presume $pK_a \geq 5$ for eq 7, k_7 is anticipated to be smaller than 1 s^{-1}. The intercept value of $k_i' = 39\ s^{-1}$ now reflects at least in part the sum $k_{-8} + k_9 + k_{11}$. This sets an upper limit to $k_9 + k_{11}$; that is, k_i' is anticipated to be greater than k_i, which is in keeping with the experimental results. In basic resolutions (pH >9), the sequence of events follows that given for the first mechanistic scheme (eq 10-12).

While a clear choice between the two schemes does not appear to be feasible at this time, we favor, for the following reasons, the second one, where the pK_a values for $*Cr(bpy)_3(H_2O)^{3+}$ and for $Cr(bpy)_3(H_2O)^{3+}$ are taken to be less than 2 and above 5, respectively. The pK_a assignment for $Cr(bpy)_3(H_2O)^{3+}$ is consistent with the recent estimate by Sriram and co-workers[11] that it is of the order of 5-6. In the context of the second mechanistic scheme (unlike the first scheme), our kinetic results are not directly applicable to the issue of the position of the inflection point observed in the plot of the steady-state quantum yields for the formation of free bipyridine vs. pH. Thus, the apparent discrepancy between the observed value near pH 8 and our higher estimate for the inflection point, made under the first scheme, is eliminated.

A final point concerns the quantum yield for release of proton where two different approaches to measuring this yield in acid both gave results that suggested the amount to be somewhat less than that in basic media. A plausible explanation for this within the second scheme is that the rate of deexcitation of $*Cr(bpy)_3(H_2O)^{3+}$ (eq 5) may be only marginally slower than that for its acidic dissociation reaction (eq 6). Owing to the slowness of release of proton from the ground-state form $Cr(bpy)_3(H_2O)^{3+}$, less amount of proton will then be generated in acidic solution relative to that in alkaline solution. In the latter case, where the ground-state dissociation reaction pertains to eq 8, the amount of $Cr(bpy)_3(OH)^{2+}$ formed will be larger and can now provide a full measure of the nascent amount of $*Cr(bpy)_3(H_2O)^{3+}$ produced. Parenthetically, if the estimate[11] for the ground-state pK_a value being in the range 5-6 is adopted along with an upper limit for k_{-8} of 39 s^{-1} ($=k_i'$), then the value for k_8 is anticipated to be in the neighborhood of $10^{10}\ M^{-1}\ s^{-1}$. This level will meet the requirements under our conditions that the rate of the reaction between $Cr(bpy)_3(H_2O)^{3+}$ and OH^- (eq 8) be at least comparable to that for the decay of the ^2E state. The second scheme offers a consistent framework in which to interpret our and others' results and at the same time points to new areas of investigation on closely related systems.

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Nuclear Magnetic Resonance Study of Ethylenediaminetetrakis(methylenephosphonic acid) and Some Metal Complexes

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The ^1H NMR spectra of ethylenediaminetetrakis(methylenephosphonic acid) and of some metal complexes were interpreted to indicate that the nitrogens are preferentially protonated in the free ligand whereas the phosphonate groups are protonated in the metal complexes. A single ABX pattern for lanthanide-ENTMP complexes is consistent with a time-averaged symmetry for the ligand about the metal involving long-lived Ln-N and short-lived Ln-O bonds. The ^{31}P NMR pattern also supports such averaged equivalence of all phosphonate groups. The CaENTMP complex has short-lived Ca-N and Ca-O bonds.

Introduction

Amino phosphonic acid ligands are of interest in biological systems and as chelating agents for metal ions. Protonation and metal ion complexation of some of these ligands have been reported by Martell et al.[2,3] using potentiometric titration and by Marov et al.[4,5] using ^1H NMR spectroscopy. These studies confirmed the existence of 1:1 metal-to-ligand complexes that became protonated at pH values below 8-10 depending on the cation. The resolution of the ^1H NMR spectra was insufficient to allow more extensive interpretation about the nature of the metal-donor atom bonding etc.

Proton resonance studies of the diamagnetic metal complexes of amino carboxylate ligands in aqueous solutions have provided information on the metal-ligand bond labilities and on structural features of the complexes.[6-9] In this paper we report the results of similar high-resolution NMR (^1H and ^{31}P) studies of ethylenediaminetetrakis(methylenephosphonic acid) and some of its metal complexes.

Experimental Section

Synthesis of ENTMP. Ethylenediaminetetrakis(methylenephosphonic acid), ENTMP, was prepared by a slight modification of the procedure reported by Krueger et al.[10] A 2.25-mol sample of phosphorous acid, 0.50 mol of H_4EDTA, and 400 mL of acetic anhydride were mixed together and heated to 130-140 °C for 1 h with vigorous stirring. The resulting lumpy mass was cooled, filtered, and rinsed with the minimum amount of water. The phosphonate ligand was dissolved in 4 equiv of sodium hydroxide solution and the

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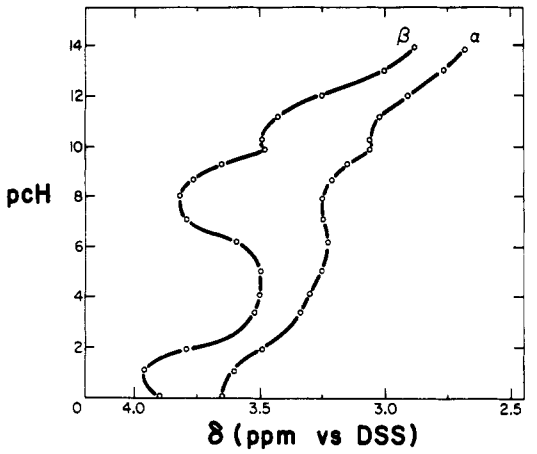

Figure 1. Variation of the chemical shift of the α and β protons with pH.

pH adjusted to approximately 5. Addition of the stoichiometric amount of lead acetate precipitated the tetralead salt, which was filtred and washed thoroughly with boiling, distilled water. The protonated ligand was obtained by treatment of an aqueous suspension of the lead salt with hydrogen sulfide followed by filtration of the PbS. The filtrate was concentrated and freeze-dried under reduced pressure. The potentiometric titration and the ^{1}H NMR spectrum of this purified product agreed exactly with similar data obtained from a sample supplied by Monsanto Chemical Corp.

Potentiometric Measurements. A Radiometer PHM 84 digital pH meter fitted with a combined glass–calomel electrode was used for the potentiometric titrations. A suitable aliquot of ENTMP acidified with perchloric acid was titrated against a standard solution of CO_2-free potassium hydroxide. The procedure was essentially that reported by Motekaitis et al.[3] except for the use of NaCl in place of KNO_3 as the supporting electrolyte to achieve an ionic strength of 3.00 M.

^{1}H NMR Measurements. A stock solution of 0.10 M Na_4D_4ENTMP in D_2O was prepared by dissolving a sample of the acid in a solution of D_2O with 4 equiv of NaOD followed by several cycles of evaporation to dryness and dilution with D_2O. The pD of the working solutions was obtained by adjustment with either NaOD or D_2SO_4. The final ionic strength was maintained at 1.0 M with use of sodium perchlorate.

Calcium, yttrium, lanthanum, and lutetium solutions were prepared by dissolving the respective oxides in concentrated perchloric acid. Solutions for NMR studies were prepared and analyzed as described previously.[9]

The proton magnetic resonance spectra were recorded with the Florida State University Bruker 270 MHz spectrometer using the pulsed Fourier transform mode with a deuterium lock. All measurements were obtained at 0 °C, ambient temperature (ca. 27 °C), and 85 °C with DSS (sodium 4,4-dimethyl-4-silapentanesulfonate) as internal standard.

^{31}P NMR Measurements. The ^{31}P NMR measurements were carried out with the SEMINOLE high-resolution spectrometer of the FSU NMR laboratory at a working frequency of 60.708 MHz. LuENTMP samples were investigated as aqueous solutions under the same experimental conditions as described previously. The chemical shifts were measured relative to phosphoric acid (85%) as an external reference.

Results

The calculation of acid constants from the potentiometric titrations gave values in close agreement with pK_{a2} through pK_{a5} of ref 7. Consequently, the pK_a values of ref 7 were used in all subsequent calculations for the concentrations of H_nENTMP species in our solutions.

The ^{1}H NMR spectra of the solutions of $H_nENTMP^{(8-n)-}$ had a singlet peak and a doublet of 1:2 total relative intensities throughout the pH range of 0–14. The upfield doublet is assigned to the eight equivalent methylenic (α) protons of the $-CH_2PO_2^{2-}$ groups. This doublet shows that these protons are equivalent and exhibit ^{1}H–^{31}P splitting. The singlet peak is assigned to the four protons of the ethylenic group (β protons). The variation of the shifts of the α and β protons as a function of the hydrogen ion concentration, pcH, agrees fairly well with that reported by Marov[5] and is presented in Figure 1. These data were used to calculate the percent protonation of the nitrogen and oxygen sites by the method of Sudmeier and Reilley.[11] In this analysis, the chemical shifts of the α and β protons are expressed in terms of the intrinsic shifts, δ°_α and δ°_β (i.e. that for $ENTMP^{8-}$), f_N and f_P (the fraction of protonation at a certain pH of the nitrogen and of the phosphonate sites), and C_P, C_N, and C'_N (the change in chemical shift due to phosphonate protonation, the change due to protonation of the N adjacent to the CH_2 group, and the change for β protons due to protonation of the nonadjacent N). The equations are

$$\delta_\alpha = \delta_\alpha + f_N C_N + f_P C_P \qquad \delta_\beta = \delta_\beta + f_N(C_N + C'_N)$$

$$\bar{n}_H = 2f_N + 8f_P$$

$\bar{n}_H$ was calculated as a function of pH from the pK_a values of ref 7. It was assumed that the first proton is associated exclusively with a nitrogen site since this is observed for $EDTA^{4-}$ (cf. ref 11) and is consistent with the pK_1 values of both $EDTA^{4-}$ and $ENTMP^{8-}$. It was found that $C_N = 0.66$ and $C'_N = 0.39$ (compared to 0.75 and 0.35 for EDTA), while C_P was a function of f_P. The results of the calculations are presented in Table I.

Table I. Estimate of Fractional Protonation at Various Basic Sites

$\bar{n}_H$	−log [H$^+$]	δ_α	f_P	δ_β	f_N	Σf_N
0	≃14.0	2.67		2.91		
1	10.51	3.04		3.48	0.54	1.09
2	8.22	3.24	0.04	3.80	0.85	1.70
3	6.65	3.22	0.19	3.70	0.75	1.50
4	5.32	3.24	0.36	3.50	0.56	1.12
5	3.79	3.32	0.48	3.51	0.57	1.14
6	2.03	3.48	0.56	3.71	0.76	1.52

Table II. Chemical Shift Values[a] (ppm) for Metal-ENTMP Solutions (pH 10.5–11.0)

metal	protons	0 °C	27 °C	85 °C
Na^{+} [b]	α		2.67	
	β		2.91	
Ca^{2+}	α	2.82[c]	2.84	2.83
	β	2.82[c]	2.86	2.86
Y^{3+}	α	broad	3.02	3.00
	β[d]	broad	3.13	3.06
La^{3+}	α	2.93[c]	2.97 ± 0.05[c]	2.95 ± 0.05[c]
	β[d]	2.93[c]	3.04	3.00
Lu^{3+}	α	3.02	3.04	3.03
	β[d]	3.13	3.10	3.07

[a] Relative to DSS. [b] These are the limiting shifts for ENTMP at pH ≃14. [c] Approximate maximum of broad peaks. [d] Baricenter of doublet (Na, Ca) or ABX quartet (Y, La, Lu).

The chemical shift of the α and β protons in a solution of pH 9.90 was measured at 0, 27, and 85 °C. At 27 °C this corresponds to a mixture of approximately equal concentrations of $HENTMP^{7-}$ and H_2ENTMP^{6-}. Both type of protons had upfield shifts with the α shifts changing from 3.11 (0 °C) to 3.04 ppm (85 °C) and the β shifts from 3.51 (0 °C) to 3.48 ppm (85 °C). The phosphorus–α-proton coupling constant, $^2J_{HCP}$, has values of 8.1 (0 °C), 10.8 (27 °C), and 11.7 Hz (85 °C).

Table II lists the observed chemical shifts for the metal ion–ENTMP solutions at pH 10.5–11.0 (except for Na^+ for which the shifts are those obtained by extrapolation of the curves in Figure 4 to $\bar{n}_H = 0$).

In the spectrum of the CaENTMP complex (pH 10.5), a β singlet and an α doublet are observed as in the Na^+–

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Table III. Observed and Calculated Spectra for LuENTMP and Y(ENTMP) (pH 10.5; 85 °C)

		LuENTMP				Y(ENTMP)			
		energy, Hz		rel intens		energy, Hz		rel intens	
transition	origin	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd
1	B	0.1	0	0.78	1.00	0	0	0.80	1.00
2	B	13.7	13.5	0.78 } 2.70		13.3	13.5	0.80 } 2.50	
3	B	14.5	15.8	1.22 }		15.3	16.2	1.20 }	
4	B	28.1	27.0	1.22	1.50	28.6	24.3	1.20	1.50
5	A	65.9	67.1	1.22	1.50	75.8	77.0	1.20 }	
6	A	79.5	78.3	1.22 } 2.60		89.1	89.1	1.20 } 3.70	
7	A	80.3	80.1	0.78 }		91.1	92.2	0.80	
8	A	93.9	93.6	0.78	1.00	104.4	101.1	0.80	1.04

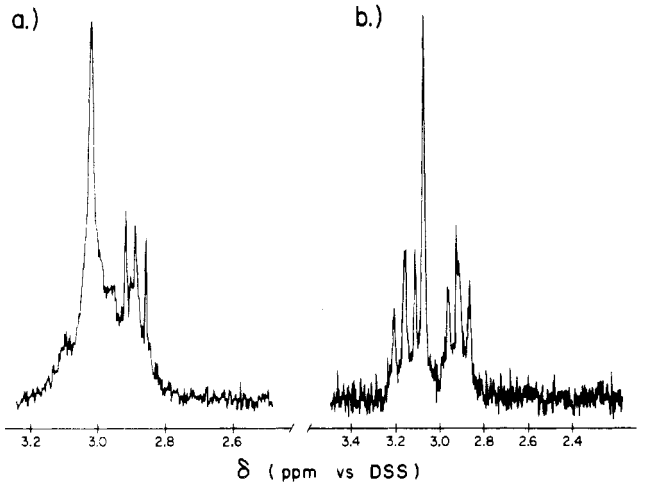

Figure 2. ^{1}H NMR spectra of (a) LaENTMP and (b) LuENTMP at 85 °C and pH 10.5.

ENTMP^{8-} system. However, for CaENTMP both the α and β resonances are shifted, and one of the peaks of the doublet merges with the β singlet peak to give a spectrum of a large, somewhat broadened peak at 2.86 ppm and a satellite at 2.80 ppm with an intensity ratio of 2:1.

The spectra of the solutions of the Y, La, and Lu complexes of ENTMP are more complex. The La and Lu spectra at 85 °C and pH 10.5 are compared in Figure 2. The Y(ENTMP) spectrum is basically similar to that of LuENTMP. The large, sharp peak in these spectra (3.0 ppm for La and 3.07 ppm for Lu) is assigned to the β protons. The remainder of the La spectrum is too poorly resolved to interpret directly. However, in the Lu spectrum, there remain five peaks of relative intensities 1:2.7:1.5:1.5:2.6:1. The peaks of 2.6 and 2.7 intensities show some structure and both probably have overlapping peaks. This pattern and the intensities are consistent with an ABX pattern. The methylenic protons in the LuEDTA complex have an AB quartet pattern, and such a pattern in the LuENTMP complex would be split by ^{31}P–^{1}H coupling into the two quartets of an ABX spectrum. Table III compares the calculated splittings and relative intensities for such an ABX spectrum with those observed in the Y(ENTMP) and LuENTMP spectra. Table IV gives the coupling constants calculated from these spectra. These calculations and the designations follow those of Bernstein et al.[12]

Figure 3 shows the effect of pH on the spectrum of the LuENTMP solutions. The peaks of the spectrum broaden as the pH is lowered and LuH_nENTMP species form. Although we are unable to define the values of n, at pH 10.5 it is almost certainly 0, while at pH 7.5 and 8.5 probably both LuHENTMP and LuH_2ENTMP are present in the solution. A similar loss of spectral resolution occurs for the pH 10.5 solutions as the temperature decreases. However, at pH 7.5, the spectrum has the reverse dependence; i.e., resolution increases with decrease in temperature.

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Table IV. Chemical Shifts (ppm) and Coupling Constants (Hz) for LuENTMP and Y(ENTMP) Species (85 °C; pH 10.5)

parameter[a]	LuENTMP	Y(ENTMP)
$\eta H_0(\sigma_B - \sigma_A)$	64.2	74.2
J_{AB}	14.4	15.3
J_{AX}	13.6 (11.4[b])	13.4
J_{BX}	13.6 (11.4[b])	13.4
D_+	32.9	37.9
D_-	32.9	37.9
$2\phi_+$, deg	12.64	11.64
$2\phi_-$, deg	12.64	11.64

[a] A and B are the *gem* α protons. [b] As estimated from ^{31}P NMR spectra.

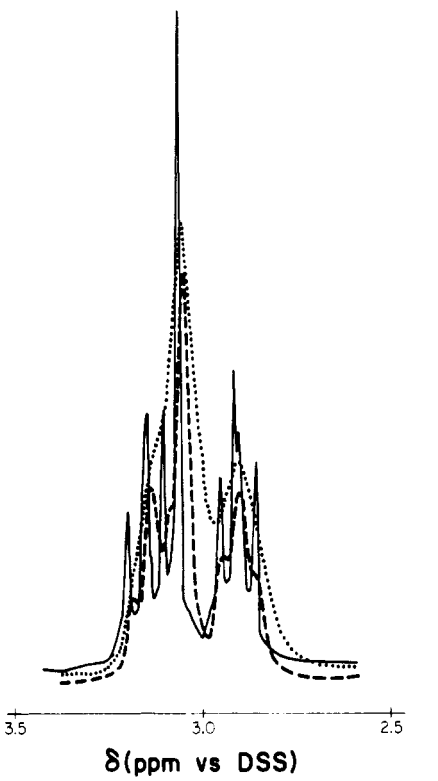

Figure 3. Spectra of LuENTMP at pH 7.5 (···), 8.5 (- - -), and 10.5 (—).

The ^{31}P spectrum of LuENTMP solutions at pH 10.5 were measured at 0, 27, and 85 °C, and a triplet of 1:2:1 relative intensity was observed, which reduced to a singlet in decoupling measurements. The shift of the central peak of the triplet was 21.56 (0 °C), 21.08 (27 °C), and 20.67 Hz (85 °C). Since the ^{31}P is part of an ABX spectrum, the triplet is consistent with an overlap of two peaks of the expected quartet for ^{31}P, which would produce the 1:2:1 intensity ratio.

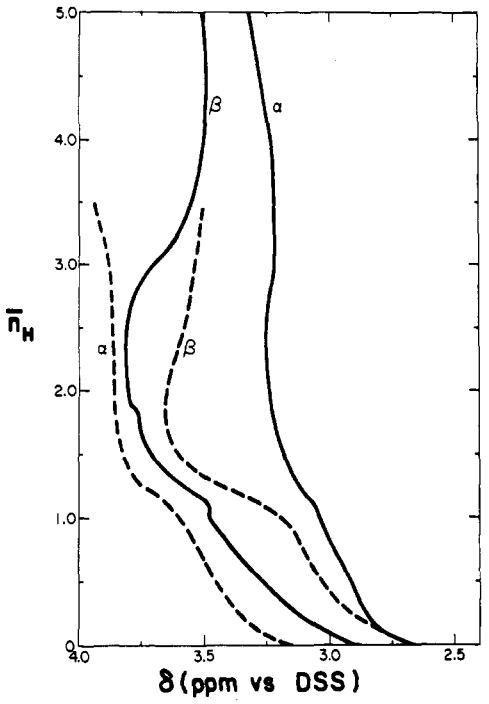

Figure 4. Comparison of the shifts of the α and β protons of EDTA (---) and ENTMP (—) as a function of $\bar{n}_H$.

Discussion

In Figure 4, the variation of the shifts of the α and β protons as a function of n_H, the protonation number, is compared for EDTA and ENTMP. The analogous protons show parallel shift behavior for $\bar{n}_H \leq 2$ in agreement with the calculations reported in Table I and those for EDTA[13] that protonation occurs at the nitrogens for the first two protons added. The rather complex behavior of the proton shifts of ENTMP for $\bar{n}_H \leq 2$ (Figure 1) is consistent with the model of Fujiwara and Reilley[14] and Letkeman and Martell[13] for amino polycarboxylates wherein hydrogen bonding occurs between the amine and the carboxylate (in this case phosphonate) groups as $\bar{n}_H$ exceeds 2.

In Figure 4, we see that the shift of the α protons in ENTMP is upfield from the corresponding protons in EDTA while that of the β protons is downfield from the EDTA β protons. Also the shift difference is much larger between the α protons of EDTA and of ENTMP than between the α protons of the two ligands. At any value of $\bar{n}_H$, the residual negative charge on the phosphonate groups of ENTMP is greater than that on the carboxylate groups of EDTA. This plus the lower electronegativity of phosphorus than that of carbon would account for a greater electron density as reflected in the upfield shift of the α protons of ENTMP. The difference in shift values would decrease, then, as the anions become highly protonated, and at pH 2 (H_6ENTMP^{2-} and H_4EDTA), the shifts for the α and the β protons are very similar for ENTMP and EDTA.

The nitrogen sites are more basic ($pK_1 = 13.0$; $pK_2 = 9.8$) for ENTMP than for EDTA ($pK_1 = 10.2$; $pK_2 = 6.1$). Accordingly, it is reasonable that the β protons have a somewhat increased electron density in EDTA than in ENTMP, in agreement with the greater downfield shift in the latter.

CaEDTA exhibited an AB pattern for the acetate protons, which was resolved at 270 MHz but not at 100 MHz.[9a,c] Such an AB pattern is expected for these ligands with a singlet pattern for the β protons, when the rate of nitrogen inversion is slower than the ^1H NMR measurement time. In complexes, this pattern is related to metal–nitrogen bonding, which is long-lived on the NMR time scale, and metal–oxygen bonding, which is short-lived on the NMR time scale, and metal–oxygen bonding, which is short-lived on that time scale. In CaEDTA, the need for 270 MHz to resolve the AB quartet indicates that the N inversion rate must be in the same time range as the NMR measurement. For the CaENTMP systems, at 270 MHz the doublet pattern observed is analogous to a singlet pattern in EDTA systems and reflects equivalence of all the α protons. This condition is associated with short-lived metal–nitrogen (fast inversion) and metal–oxygen bonding.[6] According to the stability constants[3] at the pH (10.5) of the solution studied, the complex should be about 90% CaENTMP and 10% CaHENTMP, but this small amount of protonated complex would not seem sufficient to account for the difference in the spectra of CaENTMP and CaEDTA. Moreover, CaEDTA has a stability constant ($10^{10.6}$) that is sufficiently larger than that of CaENTMP ($10^{9.40}$) to be consistent with the spectral indication of a shorter lifetime of the Ca–N bond in ENTMP, as it is this bond rupture that is rate determining[15] in the complexation kinetics of these systems.

For the lanthanide–ENTMP spectra, the ABX pattern for the α protons is analogous to the AB pattern of the protons and reflects slower nitrogen inversion (i.e., stronger Ln–N bonding) and short-lived lanthanide–oxygen bonding in both the LnEDTA and LnENTMP complexes. Poor resolution of the α-proton spectra in both types of complexes can be associated with Ln–N bonding only slightly longer than the NMR time.

The simple doublet of the CaENTMP complex, the single ABX spectrum of all the LnENTMP complexes, and the single decoupled peak for ^{31}P in the LnENTMP systems all reflect that all four phosphonate groups in these complexes within the NMR time domain have the same average interaction with the metal ion. Since the spectra are consistent with rapid metal–oxygen bond formation and rupture, such fast exchange could be expected to lead to such average behavior even if nonequivalent phosphonate binding were present when the metal–oxygen bond forms. However, the observations of a single ABX pattern does imply equivalent Ln–N bonds for both nitrogens in LnENTMP (also observed in LnEDTA but not in LnHEDTA and LnMEDTA[9a]).

In the study of diamagnetic metal–EDTA ^1H NMR spectra,[9a] the singlet β-proton peak and the baricenter of the α-proton AB quartet showed a linearly increasing downfield shift with increasing cationic charge density as measured by Z^2/R (Z = cation charge, R = cation radius). The shifts of the α and β protons of the ENTMP spectra show a similar linear behavior with a slightly smaller slope (0.035 for ENTMP vs. 0.050 for EDTA). We cannot offer a satisfactory model for such a linear deshielding trend; nevertheless, the similarity of the correlation for M(EDTA) and M(ENTMP) complexes indicates a common explanation.

Figure 3 shows the change in the spectrum of the LuENTMP complex with pH. The chemical shifts of both the α and β protons are relatively insensitive to pH in this range (7.5–10.5). These observations are consistent with structures at pH 7.5 and 8.5 wherein the protons of LnH_nENTMP bond to the oxygens of the phosphonate groups but not to the nitrogens of the ligand since the latter situation would destroy the ABX spectral pattern. Protonation of phosphonate groups would shift the baricenter of the proton spectrum of the group involved, but from the values for $\bar{n}_H \sim 1$ in Figure 4, δ would be in the range of 3.0–3.1, which is the same range as for the unprotonated groups (Table II). Consequently, protonation would seem likely to result in only small shifts in the baricenter

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of the α protons with an exchange rate between those of LuENTMP and LuHENTMP, which results in the observed line broadening. From Figure 4, we also see that the δ_β at $\bar{n}_H \sim 1$ is ca. 3.2 so the insensitivity of the β-proton shifts in LuENTMP with pH is further evidence that protonation of the complex does not occur at the nitrogen sites. Martell et al.[3] also proposed that protonation occurs on the phosphonate groups and leaves the M-N bonds intact.

A difference in LnEDTA and LnENTMP complexes is found in the temperature dependence of their ^{1}H NMR spectra. As the EDTA solutions are heated, their spectra lose resolution whereas the reverse is true for the spectra of ENTMP complexes. The loss of resolution with increasing temperature for EDTA complexes is explained by the decreased lifetime of the Ln-N bond. Such an effect would be expected to be present also in ENTMP complexes so the increased resolution with temperature must be due to another, larger effect. A probable explanation involves equilibrium between different conformers wherein the rate of transition between these conformers increases with temperature. Support for a model in which conformers have different δ values is found in ref 9a, where the α protons of LuMEDTA (*N*-methylethylenediaminetriacetate) have three separate AB quartets with baricenters of 3.25, 3.50, and 3.55 ppm (δ-(LuEDTA) = 3.40). Such different shift values for the three sets of α protons were also observed in HEDTA. The fact that the four sets of α protons in the LnEDTA complexes had identical δ (AB baricenters) values was related to an averaged symmetrical conformation while the presence of different δ values in the HEDTA and MEDTA complexes results from an averaged asymmetry in the conformation. The large residual charge in $LnENTMP^{5-}$ could lead to conformers that minimize the electrostatic repulsions. Such conformers would most likely have relatively small activation barriers to interchange so even modest increases in the temperature would increase the exchange rate. Since the values of such conformers are unlikely to be very different, exchange would lead, in the proper time domain, to line broadening and loss of resolution, as observed.

These studies have demonstrated that the metal-nitrogen bonding in the ENTMP complexes plays a significant role, comparable to that of the metal-nitrogen bond in EDTA complexes. Protonation of the complexes occurs on the phosphonate groups and does not weaken the metal-nitrogen bonding. Decreased spectral resolution with increasing temperature is interpreted to reflect the effect of exchange between different conformers in $LnENTMP^{5-}$.

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Registry No. ENTMP, 1429-50-1; H_4EDTA, 60-00-4; NaENTMP, 84961-32-0; CaENTMP, 84986-98-1; Y(ENTMP), 84986-99-2; LaENTMP, 84987-00-8; LuENTMP, 84987-01-9; phosphorous acid, 13598-36-2.

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

^{31}P NMR Investigation of the Reactions of Tetraphenyl- and Tetramethyldiphosphine and Diphenylphosphine with S_4N_4: Preparation and the Molecular and Electronic Structures of Two Structural Isomers of the Eight-Membered Ring $Ph_4P_2S_2N_4$

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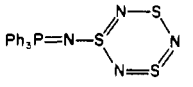
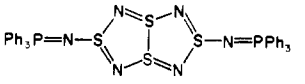
The reactions of R_2PPR_2 (R = Me, Ph) and Ph_2PH with S_4N_4 in toluene at reflux have been monitored by ^{31}P NMR spectroscopy, and the major products have been isolated and identified. In addition to the six-membered ring $R_2PS_2N_3$ reported previously and the cyclophosphazenes $(R_2PN)_{3,4}$, two structural isomers of the eight-membered ring $R_4P_2S_2N_4$ are formed and the crystal and molecular structures of the phenyl derivatives have been determined. 1,5-$Ph_2P(NSN)_2PPh_2$ crystallizes in the monoclinic space group $C2/c$ with a = 10.045 (3) Å, b = 15.930 (2) Å, c = 14.130 (4) Å, β = 93.98 (1)°, and Z = 4. The structure was solved by direct methods and refined by full-matrix least-squares techniques to give a final R = 0.045 and R_w = 0.059 for 2193 reflections with $I \geq 3\sigma(I)$. The structure consists of a folded eight-membered ring with a cross-ring S-S contact of 2.527 (1) Å. The angle between the two intersecting planes of the eight-membered ring is 117.3°. The mean endocyclic P-N and S-N bond lengths are 1.622 (3) and 1.590 (3) Å, respectively. 1,3-$(Ph_2PNPPh_2)S_2N_3$ also crystallizes in the monoclinic space group $C2/c$ with a = 15.200 (11) Å, b = 9.307 (3) Å, c = 17.675 (13) Å, β = 113.24 (3)°, and Z = 4. The structure was solved by direct methods and refined by full-matrix least-squares techniques to give a final R = 0.054 and R_w = 0.063 for 2868 reflections with $I \geq 3\sigma(I)$. The structure consists of an eight-membered ring with phosphorus atoms in the 1,3-positions. The NSNSN unit is essentially planar, and the P atoms lie out and on opposite sides of this plane by 0.697 Å. The mean endocyclic P-N and S-N bond lengths are 1.600 (3) and 1.577 (3) Å, respectively. The electronic structure of 1,3-$(Ph_2PNPPh_2)S_2N_3$ is compared with that of $Ph_2PS_2N_3$ with use of the HMO approach. The strong visible absorption band at ca. 460 nm is tentatively assigned to the HOMO (π^*) → LUMO (π^*) transition of a 10π-electron manifold.

Introduction

It was evident from our earlier studies that the nucleophilic degradation of S_4N_4 by phosphines produces a wider range of products than the corresponding reaction with other nucleophiles.[1] For example, the reaction of Ph_3P with S_4N_4 resulted in the formation of the $Ph_3P{=}N$ substituted sulfur-nitrogen rings **1** and **2**, in addition to the anion $S_4N_5^-$ (as its



1



2

$(Ph_3P{=}N)_3S^+$ salt),[2] which is a frequent product of nucleophilic attack on S_4N_4.[1] In contrast, the reaction of diphosphines, R_2PPR_2 (R = Me, Ph), with S_4N_4 produces the six-membered 8π-electron heterocycles $R_2PS_2N_3$ (**3**). These

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