the noncoordinated nitrogen atom inverts many times before the bond re-forms, and the rate-determining step is metal–nitrogen bond dissociation. In the latter case, there is statistically a 50% chance the nitrogen atom will be in an inverted state when it rebonds to the metal so that the observed rate of AB interchange will be half the rate of dissociation to IV.

Inversion rates of nitrogen atoms in multidentate ligands of the type studied here are not known; however, they have been estimated to be 10^8–10^9 sec^{-1} for nitrogen atoms in tertiary amines of the type described in the Introduction.[18-20] In the absence of more appropriate inversion rate constants, k_i for nitrogen atoms in multidentate ligands will be assumed to be of this magnitude in the following discussion.

The upper limit for the rate of formation of the metal–nitrogen bond, described by k_{-3}, is the rate of dissociation of the water molecule occupying the coordination site if the reaction occurs by the dissociative mechanism.[33] In terms of this mechanism, a water molecule is first released from a site *cis* to the site of coordination to the other nitrogen atom, and then the noncoordinated nitrogen atom bonds to the metal ion at the vacated coordination site. The rates of water release from totally aquated Cd(II) and Zn(II) are 4×10^8 and 5×10^7 sec^{-1}, respectively.[34] The rates of water release from these metal ions in IV are likely to be different from the rates for the totally aquated ions because of the effects of the ligand dentates in the inner coordination sphere.[35,36] Rates of water release from Cd(II) and Zn(II) in more appropriate model complexes are not available, however, so the rates for the aquated ions will be considered as the upper limits for k_{-3} in the following discussion.

For k_{-3} to equal the rate of water release, the rate at which the noncoordinated nitrogen atom in IV coordinates to an unoccupied coordination site has to be significantly larger than the rate at which water reoccupies the site; otherwise only solvent exchange occurs. This requires that the nitrogen atom be properly oriented for bonding at the time the metal–water bond breaks. Previous investigations of a number of fast complexation reactions of multidentate ligands suggest that the rate at which the nitrogen atom will coordinate to the unoccupied site will be less when the chelate ring formed is six membered than when it is five membered. For example, Kustin and coworkers observed that the rate constant for formation of the β-alanine complex of cobalt(II) is significantly less than that for formation of the α-alanine complex.[37] The difference was attributed to the difficulty in forming the six-membered chelate ring in the β-alanine complex. Similar differences were observed for the nickel(II) and cobalt(II) complexes of α- and β-aminobutyric acids.[38] These results suggest that, for Cd(1,3-PDTA)$^{2-}$ and Zn(1,3-PDTA)$^{2-}$, k_{-3} is somewhat less than the rates of water release from IV due to the formation of a six-membered chelate ring and, therefore, that $k_i \gg k_{-3}$ for these complexes. If so, the AB patterns for Cd(1,3-PDTA)$^{2-}$ and Zn(1,3-PDTA)$^{2-}$ are indicative of relatively inert metal–nitrogen bonding on the nmr time scale in these complexes, and the inverses of the lifetimes before AB interchange are half the first-order rate constants for partial dissociation of the complexes to form IV at the indicated temperatures.

The observation of the AB pattern for the acetate methylenic protons of Cd(EDTA)$^{2-}$ at the highest temperatures studied in this work indicates that the rate of AB interchange in Cd(EDTA)$^{2-}$ is significantly less than the rate in Cd(1,3-PDTA)$^{2-}$. This difference may be a result of more inert cadmium–nitrogen bonding in Cd(EDTA)$^{2-}$, as predicted by the observation that it is easier for a six-membered chelate ring to open than for a five-membered ring,[39,40] or it may indicate that $k_{-3} \gg k_i$ for Cd(EDTA)$^{2-}$. k_{-3} is predicted to be larger for Cd(EDTA)$^{2-}$ than for

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$Cd(1,3\text{-}PDTA)^{2-}$ because a five-membered chelate ring is formed in $Cd(EDTA)^{2-}$.

Conclusions

If the noncoordinated nitrogen atom of a partially dissociated complex of a multidentate ligand of the EDTA type inverts (IV → V in Figure 4) at least once before it rebonds to the metal (IV → III), an AB pattern for the acetate methylenic protons is indicative of inert metal–nitrogen bonding, as has been assumed.[2] If, however, the noncoordinated nitrogen atom rebonds to the metal before at least one inversion occurs, an AB pattern can result due to the slowness of the nitrogen atom inversion even when the metal–nitrogen bonding is labile. The rate at which the noncoordinated nitrogen atom rebonds to the metal depends, on the basis of previous studies of complexation reactions of multidentate ligands, in part at least on the size of the chelate ring formed. The previous studies suggest that, for the cadmium and zinc complexes of 1,3-PDTA, the rate of metal–nitrogen bond formation in IV is sufficiently less than the rate of noncoordinated nitrogen atom inversion so that the average lifetimes of the acetate methylenic protons before AB interchange are a measure of the rates of partial dissociation of these complexes.

Acknowledgments.—This research was supported in part by a grant from the National Research Council of Canada. In addition, financial support of B. J. F. by a National Research Council of Canada scholarship is gratefully acknowledged. The authors wish to thank Professor T. Schaefer and Mr. B. W. Goodwin of the University of Manitoba for the basic computer program used in simulating nmr spectra and Mr. K. Lewis for synthesizing the 1,3-PDTA used in this work.

CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF NEW SOUTH WALES, KENSINGTON, NEW SOUTH WALES, AUSTRALIA, THE DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY, UNIVERSITY OF WESTERN AUSTRALIA, NEDLANDS, WESTERN AUSTRALIA, AND THE DEPARTMENT OF CHEMISTRY, VICTORIA UNIVERSITY OF WELLINGTON, NEW ZEALAND

Temperature Dependence of the Proton Nuclear Magnetic Resonance Spectra of Some Diamagnetic *N,N*-Dialkyldithiocarbamate Complexes of Transition Metals

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Received July 23, 1971

Unusual structure and temperature dependent behavior of the proton nmr spectrum in a number of diamagnetic *N,N*-dialkyldithiocarbamate complexes of di- and trivalent transition metal ions, $[M(CS_2NR_2)_n]$, $n = 2, 3$ may be accounted for by a total line-shape analysis in terms of an appropriate and general two-proton exchange model using a density matrix formalism. This has been done in detail for a limited range of basic, well-defined, simple, and representative members of the above series, using the diethyl-, di-*n*-propyl-, diisopropyl-, diisobutyl-, and dibenzyldithiocarbamates of nickel(II) and cobalt(III). Where possible a tentative physical interpretation of the model is given.

Introduction

During studies of the temperature dependence of the proton nmr spectra of a variety of paramagnetic *N,N*-dialkyldithiocarbamate derivatives of trivalent transition metals, $[M(CS_2NR_2)_3]$,[2,3] the spectra of a range of diamagnetic analogs were determined to provide chemical shift references. In the latter, the protons near the nitrogen exhibit well-defined multiplets, some of which exhibit anomalies in structure and temperature dependence and worthy of independent study: the results are reported here, a range of di- and trivalent metals and alkyl substituents being selected which yield spectra which are well-defined, basic, and typical of the series in general. [A variety of work has recently appeared in the literature (1971) on a range of organic dialkyldithiocarbamate esters (Lemire and Thompson),[4,5] the thiuram disulfides (Wilson),[6] and a number of cobalt(III) dialkyldithiocarbamate derivatives (Siddall).[7] We refer to these in the Discussion.]

Experimental Section

Sodium salts of the *N,N*-dialkyldithiocarbamate anion, CS_2^--NR_2, are usually prepared by reacting the appropriate secondary amine with sodium hydroxide and carbon disulfide in stoichiometric amounts in ethanolic solution (the dithiocarbamate being usually formed in preference to the xanthate, CS_2^-OR)

$$Na^+OH^- + CS_2 + R_2NH \longrightarrow Na^+CS_2^-NR_2 + H_2O$$

The salt is formed as a powder or crystals and may be recrystallized from ether–ethanol; neutral coordination complexes may then be made by the addition of an aqueous solution of the sodium salt to an aqueous solution of the appropriate di- or trivalent metal ion. The filtered and dried complex may be recrystallized from chloroform–ethanol. Using this basic method, a wide range of simple dialkyldithiocarbamate derivatives was prepared for a number of transition metals, namely, (i) $[M(CS_2NR_2)_2]$ (M = Ni(II), Pd(II), Pt(II), Zn(II), Cd(II), and Hg(II)) and (ii) $[M(CS_2NR_2)_3]$ (M = Co(III), Rh(III), and Ir(III)). All of these complexes are diamagnetic and were made for the following ligand substituents: R = methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl (*i.e.*, CH_3–CH_2–CH_2R), isopropyl, *sec*-butyl (–CHR_2, –$CHRR'$), isobutyl (–CH_2–CHR_2), and benzyl (–CH_2–C_6H_5). The compounds are air stable, soluble and monomeric in chloroform solution, easily prepared, and well characterized

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