Supplementary Material Available: Listings of crystal data and structure refinement information (Table SI), distances and angles for non-hydrogen atoms (Tables SVIII and SX), anisotropic temperature factors (Tables SII and SV), atomic coordinates and thermal parameters for anions and solvent molecules (Tables SIII and SVI), and hydrogen atom coordinates and temperature factors (Tables SIV and SVII) and figures showing atom numbering for cations and unit cell and packing diagrams (21 pages); tables of observed and calculated structure factors (Tables SXI and SXII) (20 pages). Ordering information is given on any current masthead page.

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Spectroscopic Characterization of a Series of Europium(III) Amino Phosphonate Complexes in Solution

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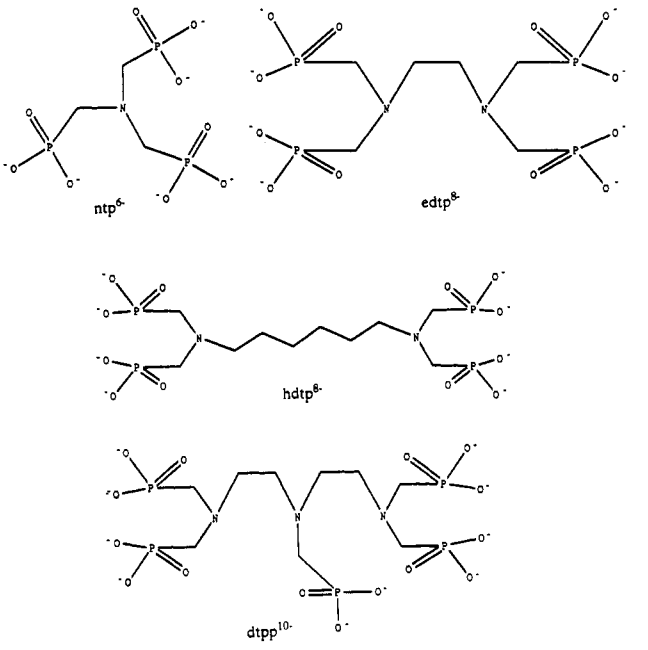
The Eu^{3+} complexes of nitrilotris(methylenephosphonic acid) (ntp), ethylenediaminetetrakis(methylenephosphonic acid) (edtp), hexamethylenediaminetetrakis(methylenephosphonic acid) (hdtp), and diethylenetriaminepentakis(methylenephosphonic acid) (dtpp) have been characterized in solution by laser-induced Eu^{3+} luminescence spectroscopy. The latter three ligands form both 2:1 and 1:1 metal-ligand complexes, while ntp forms both 1:1 and 1:2 complexes at pH 6.0. The number of water molecules directly coordinating the metal ion was determined for each complex. The $^7F_0 \rightarrow {}^5D_0$ excitation spectra of edtp, hdtp, and dtpp reveal isomeric forms for both the 2:1 and 1:1 complexes while ntp exhibits only single species for both the 1:1 and 1:2 complexes. Marked changes were observed in the Eu^{3+} $^7F_0 \rightarrow {}^5D_0$ excitation spectra of the various species as a function of pH. The temperature dependence of the excited state lifetime of the Eu^{3+}-edtp system has an activation energy of 5150 cm^{-1}, corresponding to a ligand level this far above the $^5D_0$ state, which is involved in the deexcitation process.

Introduction

The chelating ability of amino phosphonic acids has received considerable attention due to the diverse binding abilities of the phosphonate group.[1-7] Amino phosphonates have been used commercially as herbicides and sequestering agents.[8] Other potential applications include NMR imaging agents, anticorrosive agents, and metal ion separation reagents.[9,10] These ligands can also be thought of as simple models for biologically important phosphonate-containing molecules;[11] moreover, they are structural analogues of the well-known amino carboxylates. However amino phosphonic acids exhibit very different protonation and complexation properties from their aminocarboxylic acid counterparts. These differences stem from the strong pH dependence of complex formation, added bulkiness, and bidentate coordination ability of the phosphonate group, as well as their potential for formation of polymeric species.[11-14]

In order to assess the potential uses and functions of amino phosphonic acids, an understanding of the types of metal complexes formed in solution is required. The use of lanthanide luminescence spectroscopy to probe the solution complexation properties of coordination complexes and biological systems has proven to be particularly informative.[15-17] The ability of certain lanthanide ions to luminesce in solution at room temperature allows a broad amount of structural information to be obtained. Eu^{3+} and Tb^{3+} have been utilized extensively as structural probes in luminescence studies; however, Eu^{3+} is the more desirable owing to its nondegenerate ground ($^7F_0$) and first excited ($^5D_0$) states. Since neither

Chart I. Schematic Representation of the Four Amino Phosphonate Ligands Studied



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the ground nor the first excited state ($J = 0$) can be split by the ligand field, a single electronic transition is observed for each distinct Eu^{3+} environment.

The basic technique[17] employed is to monitor the $^7F_0 \rightarrow {}^5D_0$ excitation spectrum and the excited-state lifetime of Eu^{3+} under various conditions. $^7F_0 \rightarrow {}^5D_0$ spectra of Eu^{3+} complexes are obtained by scanning a tunable dye laser through the 577–581-nm range while monitoring the "hypersensitive" $^5D_0 \rightarrow {}^7F_2$ emission band at 614 nm. This method allows qualitative as well as quantitative information to be obtained, viz., the number and stoichiometries of species present in solution, the number of coordinated water molecules within the first coordination sphere of Eu^{3+}, and structural changes induced by variations in pH and temperature. We report here the application of this spectroscopic technique to probe the Eu^{3+} complexes of four amino phosphonic acids, nitrilotris(methylenephosphonic acid) (ntp), ethylenediaminetetrakis(methylenephosphonic acid) (edtp), hexamethylenediaminetetrakis(methylenephosphonic acid) (hdtp), and diethylenetriaminepentakis(methylenephosphonic acid) (dtpp). The fully deprotonated forms of these acids are shown in Chart I.

In order to facilitate our later discussion of these polyprotic ligands and their complexes, we list the pK_a values for them: H_6ntp,[18] 0.3, 1.5, 4.64, 5.86, 7.30, 12.1; H_8edtp,[4] ..., 1.33, 3.02, 5.17, 6.42, 7.94, 9.78, 12.99; H_8hdtp,[7] ..., ..., 3.25, 5.12, 5.68, 6.23, 7.71, 11.82; H_{10}dtpp,[19] 1.52, 2.64, 3.10, 3.82, 5.38, 6.28, 7.05, 7.74, 9.36, 11.12. Although complex stability and protonation constant information is unavailable for Eu^{3+} complexes of these ligands, we estimate the following to be the principal species in solution from data available[18,19] on other tripositive ions M^{3+}: at pH 6, for the ntp system, $M(Hntp)^{2-}$; for the edtp system, $M(edtp)^{5-}$ and $M(Hedtp)^{4-}$ in a ratio (former over latter) of 0.2; for the dtpp system, $M(H_3dtpp)^{5-}$ and $M(H_4dtpp)^{4-}$ in a ratio of 5. At pH 10, the principal species are as follows: for the ntp system, $M(ntp)^{3-}$; for the edtp system, $M(edtp)^{5-}$ and $M(OH)(edtp)^{6-}$ in a ratio of 0.5; for the dtpp system, $M(dtpp)^{7-}$. Thus considerable changes in the protonation states of the complexes occur over the pH range examined by us.

Experimental Section

Materials. edtp (90%) and hdtp (97%) were purchased from the Strem Chemical Co. as free acids. edtp was recrystallized three times from a hot water–ethanol mixture while hdtp was used without further purification. ntp and dtpp were purchased as 50% aqueous solutions from the Aldrich Chemical Co. and the Strem Chemical Co., respectively. Hydrated $EuCl_3$ (99.9%) and D_2O (99.8%) were also obtained from the Aldrich Chemical Co. Rhodamine 590 and 610 laser dyes were obtained from the Exciton Company and the Kodak Co., respectively. The H_2O used was deionized and doubly distilled.

Methods. The spectral and lifetime experiments were carried out by using a Quantel Series YG581C pulsed (10 Hz) Nd:YAG laser pumped tunable dye-laser, Model TDL50. The remainder of the system is identical with that previously described.[17,20] A stock solution of $EuCl_3$ was prepared at a concentration of 100 μM and standardized with edta by using an arsenazo indicator.[21] Aqueous buffered stock solutions (15 mM piperazine buffer, pH 6.0) of each ligand were prepared at a concentration of 10 mM. Metal–ligand solutions were typically prepared in a 1:1 ratio at a concentration of 100 μM unless otherwise indicated. The $^7F_0 \rightarrow {}^5D_0$ transition (580 nm) of Eu^{3+} was excited by using a mixture of Rhodamine 590 and 610 dyes while monitoring the $^5D_0 \rightarrow {}^7F_2$ emission band of Eu^{3+} at 614 nm.

Results and Discussion

Determination of Complex Stoichiometry. Stoichiometries of Eu^{3+} complexes can generally be determined by monitoring the intensity of $^7F_0 \rightarrow {}^5D_0$ excitation band as a function of added ligand.[17] Such plots of intensity vs ligand concentration, generated for each of the amino phosphonate ligands under study, resulted in binding curves that reach maximums at nonstoichiometric

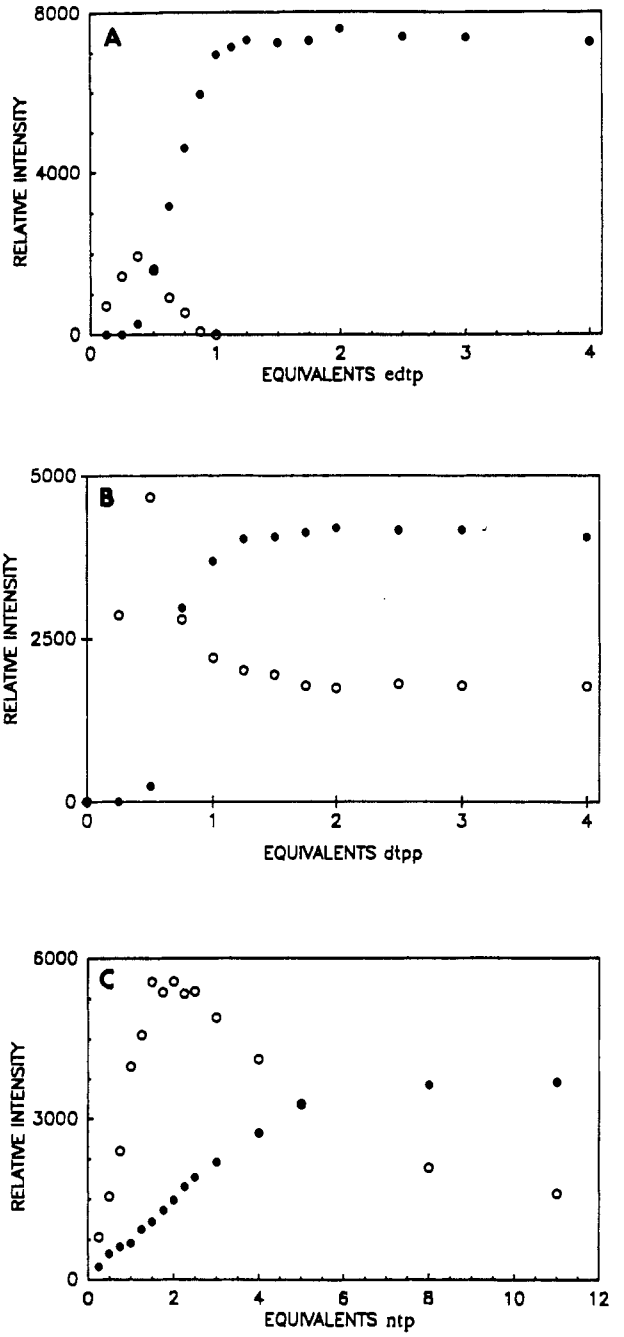

Figure 1. Time-resolved titration curves of the Eu^{3+} $^5D_0$ excited-state lifetime intensities (I_0) vs equivalents of (A) edtp, (B) dtpp, and (C) ntp all at pH 6.0.

values. These curves are difficult to interpret owing to intensity contributions from several species present in solution concurrently. A second method of obtaining complex stoichiometry when multiple species are present, known as time resolution,[22,23] consists of recording Eu^{3+} excited-state lifetimes for precise time intervals at specific wavelengths during the course of a titration. The maximum intensity (I_0) of the individual exponential components, resolved from the luminescence decay curves, are plotted vs equivalents of added ligand. This method is useful when complex exchange rates are slow on the $^5D_0$ time scale, allowing individual lifetimes to be extracted from the experimental decay curves. With this technique, interpretable binding curves were obtained for each ligand and excited-state lifetimes pertaining to the individual species present in solution were aquired.

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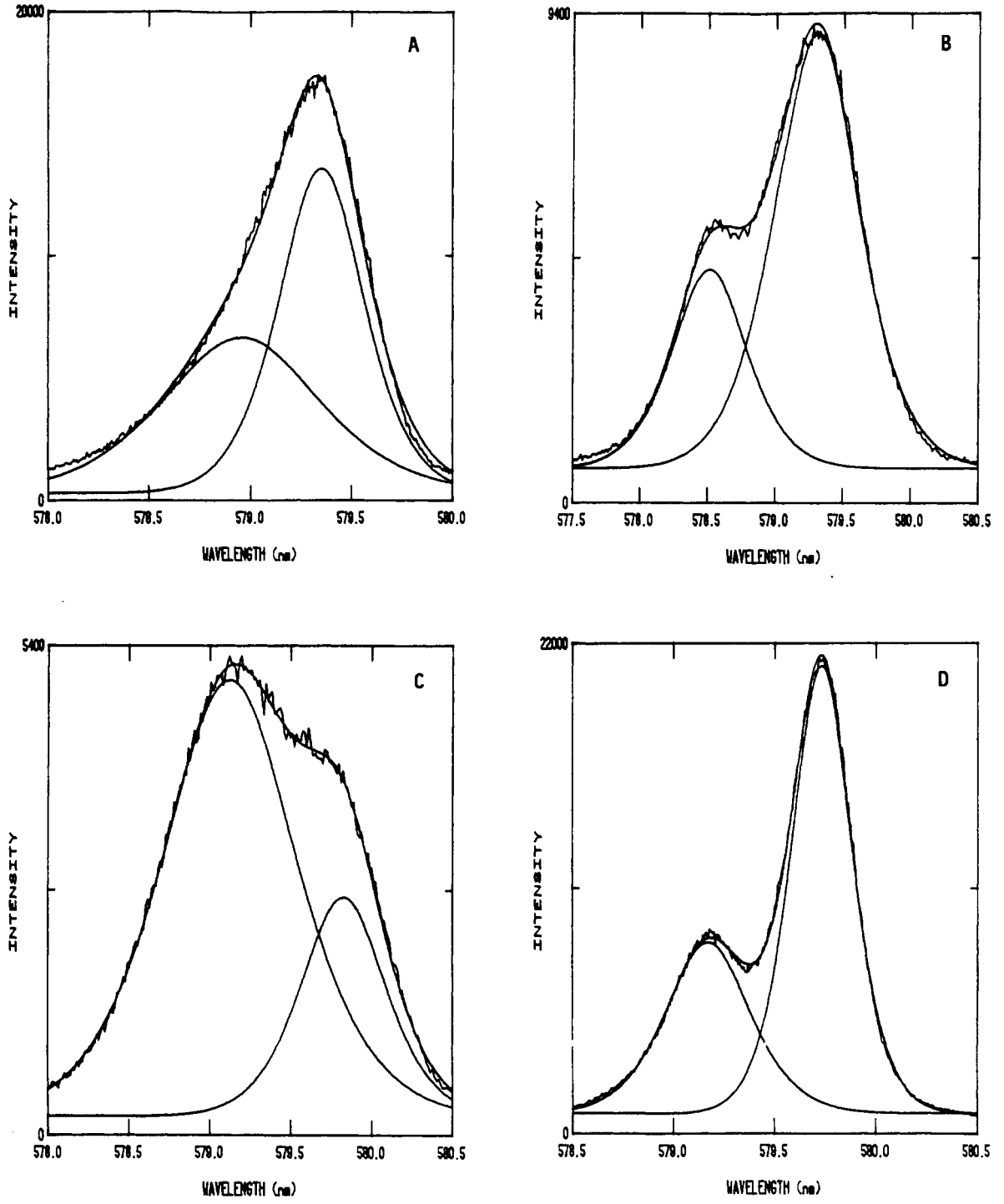

Figure 2. $^7F_0 \rightarrow {}^5D_0$ excitation spectra of the Eu^{3+} complexes of (A) edtp, (B) hdtp, (C) dtpp, and (D) ntp at pH 6.0 curve-resolved into Lorentzian-Gaussian type peaks.

The binding curves for edtp and hdtp at pH 6.0, are virtually identical with one another; the curve for edtp is given in Figure 1A. In each experiment, lifetimes were recorded at or near the peak maxima of 579.30 and 579.20 nm for edtp and hdtp, respectively (Figure 2A,C). Two distinct lifetimes were detected in each titration (Table I). The observation of two lifetimes indicates that the interconversion rate between these two species is slow on the $^5D_0$ time scale.[23] The amplitudes of the shorter lifetime component, in each titration, reach a maximum at $^1/_2$ equiv of added ligand, while the amplitude of the longer lifetime increases up to 1 equiv after which it remains constant. These data indicate the formation of 2:1 and 1:1, metal–ligand complexes corresponding to the short and long lifetimes, respectively. For edtp and hdtp, the short lifetime corresponding to the 2:1 species is undetectable after 1 equiv of ligand has been added. In contrast, the time-resolved titration of the dtpp system, while showing a sharp maximum of 0.5 equiv of added ligands, reveals a shorter lifetime species that persists throughout the course of the titration (Figure 1B). This is evidence for the presence of two isomeric forms of the 1:1 species in slow equilibrium on the $^5D_0$ excited-state time scale. Both 2:1 and 1:1 lanthanide ion complexes of edtp and dtpp have been suggested previously,[19,24,25] as well as 1:2 and 4:3 complexes of edtp and 4:3 complexes of dtpp.[5,14,25] The latter species were not detected in our experiments.

The $^7F_0 \rightarrow {}^5D_0$ excitation spectra recorded throughout the course of each titration were curve-resolved by using a Marquardt nonlinear regression algorithm[26] yielding the peak positions listed

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Table I. Observed $^7F_0 \rightarrow {}^5D_0$ Excitation Bands and Excited-State Lifetimes of the Eu(III) Complexes of ntp, edtp, hdtp, and dtpp at pH Values of 6.0 and 10.0

complex (ratio)	λ, nm	τ_{H_2O}, μs	τ_{D_2O}, μs	q[a]
		pH 6.0		
ntp (1:1)	579.14	210	600	3.5
(1:2)	579.73	910	2400	0.7
edtp (2:1)	578.95	230	2480	4.1
(1:1)	579.35, 578.95	410	2480	2.1
hdtp (2:1)	578.52	370	2450	2.4
(1:1)	579.31, 578.52	530	2450	1.6
dtpp (2:1)	579.17	370	2440	2.4
(1:1)	579.80, 579.17	940, 370	1320, 2400	0.3, 2.4
		pH 10.0		
ntp (1:10)	579.15	200	600	3.5
edtp (1:1)	578.72, 579.49	420	2320	2.1
hdtp (1:1)	579.83, 579.26	300	2450	3.1
dtpp (1:1)	578.78, 579.21	280	2440	3.3

[a] The number of coordinated water molecules $q = 1.05(\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}) \pm 0.5$.

in Table I. Spectra of the 1:1 Eu^{3+} complexes of edtp, hdtp, and dtpp at pH 6.0 were resolved into Lorentzian–Gaussian type peaks and are presented in Figure 2A–C. The resolved bands in each spectrum were identified with their respective excited-state lifetimes by recording luminescence decay curves at several wavelengths across the spectral profiles. The $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of Eu^{3+}–edtp consists of a broad asymmetric band centered at 579.25 nm, which was resolved into two bands at 578.95 and 579.35 nm (Figure 2A). Since only a single lifetime is detected for a 1:1 mixture of Eu^{3+} and edtp, the two resolved bands are assigned to isomeric forms of the 1:1 species in rapid interchange.

The Eu^{3+}–hdtp and Eu^{3+}–dtpp complexes exhibit $^7F_0 \rightarrow {}^5D_0$ excitation spectra consisting of two slightly overlapping bands. The curve-resolved spectra of hdtp and dtpp are comprised of bands at 578.52 and 579.31 nm and 579.17 and 579.80 nm, respectively (Figures 2B,C). The titration data obtained with dtpp indicate that the band centered at 579.17 nm (Figure 2C) is present from the beginning, whereas the band at 579.80 nm is detected only after $^1/_2$ equiv of ligand has been added. The longer lifetime is undetectble at shorter wavelengths, indicating that the band at 579.17 nm corresponds to the shorter lifetime species while the band at 579.80 nm belongs to an isomer with a longer excited state lifetime.

The spectral results for Eu^{3+}–ntp differ from those of the previously described amino phosphonate complexes in that two well-resolved bands are observed in the $^7F_0 \rightarrow {}^5D_0$ spectrum (Figure 2D and Table I). The $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of a 1:10 metal–ligand mixture was decomposed into bands centered at 579.14 and 579.73 nm (Figure 2D). Two distinct excited-state lifetimes of 210 and 910 μs are detected, the former corresponding to the band at 579.14 nm and the latter corresponding to the band at 579.73 nm. These two species are in slow exchange on the $^5D_0$ excited-state time scale.[23] The intensity of the shorter lifetime peak approaches its maximum value at a metal:ligand ratio of 1:1 and then decreases in intensity to a small but detectable value even at 11.0 equiv of added ligand (Figure 1B). The binding curves generated from the time-resolved component amplitudes indicate that the shorter lifetime is due to a 1:1 species. The amplitude of the longer lifetime component, on the other hand, continues to rise until ~4 equiv of ligand have been added after which it remains constant. The carboxylic acid analog of ntp is known to form both 1:1 and 1:2 metal–ligand complexes.[27] Previous studies on the lanthanide ion complexation of ntp also indicate the formation of both 1:1 and 1:2 metal–ligand complexes.[25,28] The species having the longer lifetime is assigned to the 1:2 complex. Eu^{3+} luminescence binding curves of similar character have been observed for 1:1, 1:2, and 1:3 species of dipicolinic acid.[29]

Determination of the Number of Coordinated Water Molecules. The number of inner-sphere water molecules, q, can be determined by the well-established method of replacing the OH oscillators of bound water molecules by OD oscillators.[30] The excited-state lifetimes observed separately in H_2O and D_2O for each metal–ligand complex are given, along with the number of coordinated water molecules in Table I. A 1:1 metal–ligand solution of edtp in D_2O at pH 6.0 exhibits a single lifetime of 2480 μs, independent of excitation wavelength. These data indicate that two water molecules coordinate in the 1:1 complex at pH 6.0 while the 2:1 complex coordinates four water molecules per metal ion. The Eu^{3+} complex formed with edta, the carboxylate analogue of edtp, coordinates three water molecules.[30,31] The smaller number of coordinated waters is reasonable for the Eu^{3+} complex of edtp since the phosphonate moiety is somewhat bulkier than is a carboxylate moiety. A single lifetime is also observed in D_2O for the hdtp complex with an average value of 2450 μs. This leads to the finding that the 2:1 complex coordinates either two or three water molecules per metal ion, while the 1:1 complex coordinates either one or two water molecules at pH 6.0.

The 1:1 ntp adduct displays an average excited-state lifetime of 600 μs in D_2O while the 1:2 species exhibits a value of 2400 μs. Relatively short lifetimes in D_2O such as that observed for the 1:1 species, while uncommon, have been reported previously.[22,32] Our data indicate that the 1:1 complex of ntp coordinates three or four water molecules while the 1:2 complex coordinates zero or one water molecule. The 1:1 and 1:2 nta complexes of Eu^{3+}, by comparison, coordinate five and one water molecules, respectively.[31]

A 1:1 mixture of Eu^{3+}–dtpp exhibits two lifetimes in D_2O at pH 6.0 of 1320 and 2400 μs. Both lifetimes are observed at longer wavelengths, but only the longer lifetime is detectable at shorter wavelengths. This suggests the presence of two isomers in slow (on the $^5D_0$ time scale) equilibrium. The one with the longer lifetime is devoid of coordinated water molecules while the other isomer involves two or three coordinated water ligands. By comparison, the 1:1 metal–ligand complex of the carboxylate analogue of dtpp coordinates one water molecule.[31]

Spectral Dependence on pH. The phosphonate functional group is a diprotic acid, which makes ntp a hexaprotic acid, edtp and hdtp octaprotic acids, and dtpp a decaprotic acid (Chart I). The polyprotic nature of these ligands results in highly pH-dependent metal coordination behaviors (see the Introduction for pK_a values and principal complex species present at pH values of 6 and 10). Therefore, the $^7F_0 \rightarrow {}^5D_0$ excitation spectra and excited-state lifetimes of these complexes were monitored over the pH range 2–10. All four ligands were studied at a 1:1 metal:ligand ratio at a concentration of 100 μM. At pH values below 3.0, the $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of each ligand contains only a single band, which corresponds to the Eu^{3+} aqua ion, suggesting that no complexation occurs below this pH, as these ligands are highly protonated.[4-7] The $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of edtp, shown in Figure 3A for pH 6.0, was observed throughout the pH range 4–7 with a single excited-state lifetime of 410 μs persisting throughout this range. As the pH is raised from 6 to 10, the single proton of the $Eu(Hedtp)^{4-}$ will dissociate, leading to the spectral changes shown in Figure 3A. Both $Eu(Hedtp)^{4-}$ and $Eu(edtp)^{5-}$ appear to involve two-coordinated water molecules (Table I). The two bands observed for $[Eu(edtp)(H_2O)_2]^{5-}$ correspond to the

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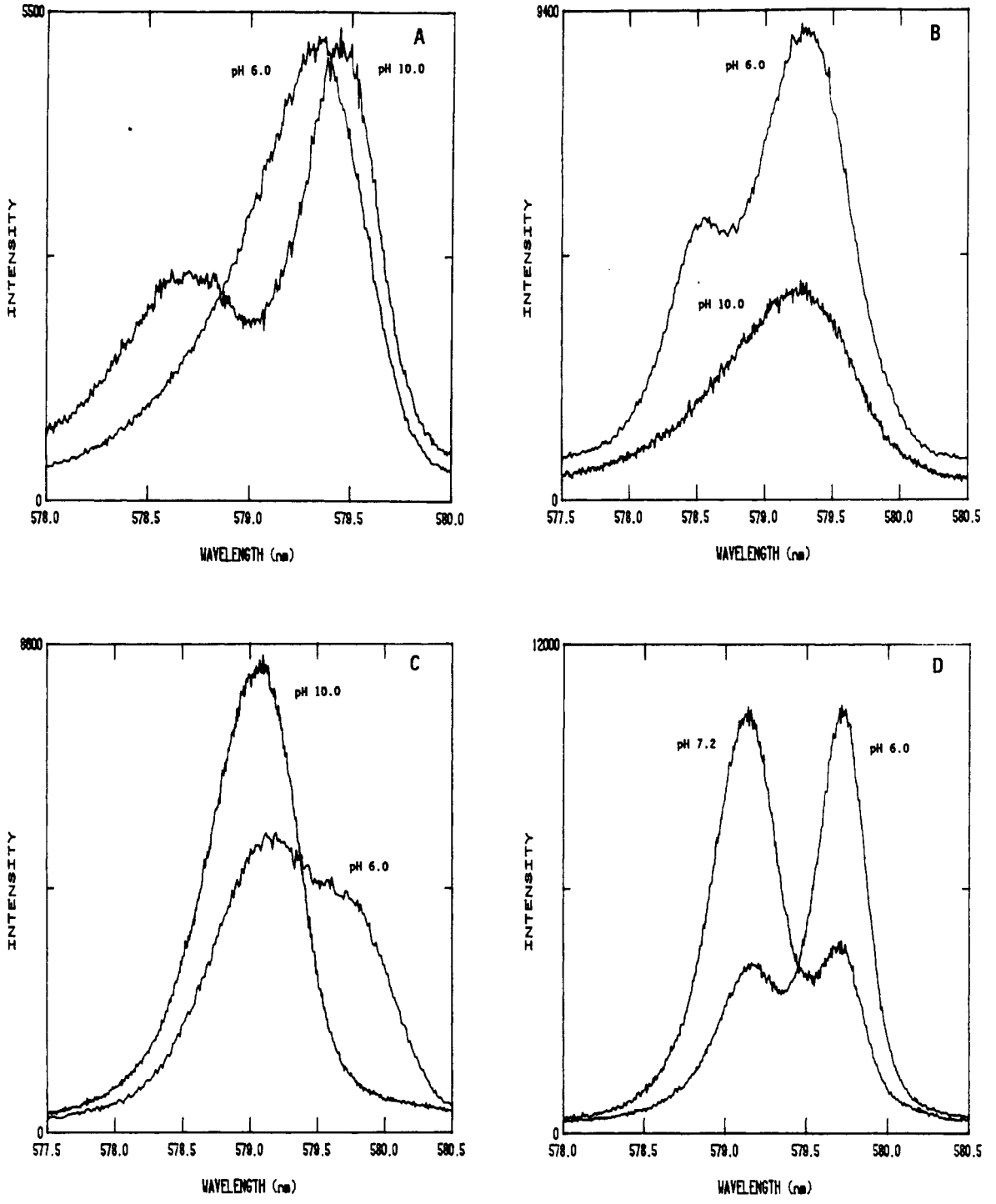

Figure 3. Comparison of the $^7F_0 \rightarrow {}^5D_0$ excitation spectra of the 1:1 Eu^{3+} complexes of (A) edtp, (B) hdtp, and (C) dtpp at pH values of 6.0 and 10.0 and (D) ntp (1:10) at pH values of 6.0 and 7.2.

presence of two isomers as is observed in the analogous edta complex.[34]

The $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of the 1:1 Eu^{3+}–hdtp complex at pH values between 3.0 and 4.0 consists of an asymmetric band centered at 579.31 nm. A shorter wavelength component centered at 578.52 nm does not appear until pH values greater than 4.0 have been reached. When the pH is increased to 6.0, both peaks reach their maximum intensity values. These features remain constant up to pH 9.0 after which the overall spectral intensity decreases with the band at 578.52 nm virtually disappearing (Figure 3B). The excited-state lifetime also decreases (Table I). While the protonic equilibria for H_8hdtp and H_8edtp are fairly similar, with the former being slightly more acidic until the final deprotonation step, the significant difference (Figure 3A,B) is probably due to the fact that the 1:1 Eu^{3+}–hdtp complex has been shown to be a dimer from Ce^{3+} to Tb^{3+} and Ce^{3+} to Eu^{3+} energy-transfer experiments in this laboratory,[35] while the 1:1 Eu^{3+}–edtp system is monomeric.

The $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of the 1:1 Eu^{3+}–dtpp complex remains relatively unchanged between pH values of 3 and 6. The only observable change is an overall increase in spectral intensity over this range. Two exicted-state lifetimes are observed, which indicate that two isomers are present at each of these pH values. While no potentiometric data for Eu^{3+} complexes of dtpp are available, one can infer from protonation data on the free ligand and the Y^{3+} complex[5,19] that $Eu(H_3dtpp)^{4-}$ predominates

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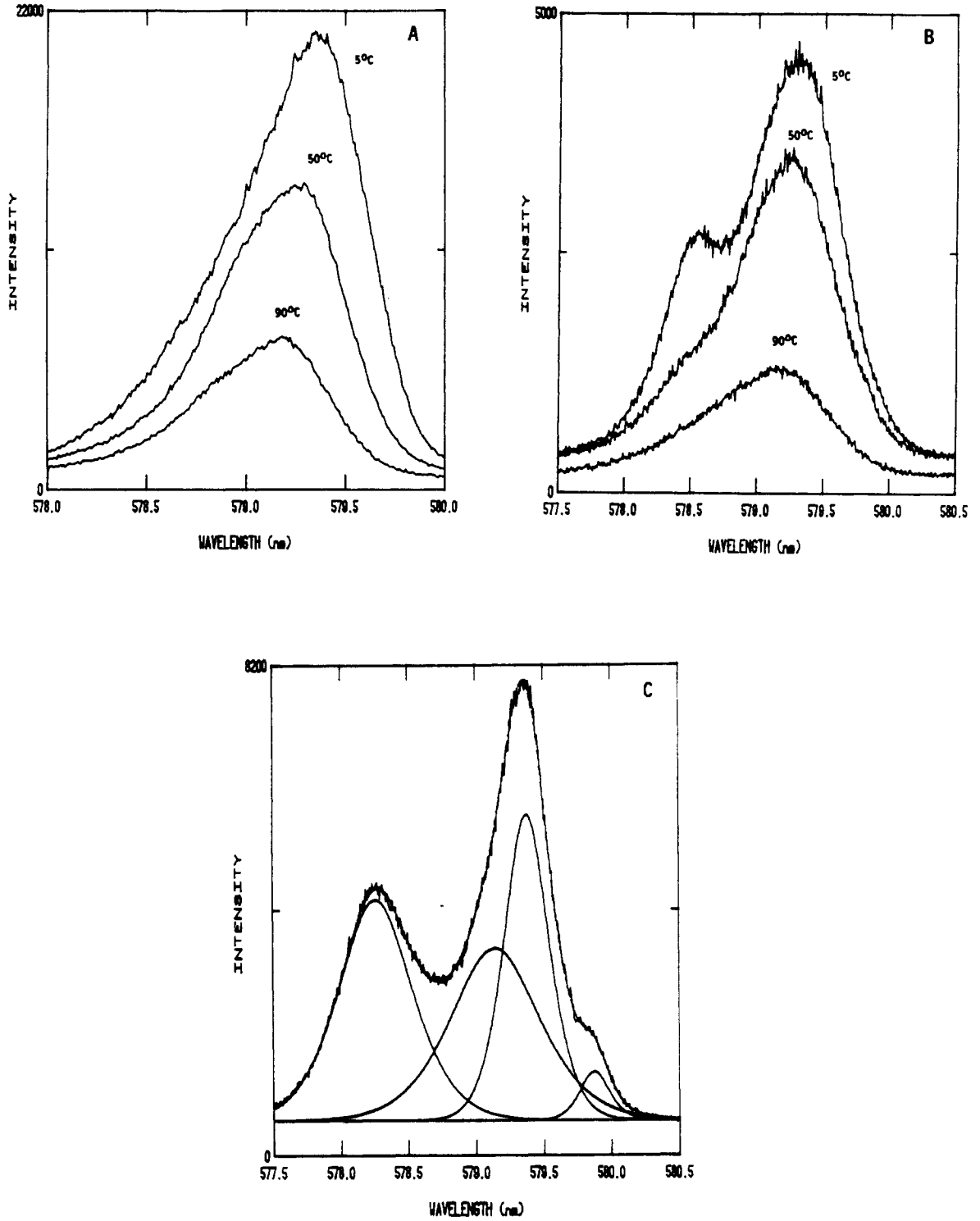

Figure 4. Temperature dependence of the $^7F_0 \rightarrow {}^5D_0$ excitation spectra of the Eu^{3+} adducts of (A) edtp, (B) hdtp, and (C) dtpp (90 °C only) at pH 6.0.

at pH 6. As the pH is increased above 6.0, the band centered at 579.80 nm decreases in intensity with a concomitant increase in intensity of the band centered at 579.17 nm. A decrease in amplitude of the former lifetime component is also observed at pH values above 6.0. At pH values of 8.0 or greater, only an asymmetric band centered at 579.21 nm is observed (Figure 3C), which exhibits a single lifetime of 280 μs. The curve-resolved spectrum contains two bands centered at 578.93 and 579.21 nm.

Both the 1:1 and 1:2 complexes of ntp were analyzed for changes due to pH by monitoring the $^7F_0 \rightarrow {}^5D_0$ excitation spectra of solutions containing metal:ligand ratios of 1:0.75 and 1:10. As the pH is increased from 3.0 to 6.0, both the Eu^{3+} aqua ion and the 1:1 species are observed for the 1:0.75 metal–ligand solution. The 1:1 and 1:2 species are both present for the 1:10 metal–ligand solution; however, the 1:2 band dominates the spectrum. Potentiometric data for lanthanide ion complexation with ntp is not available, however, protonation data for the free ligand and Ca^{2+} complex and the dissociation constant of the Eu^{3+} 1:1 complex have been reported.[3,12,13] On the basis of these data, $Eu(Hntp)^{2-}$ is believed to be the principal species present at pH 6.0. As the pH of the 1:0.75 metal–ligand solution is increased to 8.0, a single band at 579.15 nm appears. The intensity of this band reaches a maximum at pH 8, after which it decreases. For the 1:10 Eu^{3+}–ntp sample above pH values of 6.0, the band centered at 579.73 nm (1:2 species), decreases in intensity with a concomitant increase in intensity of the 1:1 band centered at 579.14 nm (Figure

Table II. Luminescence Lifetimes, τ, and Activation Energies, ΔE, of the 1:1 Eu^{3+}–edtp System in H_2O and D_2O as a Function of Temperature at pH 6.0

T,[a] K	$\tau^{-1}(H_2O)$,[b] μs	$\tau^{-1}(D_2O)$,[b] μs	T,[a] K	$\tau^{-1}(H_2O)$,[b] μs	$\tau^{-1}(D_2O)$,[b] μs
278	2.44	0.39	333	4.17	0.67
288	2.47	0.40	343	5.62	0.85
303	2.63	0.42	353	7.87	1.26
318	3.15	0.48	363	13.24	1.80

solvent	ΔE,[c] cm^{-1}	solvent	ΔE,[c] cm^{-1}
H_2O	5300	D_2O	5000

[a] Temperatures are estimated to be accurate to within ±1 K. [b] Excited-state lifetimes are accurate to ±10%. [c] Errors associated with activation energies are estimated to be ±500 cm^{-1}.

3D). As the pH is increased to 10.0, the band attributed to the 1:2 species becomes unobservable. The $^7F_0 \rightarrow {}^5D_0$ excitation spectrum contains only a single band centered at 579.15 nm along with a single excited-state lifetime of 200 μs. These data suggest a shift in equilibrium toward the 1:1 metal–ligand complex at high pH values, as previously reported.[28]

Spectral Dependence on Temperature. An additional method of studying variations in complex equilibria is to alter the sample temperature. The $^7F_0 \rightarrow {}^5D_0$ spectra and excited-state lifetimes of each of the Eu^{3+} amino phosphonate complexes was monitored over the temperature range 5–90 °C. The spectral profile of the 1:1 Eu^{3+}–edtp complex at pH 6.0 does not change appreciably as the temperature is increased (Figure 4A); however, the excited-state lifetime decreases markedly (Table II). An identical sample in D_2O at pH 6.0 was prepared and examined over the same temperature range. The deuterated solvent eliminates the nonradiative deexcitation pathway due to OH oscillators, allowing the Eu^{3+} aqua ion to be easily detected if it is present. No Eu^{3+} aqua ion signal is detectable, but a similar decrease in lifetime with increasing temperature is observed (Table II). These observations suggest that an additional deexcitation pathway is present, which becomes accessible as the temperature is increased.

Thermal quenching of the $^5D_0$ level by higher excited states has been reported by Kropp and Dawson[36] for $Eu(NO_3)_3$ in methanol and deuterated methanol. They observed a decrease in $^5D_0$ lifetime at temperatures above 310 K, corresponding to an activation energy of 2000 cm^{-1}, in good agreement with the separation between the $^5D_0$ and $^5D_1$ excited-states of Eu^{3+}. The rate constant for this temperature-dependent deexcitation can be calculated by using eq 1, where τ is the excited-state lifetime at

$$k(T) = [(1/\tau) - (1/\tau_m)] = A \exp(-\Delta E/RT) \qquad (1)$$

temperature T (K) and τ_m is the excited-state lifetime in the absence of quenching. A plot of log $[(1/\tau) - (1/\tau_m)]$ vs T^{-1} should be linear with a slope of $-\Delta E/2.3R$, where ΔE is the difference in energy between the $^5D_0$ state and the level responsible for the deexcitation. Such plots for the thermal quenching of Eu^{3+}–edtp in H_2O and D_2O are linear with identical slopes (Figure 5). The average energy difference calculated from these plots (5150 cm^{-1}) is greater than that expected if the $^5D_1$ or $^5D_2$ levels are responsible for the observed thermal quenching. A ligand energy level therefore appears to be responsible for the nonradiative deexcitation pathway. Indeed, ligand absorption bands are present at shorter wavelengths (<500 nm) for each ligand studied with a distinct absorption shoulder appearing at 430 nm in the case of edtp.

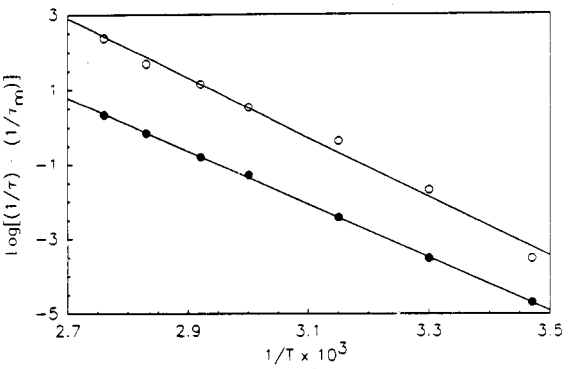

Figure 5. Thermal quenching of the Eu^{3+} complexes of edtp in H_2O (○) and D_2O (●).

The behaviors as a function of temperature of the spectral intensities and lifetimes of the Eu^{3+} complexes of ntp, hdtp, and dtpp to some extent parallel that of the edtp system discussed above, but complications arising from the biexponential nature of some of the decay curves prohibit a straightforward analysis. Further data on, and discussion of, these systems can be found in a thesis.[37]

Conclusions

When presented with excess Eu^{3+} each of the di- and triamino ligands, edtp, hdtp, and dtpp all form 2:1 metal–ligand complexes. This finding is corroborated by independent Ce^{3+} to Eu^{3+} and Ce^{3+} to Tb^{3+} energy-transfer experiments on the corresponding mixed metal systems.[35] When mixed in a 1:1 Eu^{3+}:ligand ratio at pH 6, edtp forms a monomeric complex that, on the basis of equilibrium data and the measured lifetimes in H_2O and D_2O, can be formulated as $[Eu(Hedtp)(H_2O)_2]^{4-}$. Under the same conditions, dtpp forms an equilibrium mixture of $[Eu(H_3dtpp)(H_2O)_2]^{5-}$ and $[Eu(H_3dtpp)]^{5-}$, accounting for the short and long excited-state lifetimes, respectively. The former species presumably involves coordination by only three phosphonate moieties, while the latter involves coordination of four or five phosphonates utilizing both ends of the molecule. Independent energy-transfer experiments[35] suggest that the Eu^{3+}–hdtp system involves dimeric units $[Eu(Hdtp)(H_2O)_2]_2^{10-}$, where each Eu^{3+} is coordinated to an end of two different hdtp ligands.

As the pH is raised from 6 to 10, deprotonation occurs for all the systems, leading to structural changes that are reflected in spectral changes and the observation of only a single excited-state lifetime in each case at pH 10. $[Eu(edtp)(H_2O)_2]^{6-}$, $[Eu(hdtp)(H_2O)_3]_2^{12-}$, and $[Eu(dtpp)(H_2O)_3]^{7-}$ appear to be the principal species at pH 10.

At pH 6, ntp forms complexes that can be formulated as $[Eu(Hntp)(H_2O)_{3\text{ or }4}]^{2-}$ and $[Eu(Hntp)_2(H_2O)]^{8-}$ while at pH 10 only $[Eu(ntp)(H_2O)_{3\text{ or }4}]^{3-}$ appears to form. At pH 6, the excited-state lifetime of $[Eu(Hedtp)(H_2O)_2]^{4-}$ decreases with increasing temperature at a rate corresponding to an activation energy of 5150 cm^{-1}. A ligand absorption at ~430 nm is implicated in the deexcitation mechanism.

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