The effect of the metal–ligand bond covalency on the paramagnetic shielding has been quantified by introducing the circulation-removing ratio. This ratio for a series of ligands follows closely the electronegativities of the ligating atoms. The circulation-removing ratio has nearly constant value for a given chromophore, irrespective of the ligand field splitting magnitude. It may be added that it is surprising how independent the ratio is of the value of ligand field splitting, when both parameters reflect properties of the same metal–ligand bond.

As a measure of metal–ligand bond covalency in spin-paired d^6 transition-metal complexes, the circulation-removing ratio $\eta_{\sigma\pi}$ seems supplementary to the nephelauxetic ratio. However, the former ratio has some distinct advantages. Unlike the nephelauxetic ratio, $\eta_{\sigma\pi}$ may be related to the metal–ligand bond properties by a simple theoretical calculation, and it may be determined in complexes for which only the first spin-allowed d–d transition is discernible.

The results obtained suggest that central-ion NMR spectroscopy can be used as a powerful new means of examinning metal–ligand bond covalency in spin-paired d^6 transition-metal complexes.

Experimental Section

The ^{59}Co magnetogyric ratios of the examined complexes were determined with a Bruker SXP-100 pulse Fourier transform NMR spectrometer operating at 21.5 MHz. Absorption spectra were taken by a Varian Super Scan 3 spectrophotometer. All measurements were performed at room temperature (~25 °C).

For measurements we used aqueous solutions of the tris(1,4-butanediamine)cobalt(III) complex and of the hexakis(fulminato) complex, while tris(*o*-phenylenebis(dimethylarsine)cobalt(III), tris(dimethylglyoximato)cobalt(III), and tris(trithiocarbonato)cobalt(III) complexes were dissolved in Me_2SO. Tris(dithiophenylacetato)cobalt(III) was dissolved in chloroform. Concentrations of ~0.2 M for NMR spectra and ~10^{-2} M for spectrophotometric measurements were used.

All the complexes were synthesized by the reported procedures (for references see Table I).

Acknowledgment. The author is grateful to Professor M. B. Čelap for helpful discussion and to Professor D. Vučelić, who kindly provided access to the NMR spectrometer.

Registry No. $[Co(CNO)_6]^{3-}$, 45225-00-1; $[Co(diars)_3]^{3+}$, 47778-65-4; $[Co(NH_2(CH_2)_4NH_2)_3]^{3+}$, 83897-72-7; $Co(dmg)_3$, 14877-98-6; $Co(S_2CCH_2C_6H_5)_3$, 20963-66-0; $[Co(S_2CS)_3]^{3-}$, 51475-74-2; Co, 7440-48-4.

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Aluminum-27 Nuclear Magnetic Resonance Study of Aluminum(III) Interactions with Carboxylate Ligands

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Aluminum-27 NMR in high field has been employed in aqueous solution, at 10 mM concentration, for the study of the interactions of Al(III) with citrate, lactate, and ethylenediaminetetraacetate (EDTA). In the reaction with lactate, slow-exchange phenomena make possible the observation of distinct peaks for hydrated Al(III), 1:1 and 1:3 Al–lactate complexes, as well as mixed aquo–lactato and hydroxo–lactato complexes. Increasing pH leads to substitution of water in the Al(III) coordination sphere by lactate and eventually to substitution of lactate by hydroxide. A 1:3 Al(III)–lactate complex produced in the presence of excess lactate remains in a metastable condition and does not readily dissociate when more Al(III) is added. Increased pH has similar effects on the reaction of Al(III) with citrate, but the reaction with EDTA leads to only one peak that corresponds to a very stable complex; apparently no mixed aquo–EDTA or hydroxo–EDTA complexes can be observed.

Introduction

Our interest in the interactions of aluminum with various ligands in aqueous solution originates in the recent observations of increased aluminum concentrations in two human pathological conditions. Specific increased aluminum levels have been detected in Alzheimer's disease,[2-4] the prevalent form of senile dementia, and dialysis encephalopathy[5-7] resulting from renal dialysis. Furthermore, aluminum may play a key role in the toxic processes associated with acidification of the environment by pollutants.[8,9]

The present series of experiments was carried out to determine the suitability of ^{27}Al NMR as a probe for Al(III) complexation in dilute aqueous solution. Most of the previous studies employing ^{27}Al NMR have been performed in organic solvents at 0.1 M concentration or greater.[10-12] The hydrolysis of Al(III)[13-18] and chelation by a variety of ligands[19,20] has

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also been examined by Akitt et al. at Al(III) concentrations $\geq$0.2 M. Carboxyl ligands were selected because they are known to form soluble complexes with aluminum.[21] The high natural abundance (100%) and sensitivity (20% relative to protons) make the ^{27}Al nucleus favorable for these NMR studies.

Even in the absence of ligands other than water and OH^- a complex equilibrium exists among a variety of Al species.[22] We have demonstrated that aluminum forms a number of different complexes with DNA[23] and ATP[24] and that these vary with pH. In the experiments reported here, the simultaneous presence of different aluminum complexes in solution has been demonstrated by ^{27}Al NMR. We have studied equilibria in which carboxyl ligands and hydroxide participate in the binding to the Al(III) nucleus. Most interestingly, we have found that some of the Al complexes are not readily dissociated, once formed, and are therefore present as metastable products under nonequilibrium conditions. Thus different products are obtained under different mixing conditions.

Materials and Methods

Reagent grade sodium salts of citric and ethylenediaminetetraacetic (EDTA) acids (Fisher Chemical) were used without further purification. Sodium *dl*-lactate was purchased from ICN Pharmaceuticals as the 40% aqueous solution, and $AlCl_3 \cdot 6H_2O$ (99.9995%) was purchased from Gallard-Schlesinger.

Tris(lactato)aluminum(III) was prepared by mixing concentrated aluminum chloride and sodium lactate solutions in a small volume (2–3 mL) at pH 1. The pH was raised to 5, and approximately 50 volumes of methanol was added, precipitating NaCl. The methanol was removed by evaporation, and the aluminum lactate was recrystallized twice from methanol. Other Al(III) salts of lactate, citrate, and EDTA were prepared by mixing aluminum chloride and the corresponding sodium salt at pH ~1, unless otherwise noted. No precipitation was detected in any solution.

^{27}Al NMR spectra were obtained on a Varian XL-200 spectrometer at ambient temperature (~22 °C) using a tunable broad-band probe operating at 52.1 MHz. All samples were observed in 10-mm o.d. tubes with a concentric 4-mm o.d. tube containing D_2O for a lock. Spectra were obtained with a spectral window of 10 KHz, line broadening of 1 Hz, and 90° pulse width of 12 μs. Typically, 1000–2000 transients were collected with a 0.5-s repetition time. The relaxation time (T_1) for this quadrupolar nucleus was 0.1 s or less over a variety of conditions. All chemical shifts are reported with respect to $Al(H_2O)_6^{3+}$, and downfield chemical shifts are shown as positive. Peak integration of spectra was performed by an automatic spectrometer routine.

Factors That Affect the ^{27}Al NMR Parameters

To allow full interpretation and assignment of the complex ^{27}Al spectra, we must consider various contributions to the NMR signal parameters. The chemical shift and line widths of quadrupolar nuclei are primarily dependent on four factors: ligand type, coordination number, ligand field symmetry, and the rate of chemical exchange among the various species in equilibrium.

(1) Ligand. A wide range of chemical shifts has been observed in aqueous solution for aluminum complexes with a variety of ligands. Anions such as phosphate and sulfate produce upfield shifts in the ^{27}Al spectra (−3 to −20 ppm).[19,20]

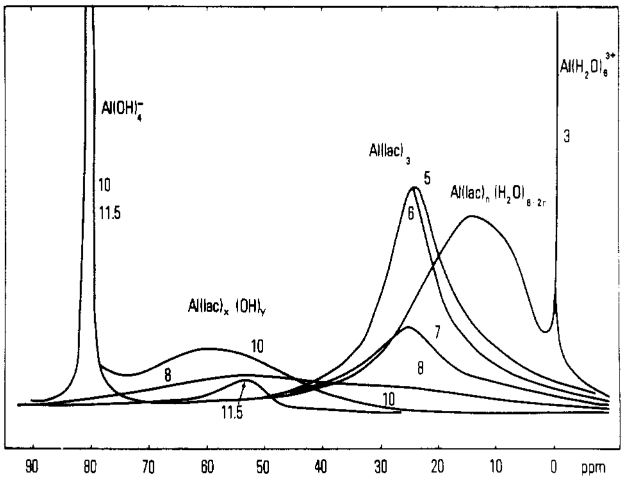

Figure 1. ^{27}Al NMR spectra for a 10 mM aluminum tris(lactate) solution adjusted from pH 3.0 to 11.5. The pH values are indicated; see text for discussion of assignments.

The chemical shift of Al(III) fluoride complexes ranges from 2 to 15 ppm,[20] and hydroxide complexes also lie downfield;[25] for example, the dimer $Al_2(OH)_2^{4+}$ is found at 3 ppm, $Al_{13}(OH)_{24}O_4^{7+}$ at 62.5 ppm, and $Al(OH)_4^-$ at 80 ppm.[10,26] Aluminum chemical shifts for chelates with hydroxy carboxylic acids have been observed between 0 and 6 ppm at acidic pH.[27]

(2) Coordination Geometry. Aluminum exists in two coordination geometries: octahedral and tetrahedral. Octahedral species such as $Al(H_2O)_6^{3+}$ and $[AlMo_6O_{21}]^{3-}$ may be observed at chemical shifts near 0 ppm, whereas tetrahedral complexes are observed further downfield (e.g., $Al(OH)_4^-$ at 80 ppm and $[AlW_{12}O_{40}]^{5-}$ at 72 ppm).[28] However, there is considerable overlap in the chemical shift ranges of octahedral and tetrahedral complexes, and therefore care must be taken in applying chemical shift data to determine the geometry of a complex. In nonaqueous solvents, the chemical shift range of octahedral complexes covers nearly 70 ppm (from −46 to +20 ppm) while that of tetrahedral complexes extends from −28 to +221 ppm.[11] In general, therefore, tetrahedral complexes are in the more downfield portion of the chemical shift range but much overlapping exists.

(3) Symmetry. The aluminum nucleus, with spin $+^5/_2$, possesses a quadrupolar moment ($Q = 0.149 \times 10^{-24}$ cm^2), which interacts with surrounding electric field gradients. The ^{27}Al line width in the NMR spectrum reflects the degree of symmetry and arrangement of ligands around the Al(III) nucleus, i.e., the more symmetric the complex, the smaller the resulting line width. The sensitivity of aluminum spectra to ligand field alterations has been employed to examine variations in symmetry for aluminum-substituted ferrichromes.[29]

In addition, ^{27}Al NMR has been able to differentiate stereoisomers of hexacoordinated complexes.[30]

(4) Exchange Rates. The variation in line width for this quadrupolar nucleus as a function of chemical exchange rate is a phenomenon common to all NMR nuclei. In the experiments reported here and in others carried out in our laboratory, it appears that some aluminum complexes in aqueous solution are in slow exchange relative to their chemical shift difference. This conclusion is based on the appearance of multiple peaks corresponding to a variety of complexes in the ^{27}Al NMR spectra.

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In summary, the sensitivity of the ^{27}Al NMR chemical shift to ligand type and coordination geometry and the dependence of the line width on the symmetry of the complex provide an effective tool in the elucidation of the structures of aluminum complexes. Under conditions of extreme asymmetry and/or very high exchange rate, however, resonances may be so broad as to be undetectable.

Results and Discussion

Aluminum Lactate. Lactate was selected as the primary ligand for this investigation for the following reasons: (1) Its reaction with Al is of longstanding interest, since it is often used to solubilize Al(III). (2) Coordination of lactate is simple; one hydroxyl and one carboxyl group are the only donors, producing a bidentate ligand that generates a six-membered chelate ring. The ^{27}Al NMR spectra of tris(lactato)aluminum(III) in the pH range 3–11.5 are shown in Figure 1. It can be seen that increasing pH leads to downfield shifts in the NMR resonances.

At pH 3 the spectrum consists of two resonances: a sharp line ($\Delta\nu \approx 5$ Hz) at 0 ppm, which corresponds to $Al(H_2O)_6{}^{3+}$, and a broad line ($\Delta\nu \approx 1200$ Hz) centered at 14 ppm, which corresponds to aluminum lactate complexes. At pH <3, the hydrated aluminum line increases in intensity and the broad peak decreases in a reciprocal fashion (not shown). Thus under these experimental conditions, slow exchange between hydrated and lactate-bound aluminum with respect to the ^{27}Al chemical shift time scale is indicated. At pH 3, intensity analysis reveals that ~96% of the aluminum is bound to lactate.

As the pH is raised from 3 to 5, a downfield-shifted line emerges at 24 ppm that gradually sharpens with increasing pH. Careful examination of the spectrum reveals that the 14-ppm peak, observed at pH 3, remains as a shoulder on the 24-ppm peak that appears at pH 5. At pH >6.5, the resonance at 24 ppm ($\Delta\nu \approx 500$ Hz) decreases in intensity while the chemical shift does not change. At pH 8, it is masked by an emerging broad line centered at ~53 ppm. As the pH is increased further, up to pH 10, the spectrum consists of a broad peak at 60 ppm and a sharper line ($\Delta\nu \approx 120$ Hz) at 80 ppm; the latter corresponds to the chemical shift[10] observed for the aluminate anion $Al(OH)_4{}^-$. At pH 11.5, the aluminate resonance is accompanied by an asymmetrical resonance at 53 ppm. Thus the NMR spectrum of tris(lactato)aluminum(III) is profoundly affected by variations in pH.

The changes observed in the ^{27}Al spectra are explained by the gradual displacement of H_2O by lactate, and of the latter by OH^-, with increasing pH. Two events accompany an increase in pH: deprotonation of the lactate ligand and an increase in the competition between lactate and OH^- for Al(III). The chemical shift and broad line width of the 14-ppm peak at pH 3 leads us to conclude that the aluminum complex is probably octahedrally coordinated but the symmetry is distorted relative to that of $Al(H_2O)_6{}^{3+}$. At this low pH, the contribution from hydroxide binding is probably not significant. Thus the two separate peaks in the spectrum indicate that hydrated aluminum is in slow exchange with an aluminum species in which lactate has displaced waters of hydration. The skew of the peak suggests the presence in slow equilibrium of more than one lactate-containing species. The upper limit for the exchange rates has been calculated to be from 2000 to 5000 s^{-1}. (The water-exchange rate for $Al(H_2O)_6{}^{3+}$, as determined by ^{17}O NMR, is ~6 s).[31] We interpret the peak centered at 14 ppm as resulting from the overlap of two peaks at ~9 and 15 ppm from $[Al(lac)(H_2O)_4]^{2+}$ and $[Al(lac)_2(H_2O)_2]^+$, respectively. Probably there is also a contribution from the emerging $Al(lac)_3$ line at 24 ppm. Line broadening may be due to distortion of ligand field symmetry through the displacement of two water molecules by chelating hydroxyl and carboxyl groups of lactate ions. There might be some broadening contributions also from intermediate exchange among the three complexes $[Al(lac)_n(H_2O)_{6-2n}]^{3-n}$ (n = 1–3).

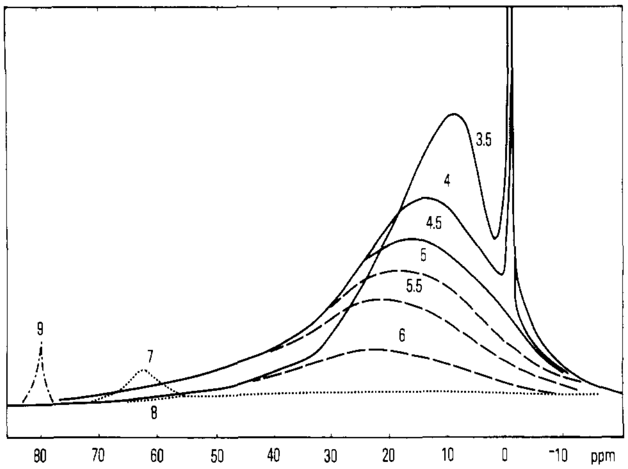

Figure 2. ^{27}Al NMR spectra for a 10 mM equimolar mixture of $AlCl_3$ and sodium lactate mixed at pH 2 and adjusted between pH 3.5 and 9. The pH values are indicated.

The peak at ~24 ppm observed at pH 5–7 (Figure 1) is sharper than any other complex peaks and remains stable over a considerable pH range; we assign it to tris(lactato)aluminum(III), which has lactate carboxyls and hydroxyls occupying the six positions in the coordination sphere.[32] At pH 7, the intensity of the tris(lactato)aluminum(III) peak decreases, and the peak becomes skewed, with higher intensity in the downfield region. It appears that much of the $[Al(lac)_3]$ complex has been partly hydroxylated. At pH 8 the spectrum is very broad and unresolved and may contain a residual peak of the tris(lactato) complex but presumably is mainly due to mixed hydroxo–lactato complexes. The breadth of the 60-ppm peak observed at pH 10 is probably due to the distorted symmetry of the mixed lactate–hydroxide complexes and also perhaps some exchange broadening. At this pH, somewhat more than half of the aluminum exists as aluminate; the tetrahedral symmetry produced by four hydroxide molecules results in a sharper line at 80 ppm in slow exchange with aluminum still coordinated to lactate.

By pH 11.5, most of the aluminum has been converted to $Al(OH)_4{}^-$, but about 8% of it is reflected by a peak at ~52 ppm. Presumably this peak represents the signal from the mixed lactate–hydroxide species, which is the last to convert to aluminate with an increase in pH.

In summary, the complex spectra illustrated in Figure 1 can be interpreted in terms of a series of equilibria in which waters of hydration of aluminum are successively displaced by first lactate and then hydroxide with increasing pH. The types of equilibria that may occur are illustrated in eq 1–6, which are partly speculative.

$$Al(H_2O)_6{}^{3+} + lac^- \rightleftarrows [Al(lac)(H_2O)_4]^{2+} + 2H_2O \quad (1)$$

$$[Al(lac)(H_2O)_4]^{2+} + lac^- \rightleftarrows [Al(lac)_2(H_2O)_2]^+ + 2H_2O \quad (2)$$

$$[Al(lac)_2(H_2O)_2]^+ + lac^- \rightleftarrows [Al(lac)_3] + 2H_2O \quad (3)$$

$$[Al(lac)_3] + 2OH^- \rightleftarrows [Al(lac)_2(OH)_2]^- + lac^- \quad (4)$$

$$[Al(lac)_2(OH)_2]^- + OH^- \rightleftarrows [Al(lac)(OH)_3]^- + lac^- \quad (5)$$

$$[Al(lac)(OH)_3]^- + OH^- \rightleftarrows Al(OH)_4{}^- + lac^- \quad (6)$$

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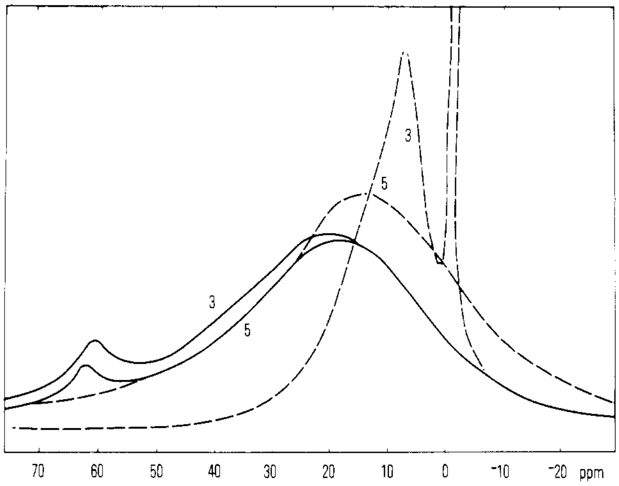

Figure 3. ^{27}Al NMR spectra for a 10 mM equimolar mixture of sodium lactate (pH 7) and $AlCl_3$ (pH 3) mixed in two different ways. The dashed lines result from the mixing of sodium lactate into aluminum chloride (temporary aluminum excess). The solid lines result from the mixing of aluminum into sodium lactate (temporary lactate excess).

Aluminum Lactate, 1:1. Figure 2 illustrates spectra for an equimolar mixture of aluminum chloride and sodium lactate mixed at pH 2 and adjusted so that solutions from pH 3.5 to 9 were obtained. The same spectra result when lactate is added to aluminum (temporary aluminum excess) or aluminum to lactate (temporary lactate excess). At pH 3.5, the ^{27}Al NMR spectrum consists of the $Al(H_2O)_6{}^{3+}$ peak at 0 ppm, another peak at ~9 ppm, and others on the downfield shoulder of the latter. Slow exchange appears to exist. The 9-ppm peak is presumably the 1:1 aluminum lactate complex with waters of hydration occupying the other four coordination sites; this peak was observed in the 3:1 mixture at pH 3 (Figure 1). The signal on the downfield shoulder of this peak gradually increases as the pH rises. The peak at 8 ppm decreases concomitantly. These changes for a 1:1 mixture as the pH is increased from 4 to 6 probably arise from substitution of hydroxide for water in the aluminum coordination sphere. The fact that this phenomenon occurs at lower pH than in the 3:1 lactate–Al system suggests that the hydration sphere of an equimolar complex is more easily displaced by hydroxides than the lactate ligands from $Al(lac)_3$ and $[Al(lac)_2(H_2O)_2]^+$. The peak at ~22 ppm is probably due to a partly hydroxylated lactate complex, $[Al(lac)(OH)_n(H_2O)_{4-n}]$.

At pH 7, a small peak is observed at ~62 ppm (the chemical shift[14] for $[Al_{13}(OH)_{24}O_4]^{7+}$), and the spectrum is featureless at pH 8. Finally, at pH 9 the formation of aluminate is indicated by a small resonance at 80 ppm. In the 3:1 system this conversion to completely hydroxylated aluminum does not appear until pH 10.

The spectra of Figure 2 result from the preparation of aluminum–lactate mixtures at acid pH. When the solutions are not acidic during mixing, the order of mixing becomes important.

The spectra of Figure 3 result from mixing equimolar amounts of aluminum chloride at pH 3 and sodium lactate at pH 7. At these initial pHs, aluminum is fully hydrated and the sodium lactate is fully ionized (p*K* = 3.08). Spectra obtained from the addition of the lactate solution to the aluminum, when there is temporary aluminum excess, are shown in broken lines. The pH of this Al solution rises to 5 when the lactate is added; this spectrum is identical with that observed for an equimolar complex that had been mixed at pH 2 and then adjusted to pH 5 (Figure 2). When the pH of this solution is readjusted to 3, the hexaaquoaluminum line emerges, which indicates partial dissociation of aluminum from lactate (Figure 3). The spectra for aluminum chloride (pH 3) added to sodium lactate (pH 7), i.e., with a temporary excess of lactate, are illustrated by the solid lines in Figure 3. The NMR spectrum at pH 5 contains two components, a broad line at ~21 ppm and a sharper small resonance at 62 ppm. The 21-ppm peak is far removed from the 9-ppm peak characteristic of the 1:1 complex and close to the 24-ppm peak observed in Figure 1 for the 1:3 complex. Evidently the addition of Al to excess lactate during the initial mixing produces predominantly the 3:1 complex, and this complex does not dissociate on further addition of aluminum. The aluminum added last, rather than removing lactate from $Al(lac)_3$, instead associates into the isopolyanion $[Al_{13}(OH)_{24}O_4]^{7+}$.[33] Decreasing the pH to 3 alters this spectrum only very slightly.

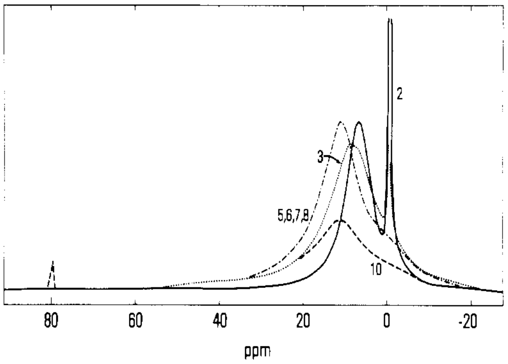

Figure 4. ^{27}Al NMR spectra for a 10 mM equimolar mixture of aluminum chloride and sodium citrate adjusted from pH 2 to 10. The pH values are indicated.

Since different products are obtained when the order of mixing is varied during the formation of the Al–lactate complexes, and since these complexes are stable for months, the formation of metastable products, which tend toward equilibrium so slowly that the rates cannot be measured, seems to characterize these species.

Aluminum Citrate. Citrate has hydroxyl and carboxyl donors and therefore has characteristics similar to those of lactate, as is borne out by NMR experiments. An equimolar mixture of aluminum chloride and sodium citrate was prepared at pH 2 and the pH increased to 10 (Figure 4). The ^{27}Al NMR spectrum at pH 2 consists of two peaks, a sharp line at 0 ppm and a broader peak ($\Delta\nu \approx 750$ Hz) at 8 ppm. Therefore, at pH 2, aluminum is in slow exchange between the hydrated and ligand-bound forms, as observed earlier wtih lactate, and ~70% of the aluminum is bound to citrate. The upper limit for the observed exchange rate is ~3000 s^{-1}, similar to that for the lactate. At pH 3, the broad peak is shifted to 10 ppm and the hydrated aluminum peak decreases to <10% of the total area. From pH 5 to 8 the ^{27}Al spectrum of the aluminum–citrate mixture remains constant and appears to consist of two components: a large peak at 12 ppm with a shoulder on the upfield side at 0 ppm. At pH 10, the intensity of these two components decreases without the appearance of any other signals in the spectrum, and a small amount of aluminate is observed.

Thus, in a general way, the NMR spectrum of the Al(III)–citrate system is affected by pH in the same manner as the Al(III)–lactate system. Increasing pH leads to progressive shifts downfield and eventually to broadening. The explanation is also the same; water molecules are first displaced by citrate, then mixed hydroxo–citrato complexes are formed, and finally all the citrate ligands are displaced. The gradual shifts in the spectra between pH 2 and 8 may result from fast exchange

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(33) Although this peak is quite small, it stands only for the central tetrahedrally coordinated aluminum.[25]

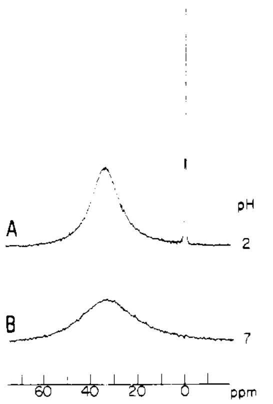

Figure 5. ^{27}Al NMR spectra for a 10 mM equimolar mixture of aluminum chloride and EDTA adjusted to pH 2 (A) and 7 (B).

among species containing different numbers of citrate and water molecules.

Because of the greater complexity of the citrate ligand, ^{27}Al NMR cannot define the structural characteristics of its Al complexes as well as those of the lactate complexes: citrate has three carboxyl groups and one hydroxyl group; numerous coordination possibilities can be generated from this combination. The most likely structure for the most stable complex, i.e., the one corresponding to the peak at 12 ppm, which remains constant between pH 5 and 8, has Al bound to citrate via two carboxyls and one hydroxyl, producing two six-membered rings. Evidence for such a structure has been obtained potentiometrically.[34,35]

Aluminum Complex of EDTA. EDTA contains six electron donor groups—four carboxyls and two nitrogens—that can completely saturate the coordination sphere of an octahedral metal and produce remarkably stable complexes.[21,36,37] As a consequence of the great stability of the complex of Al(III) bound to all six of the coordination positions, the ^{27}Al NMR spectrum exhibits only one bound peak, at ~32 ppm, corresponding to an Al(III)–EDTA complex (Figure 5). This complex is presumably the one in which the electron donor atoms of the ligand are bound to the Al.

At pH 2 the spectrum consists of two peaks corresponding to hydrated and EDTA-bound aluminum in slow exchange (upper limit ~10^4 s^{-1}). As the pH is increased to 4, the former disappears. The Al(III)–EDTA peak remains at the same position throughout the observed pH range but is broadened from 850 Hz at pH 2 to 1400 Hz at pH 7, and at pH 10 the peak is no longer detectable. Thus, EDTA coordination results in the apparently simultaneous displacement of water molecules from $[Al(H_2O)_6]^{3+}$; displacement of EDTA by OH^- at high pH presumably occurs in the same way. Thus no peaks with positions intermediate to those of $[Al(H_2O)_6]^{3+}$ and Al(III)–EDTA can be detected, because no intermediate complexes exist. Therefore the pH profile of the Al(III)–EDTA system is more monotonous than the pH variation of the NMR spectra of the lactate and citrate complexes. The broadening of the complex peak at pH 7 in Figure 5B may perhaps be attributed to changes in the outer coordination sphere.

Conclusions

We have demonstrated the ability of ^{27}Al NMR to identify complexes generated by three chelating ligands in aqueous solution at 10 mM aluminum concentration. pH-stable complexes have been observed in a unique chemical shift position for each ligand. It has been possible to directly observe substitution equilibria in which chelating ligands displace waters of hydration and hydroxides displace the ligands, as a function of increasing solution pH. Metastable reaction products have been observed under altered mixing conditions. These results demonstrate the utility of ^{27}Al NMR in the examination of Al complexes, including those involving biological ligands. ^{27}Al NMR clearly provides a significant tool in the identification and interaction of aluminum complexes in aqueous solution.

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Study by Oxygen-17 Nuclear Magnetic Resonance and Other Methods of the Nickel(II) 1,4,8,11-Tetraazaundecane and 1,4,8,11-Tetraazacyclotetradecane Complexes in Aqueous Solution

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Oxygen-17 NMR, spectrophotometric, and magnetic susceptibility measurements have been made on the Ni(II)–2,3,2-tet (1,4,8,11-tetraazaundecane) and Ni(II)–cyclam (1,4,8,11-tetraazacyclotetradecane) systems. The high-spin–low-spin equilibria were studied. The high-spin forms contain 2 H_2O/Ni. Water-exchange rate parameters for the high-spin forms are as follows: for Ni(II)–2,3,2 tet k_1(25 °C) = 4 × 10^6 s^{-1}, $\Delta H^* = 9.7$ kcal mol^{-1}, and $\Delta S^* = 4$ cal mol^{-1} K^{-1}; for Ni(II)–cyclam k_1(25 °C) = 2 × 10^7 s^{-1}, $\Delta H^* = 9$ kcal mol^{-1}, and $\Delta S^* = 7$ cal mol^{-1} K^{-1}.

Introduction

We have previously reported[1] on the tetraaza system (1,4,7,10-tetraazacyclododecane)nickel(II) (Ni^{II}(cyclen)), where a "high-spin–low-spin" equilibrium exists. This report[2] adds two more examples in which kinetic and equilibrium data are obtained. Water-exchange kinetic data were obtained on the high-spin forms, some independent information on slow cis–trans conversion was obtained, and the positions of the

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