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Strong Metal Ion Size Based Selectivity of the Highly Preorganized Ligand PDA (1,10-Phenanthroline-2,9-dicarboxylic Acid) with Trivalent Metal Ions. A Crystallographic, Fluorometric, and Thermodynamic Study

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The selectivity of the rigid ligand PDA (1,10-phenanthroline-2,9-dicarboxylic acid) for some M(III) (M=metal) ions is presented. The structure of $[Fe(PDA(H)_{1/2})(H_2O)_3]\,(ClO_4)_2\cdot 3H_2O\cdot {}^1/_2H_5O_2$ (**1**) is reported: triclinic, $P\bar{1}$, a=7.9022(16) Å, b=12.389(3) Å, c=13.031(3) Å, α=82.55(3)°, β=88.41(3)°, γ=78.27(3)°, V=1238.6(4) Å^3, Z=2, R=0.0489. The coordination geometry around the Fe(III) is close to a regular pentagonal bipyramid, with Fe−N lengths averaging 2.20 Å, which is normal for a 1,10-phenanthroline type of ligand coordinated to seven-coordinate Fe(III). The Fe−O bonds to the carboxylate oxygens average 2.157 Å, which is rather long compared to the average Fe−O length of 2.035 Å to carboxylates in seven-coordinate Fe(III) complexes. The structure of **1** supports the idea that the Fe(III) is too small for ideal coordination in the cleft of PDA, and the structure shows that the Fe(III) adapts to this by inducing numerous small distortions in the structure of the PDA ligand. The log K_1 values for PDA at 25 °C in 0.1 M $NaClO_4$ were determined by UV spectroscopy with Al(III) (log K_1=6.9), Ga(III) (log K_1=9.7), In(III) (log K_1=19.7), Fe(III) (log K_1=20.0), and Bi(III) (log K_1=26.2). The low values of log K_1 for PDA with Al(III) and Ga(III) are because these ions are too small for the cleft in PDA, which requires a large metal ion with an ionic radius (r^+) of 1.0 Å. In(III) and Fe(III) (r^+=0.86 and 0.72 Å for a coordination number (CN) of 7) are somewhat too small for the cleft in PDA but may adapt by increasing the coordination number, which increases the metal ion size, and have high log K_1 values. Very large log K_1 values are found, as expected, for Bi(III) (r^+=1.17 Å, CN=8), which fits the cleft quite well. Fluorescence studies show that Y(III) produces the largest CHEF (chelation enhanced fluorescence) effects, followed by La(III) and Lu(III), in the PDA complexes. Metal ions with nonfilled d or f subshells produce very large quenching of the fluorescence, as do heavy-metal ions such as In(III) and Bi(III), which have large spin−orbit coupling effects. The Al(III)/PDA complex produced an intense broad band at longer wavelength than the $\pi^*-\pi$ emissions of the PDA ligand, which is at a maximum at pH 6, and the possibility that this might reflect an exciplex, where one PDA ligand in the Al(III) complex π-stacks with the excited state of a second PDA ligand, is discussed.

Ligand preorganization[1] is of considerable interest, as seen in the use of preorganized ligands such as macrocycles[2] and cryptands[3,4] in a range of applications from biomedical[5,6] to the development of sensors for metal ions.[7−12] A preorganized[1] free ligand has the same conformation as is required to complex the target metal ion. Recently, metal ion complexing properties of the ligands PDA,[13,14] PDALC,[15] and DPP[16] were reported (see Figure 1 for a key to the ligand

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abbreviations). These ligands have a rigid phen backbone, with only limited movement possible for the donor groups at the 2- and 9-positions of the phen, leading to high[13−16] levels of preorganization. These ligands do not have a cavity, as do macrocycles and cryptands, but rather a rigid cleft that controls metal ion size based selectivity. Theoretical calculations[13] on PDA suggest that the carboxylates participate in the delocalization of the phen system and are somewhat constrained to lie in the plane of the ligand. PDA is thus highly preorganized for the complexation of large metal ions with an ionic radius (r^+) close to 1.0 Å. This corresponds to metal ions such as Ca^{2+} (1.12 Å, 8), Cd^{2+} (0.96 Å, 6), Gd^{3+} (1.11 Å, 9), or Th^{4+} (1.05 Å, 8) (ionic radii[17] (r^+) in parentheses, followed by a more typical coordination number for the metal ion to which r^+ refers[17]). The preference for large metal ions arises from the presence of three five-membered chelate rings in PDA, which leads to a preference for large metal ions,[18,19] as indicated in the following graphic:

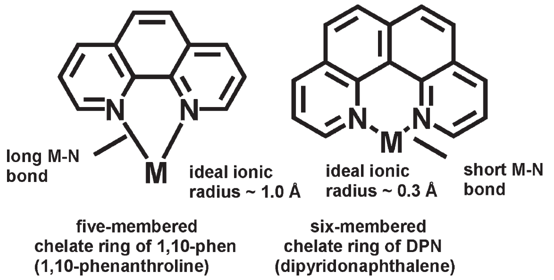

Table 1 shows the effect of high levels of preorganization of PDA on the log K_1 values[20] for PDA complexes, as compared to those of its much less preorganized analogue EDDA. Table 1 indicates that small metal ions such as Cu(II) and Zn(II) form complexes with PDA that are less stable than those with EDDA, due to these ions being too small for the rigid cleft[13] of PDA. Large divalent metal ions such Cd^{2+} and Ca^{2+}, which are close to the right size for the cleft of PDA, show quite large stabilizations compared to those of the EDDA complexes, while the too-large Pb^{2+} shows only a modest stabilization. What is of interest is the large stabilization of the PDA compared to the EDDA complexes shown by the Gd^{3+} and Th^{4+} complexes. The effect of higher cationic charge on the stability of complexes of PDA has been interpreted[14] in terms of the need for metal ions of higher charge to stabilize their complexes by H bonding with the solvent. A ligand such as phen has low[21a] affinity for Th^{4+} log $K_1 \approx 2$ (corrected[21b] to ionic strength 0.1 compared to 5 M NaCl in which log K_1 was determined). The low log K_1(phen) for Th(IV) arises because the coordinated phen is not able to H bond with the solvent. However, in a ligand such as PDA there is a synergistic effect between the negatively charged carboxylate groups, which act to lower the charge on the Th(IV), and the phen group, which now does not cause loss of stability because of the high charge on the Th(IV). One sees the remarkable increase in log K_1 in passing from the phen complex of Th(IV) with log $K_1 \approx 2$ to the PDA complex,[21] with log $K_1 = 25.7$, brought about simply by adding two carboxylate groups to phen to give PDA.

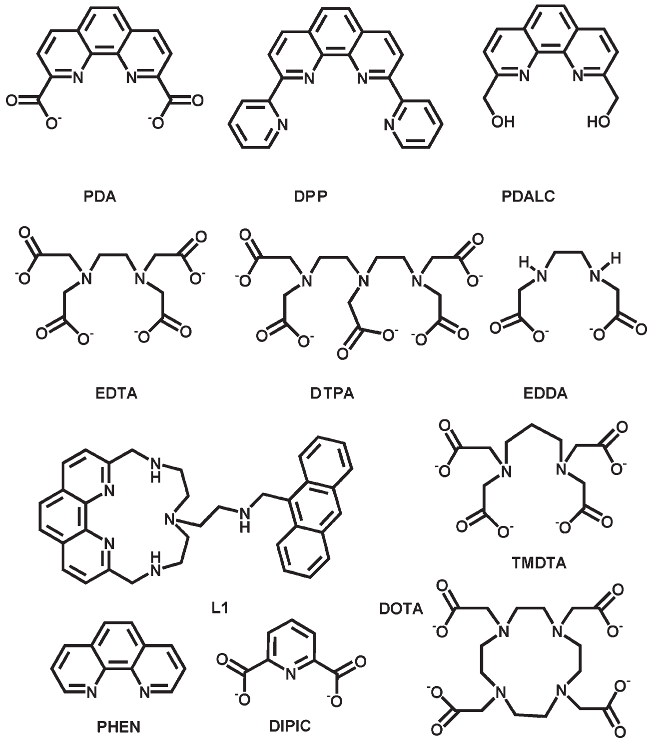

Figure 1. Ligands discussed in this paper.

The high affinity of PDA for metal ions of higher charge suggests that it would be of interest to study its complex formation with other trivalent metal ions in addition to the large Gd(III) and La(III) ions already studied.[13] In order to study M(III) ions covering a range of sizes and CN values, we report here a UV−visible study of the complex formation of the following M(III) ions (r^+, followed by CN to which r^+ refers in parentheses[17]): Al(III) (0.54 Å, 6), Ga(III) (0.62 Å, 6), Fe(III) (0.72 Å, 7), In^{3+} (0.86 Å, 7), and Bi^{3+} (1.17 Å, 8).

Since fluorescence sensing of metal ions by the CHEF (chelation enhanced fluorescence) effect is of considerable importance,[7−12] a fluorescence study of PDA and its complexes with trivalent metal ions in solution is reported here. The fluorescence studies are particularly useful in identifying species present at different pH values in solutions of M(III) ions and PDA. For example, unlike the absorption spectrum, the emission spectrum of the $PDAH_2$ species is very different from that of any of the other species present and allows one to be certain that at lower pH the complex is breaking down to produce $PDAH_2$ as in eq 1 (see below). Since it is of interest to know how an apparently too small metal ion such as

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[17] (a) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751. (b) The on-line listing of ionic radii from the paper of Shannon by D. J. van Horn, as an Excel file, was also consulted. (c) Note that ionic radii are used here, not to be confused with crystal radii, which are uniformly 0.14 Å larger.

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[21] (a) Xia, Y. X.; Chen, J. F.; Choppin, G. R. *Talanta* **1996**, *43*, 2073. (b) log $K_1 \approx 3.5$ (average of two values) for phen with Th(IV) was reported[21a] in 5 M NaCl. High ionic strength causes a considerable rise[20] in log K_1 for neutral ligands, so that one should estimate log K_1 at ionic strength 0.1 for comparison with other log K_1 values in this paper. Suitable examples of log K_1(phen) at both high and low ionic strength are not available, but for en log K_1 for Cu(II) varies linearly with ionic strength: μ=0.1, 10.49; μ=1.0, 10.80; μ=2.0, 10.96; μ=3.0, 11.38. To compare log K_1(phen) with log K_1(PDA), they both need to be at μ=0.1, so that a correction of about $^5/_3 \times (11.38 - 10.49)$ or 1.5 log units needs to be made, which suggests a rough value of log K_1(phen) for Th(IV) of ~2.

Table 1. Comparison of log K_1 Values for the Highly Preorganized Ligand PDA Compared to EDDA

	metal ion						
	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ca^{2+}	Th^{4+}	Gd^{3+}	Pb^{2+}
ionic radius[a] (Å)[17]	0.57	0.74	0.96	1.12	1.05	1.11	1.29
log K_1 PDA[13,14]	12.8	11.0	12.8	7.3	25.7	16.1	11.4
log K_1 EDDA[20]	16.8	11.1	9.1	4.0	13.9[b]	8.0	10.6
difference in log K_1 (log K_1 PDA vs EDDA)	−4.0	−0.1	+3.7	+3.3	+11.8	+8.1	+0.8

[a] Ionic radii (r^+) refer to more common coordination numbers (CN) of metal ions: Cu^{2+}, 4; Zn^{2+}, Cd^{2+}, 6; Ca^{2+}, Th^{4+}, Pb^{2+}, 8; Gd^{3+}, 9. A CN of 4 is appropriate for Cu(II), since it is Jahn−Teller distorted, and its effective size is then dictated by the four in-plane bonds lying in the plane of PDA. [b] Estimated from log K_1 for other aminocarboxylates as described previously.[14]

Fe(III) would coordinate with PDA, the crystal structure of $[Fe(PDA(H)_{1/2})(H_2O)_3](ClO_4)_2 \cdot 3H_2O \cdot {}^1/_2H_5O_2$ is reported here.

Experimental Section

Materials and Methods. PDA was synthesized by a literature method.[22] The metal perchlorates were obtained from VWR or Strem in 99% purity or better and used as received. All solutions were made up in deionized water (Milli-Q, Waters Corp.) of >18 MΩ cm^{-1} resistivity.

Synthesis of $[Fe(PDA(H)_{1/2})(H_2O)_3](ClO_4)_2 \cdot 3H_2O \cdot {}^1/_2H_5O_2$ (1). The ligand PDA (0.035 g, 0.132 mmol) was dissolved in 30 mL of absolute ethanol in a 50 mL three-necked round-bottomed flask. The pH of this solution was adjusted to approximately 4.0 using 1.0 mol dm^{-3} perchloric acid. The flask was attached to a condenser and allowed to reflux. Iron(III) perchlorate (0.0466 g, 0.132 mmol) was dissolved in absolute ethanol and added to the ligand solution dropwise over a period of 1 h. (*Caution!* Heating perchlorates with organic compounds may be explosive.) The solution of the complex was left to reflux for a further 1 h. This solution was then allowed to evaporate slowly. Yellowish orange rodlike crystals were deposited after 2 weeks. Anal. Calcd for $C_{14}H_{21}Cl_2FeN_2O_{19}$: C, 25.95; H, 3.27; N, 4.32. Found: C, 25.82; H, 2.92; N, 4.16.

Formation Constant Determination. These were determined by UV−visible spectroscopy following procedures similar to those reported previously[13,14] for studying PDA complexes. UV−visible spectra were recorded using a Varian 300 Cary 1E UV−visible spectrophotometer controlled by Cary Win UV Scan Application version 02.00(5) software. A VWR sympHony SR60IC pH meter with a VWR sympHony gel epoxy semimicro combination pH electrode was used for all pH readings, which were made in the external titration cell, with N_2 bubbled through the cell to exclude CO_2. The pH meter was calibrated prior to every titration, by means of titration of standard acid with standard base: the value of $E°$ for the cell, as well as the Nernstian slope, was obtained from a linear plot of measured values of E versus the calculated pH. The cell containing 50 mL of ligand/metal solution was placed in a bath thermostated to 25.0 ± 0.1 °C, and a peristaltic pump was used to circulate the solution through a 1 cm quartz flow cell situated in the spectrophotometer. The pH was altered in the range 2−12 by additions to the external titration cell of small amounts of standard $HClO_4$ or NaOH as required using a micropipet. After each adjustment of pH, the system was allowed to mix by operation of the peristaltic pump for 15 min prior to recording the spectrum, and to ensure proper mixing, the solution in the external cell was agitated with a magnetic stirrer.

For metal ions bound more weakly by PDA, such as the alkali-earth-metal ions, with log $K_1 < 10$, it is possible[13] to use the intense bands in the UV spectrum of PDA to monitor equilibria such as eq 1 as a function of pH and to calculate log K_1 from the known protonation constants of PDA:

$$M(PDA) + 2H^+ \leftrightarrows M^{2+} + PDAH_2 \qquad (1)$$

The approach in eq 1 is not practicable for metal ions with log $K_1 > 10$, but could be used here for Al(III) and Ga(III), which have quite low log K_1 values. For many metal ions, using the UV spectra to monitor competition as a function of pH between PDA and EDTA or DTPA for complexation of the metal ion proved feasible, as in eq 2. EDTA and DTPA usually have slightly higher log K_1 values[20] than the corresponding PDA complexes of these metal ions, but at lower pH values the PDA complexes are present because of the higher protonation constants of the EDTA and DTPA ligands:

$$M(PDA) + EDTAH_2{}^{2-} \leftrightarrows M(EDTA)^{2-} + PDA^{2-} + 2H^+ \qquad (2)$$

The transition from the PDA complex to the EDTA complex plus the free PDA ligand occurs at pH values typically above 6, so that the PDA is not protonated (the first protonation constant, pK_1, is equal to 4.75[13]). The approach in eq 2 proved suitable for all M(II) ions, as well as for La(III) and Gd(III), which are weaker Lewis acids compared to most non-lanthanide M(III) ions, and was used here for Fe(III). However, for Th(IV) and the $UO_2{}^{2+}$ ion, this approach proved to be of no use, since EDTA or DTPA were not able to displace PDA from its complexes. Only above pH 12, where the PDA was displaced by OH^- as shown in eq 3, could log K_1 values be calculated from a knowledge of the formation constants[20] of the $M(OH)_n$(aq) species:

$$M(PDA)^{(n-2)+} + n\,OH^- \leftrightarrows M(OH)_n(aq) + PDA^{2-} \qquad (3)$$

This is a well recognized approach[23] and was used[14] to measure log K_1 for the PDA complex of Th(IV). The same approach was used here to determine the log K_1 values for the PDA complexes of In(III) and Bi(III).

Fitting of theoretical absorbance versus pH curves was accomplished using the SOLVER module of EXCEL.[24] For a set of spectra for any one metal ion with PDA, SOLVER was used to fit protonation constants and molar absorptivities for the species in solution involving PDA. Most of the metal ions produced some absorbance down toward 200 nm, so that for simplicity wavelengths used in calculating log K_1 were limited to those above 250 nm. A further reason for not using absorbances below 250 nm is that a tiny fraction of the low-solubility PDA can form nanoparticles that cause strong absorbances down toward 200 nm, although we have found that extensive sonication removes this problem. For the determination of log K_1 the approach[14] for Al(III) and Ga(III) was based on eq 1, for

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Table 2. Formation Constants for PDA Complexes of Trivalent Metal Ions in 0.1 M $NaClO_4$ at 25 °C

metal ion	equilibrium	log *K*	method[a]	ref
H^+	$H^+ + OH^- \rightleftarrows H_2O$	13.78		20
	$PDA^{2-} + H^+ \rightleftarrows PDAH^-$	4.75		13
	$PDAH^- + H^+ \rightleftarrows PDAH_2$	2.53		13
Al^{3+}	$Al^{3+} + PDA^{2-} \rightleftarrows Al(PDA)^+$	6.9(1)	pH	this work
Ga^{3+}	$Ga^{3+} + PDA^{2-} \rightleftarrows Ga(PDA)^+$	9.7(1)	pH	this work
	$Ga(PDA)^+ + OH^- \rightleftarrows Ga(PDA)(OH)$	10.0(1)	pH	this work
	$Ga(PDA)OH + OH^- \rightleftarrows Ga(PDA)(OH)_2^-$	7.44(5)	pH	this work
In^{3+}	$In^{3+} + PDA^{2-} \rightleftarrows In(PDA)^+$	19.7(2)	OH^-	this work
	$In(PDA)^+ + H^+ \rightleftarrows In(PDA)H^{2+}$	2.6(1)	pH	this work
	$In(PDA)^+ + OH^- \rightleftarrows In(PDA)(OH)$	8.00(5)	pH	this work
	$In(PDA)(OH) + OH^- \rightleftarrows In(PDA)(OH)_2^-$	5.35(5)	pH	this work
	$In^{3+} + 4\,OH^- \rightleftarrows [In(OH)_4]^-$	33.9		20
Fe^{3+}	$Fe^{3+} + PDA^{2-} \rightleftarrows Fe(PDA)^+$	20.0(1)	EDTA	this work
	$Fe(PDA)^+ + H^+ \rightleftarrows Fe(PDA)H^{2+}$	2.5(1)	pH	this work
	$Fe(PDA)^+ + OH^- \rightleftarrows Fe(PDA)(OH)$	8.37(5)	pH	this work
	$Fe(PDA)(OH) + OH^- \rightleftarrows Fe(PDA)(OH)_2^-$	5.35(5)	pH	this work
	$Fe^{3+} + EDTA^{4-} \rightleftarrows Fe(EDTA)^-$	25.1		20
Bi^{3+}	$Bi^{3+} + PDA^{2-} \rightleftarrows Bi(PDA)^+$	26.2(1)	OH^-	this work
	$Bi(PDA)^+ + H^+ \rightleftarrows Bi(PDA)H^{2+}$	2.6(1)	pH	this work
	$Bi^{3+} + 4\,OH^- \rightleftarrows [Bi(OH)_4]^-$	31.9		20

[a] Methods of determination of log *K*: the pH method refers to determination of equilibrium constants directly from the variation of absorbance as a function of pH, which for the calculation of log K_1 values refers to eq 1; the OH^- method refers to determination of log K_1 from displacement of the metal ion from its PDA complex to form $M(OH)_n$(aq) species at high pH according to eq 3; the EDTA method refers to displacement of the metal ion from its PDA complex in the presence of EDTA as the pH is raised according to eq 2.

In(III) and Bi(III) the approach was based on eq 3, and for Fe(III) the approach was based on eq 2. The values obtained are given in Table 2, together with necessary literature values used in calculating log K_1 for PDA. The standard deviations given for log *K* values in Table 2 were calculated using the SOLVSTAT macro provided with ref 24.

Crystallography. A Rigaku Mercury diffractometer, using the ω scan mode, was employed for crystal screening, unit cell determination, and data collection. The structure of **1** $[Fe(PDA(H)_{1/2})(H_2O)_3](ClO_4)_2 \cdot 3H_2O \cdot {}^1/_2H_5O_2$ was solved by direct methods and refined to convergence.[25] Some details of the structure determination are given in Table 3, and crystal coordinates and details of the structure determination of **1** have been deposited with the CSD (Cambridge Structural Database).[26] A selection of bond lengths and angles for **1** is given in Table 4.

Fluorescence Measurements. .Emission spectra were determined on a Horiba Jobin Yvon Fluororlog-3 scanning fluorometer equipped with a 450 W Xe short arc lamp and a R928P detector. The instrument was configured to collect the signal in ratio mode with dark offset using 5 nm bandpasses on both the excitation and emission monochromators. The emission spectra were determined by measurements every 5 nm from 335 to 480 nm at 280 nm excitation wavelength. Scans were corrected for instrument configuration using factory-supplied correction factors. Postprocessing of scans was performed using the FluorEssence program.[27] The software eliminates Rayleigh and Raman scattering peaks by excising portions (±10−15 nm FW) of each scan centered on the respective scatter peak. Following removal of scatter peaks, data were normalized to a daily determined water Raman intensity (275ex/303em, 5 nm bandpasses). Replicate scans were generally within 5% agreement in terms of intensity and within bandpass resolution in terms of peak location. The fluorescence spectra of 2×10^{-5} M PDA plus a selection of M(III) PDA complexes were recorded in 10% methanol/90% water.

Table 3. Crystallographic Data for the Structure of **1**, $[Fe(PDA(H)_{1/2})(H_2O)_3](ClO_4)_2 \cdot 3H_2O \cdot {}^1/_2H_5O_2$

empirical formula	$C_{14}H_{21}Cl_2FeN_2O_{19}$
formula wt	646.08
T (K)	163(2)
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	7.9022(16)
b (Å)	12.389(3)
c (Å)	13.031(3)
α (deg)	82.55(3)
β (deg)	88.41(3)
γ (deg)	78.27(3)
V (Å^3)	1238.6(4)
Z	2
no. of rflns collected	4641
no. of indep rflns	4078
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0481 wR2 = 0.1268
R indices (all data)	R1 = 0.0552 wR2 = 0.1396

Results and Discussion

Formation Constants. The formation constants for the PDA complexes with M(III) ions determined here are seen in Table 2. In Table 5, a comparison is made between the log K_1 values for PDA complexes of M(III) ions and those of the less preorganized EDDA analogues. In parts a−g of Figures 2 are shown the sets of spectra obtained as a function of pH, all with 2×10^{-5} M PDA and, if present, 1:1 metal ion: (a, b) PDA ligand alone; (c) Al(III)/PDA; (d) Ga(III)/PDA; (e) In(III)/PDA; (f) Bi(III)/PDA; (g) Fe(III)/PDA. The spectra for the PDA ligand alone in Figure 2a,b are shown for purposes of comparison with the titrations in the presence of metal ions and have been previously analyzed[13] to yield $pK_1 = 4.75$ and $pK_2 = 2.53$.

A reviewer has pointed out that Moghimi et al.[28] have reported a glass-electrode study of the protonation constants of PDA in 50% ethanol/50% water, which

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(26) Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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Table 4. Bond Angles and Bond Lengths of Interest in **1**, $[Fe(PDA(H)_{1/2})(H_2O)_3](ClO_4)_2\cdot 3H_2O\cdot {}^1/_2H_5O_2$

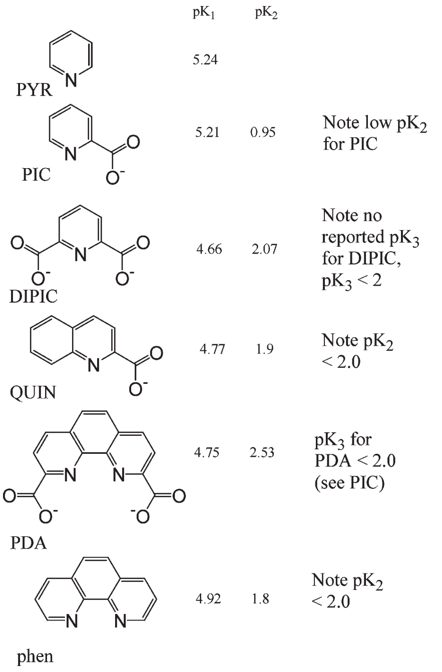
	Bond Lengths (Å)		
Fe(1)−O(5)	1.9682(12)	Fe(1)−O(6)	2.0032(12)
Fe(1)−O(7)	2.0590(11)	Fe(1)−O(3)	2.1211(12)
Fe(1)−N(2)	2.1891(13)	Fe(1)−O(2)	2.1938(12)
Fe(1)−N(1)	2.2157(13)		
	Bond Angles (deg)		
N(2)−Fe(1)−N(1)	70.57(5)	N(1)−Fe(1)−O(2)	69.77(5)
O(2)−Fe(1)−O(7)	74.06(4)	O(7)−Fe(1)−O(3)	75.62(5)
O(3)−Fe(1)−N(2)	71.17(5)	O(5)−Fe(1)−O7	94.93(5)
O(5)−Fe(1)−O(6)	178.53(5)	O(6)−Fe(1)−O(7)	84.71(5)
O(3)−Fe(1)−O(2)	148.26(4)	Fe(1)−N(1)- C(2)	121.36(10)
N(1)−C(2)−C(1)	110.18(13)	C(2)−C(1)−O(2)	116.75(14)
C(1)−O(2)−Fe(1)	121.49(10)	N(1)−C(13)−C(12)	115.04(14)
Fe(1)−N(1)−C(13)	119.36(11)	C(3)−C(2)−C(1)	127.60(15)

Table 5. Comparison of log K_1 Values for PDA Complexes of Trivalent Metal Ions with Those for the Much Less Preorganized EDDA Analogue [a]

	metal ion						
	Al^{3+}	Ga^{3+}	Fe^{3+}	In^{3+}	Gd^{3+}	La^{3+}	Bi^{3+}
ionic radius[b] (Å)	0.54	0.62	0.72	0.86	1.11	1.22	1.17
log K_1 PDA (this work)	6.9	9.7	20.0	19.7	16.1	13.5	26.2
log K_1 EDDA[20]	9.5[c]	14.0[d]	16.9[e]	16.5[c]	8.1	7.0	20.1[c]
diff in log K_1: (PDA vs EDDA)	−2.6	−4.3	+3.1	+3.2	+8.0	+6.5	+6.1
log K_1 DOTA[20]	17.0	21.3	29.4	23.9	22.4	22.0	

[a] The log K_1 values for DOTA are given to illustrate the weaker size-based selectivity of a macrocyclic ligand. [b] The ionic radii[17] refer to more common coordination numbers of the elements involved in complexes of polyaminocarboxylates[26] such as EDTA: Al^{3+} and Ga^{3+}, six-coordinate; Fe^{3+} and In^{3+}, seven-coordinate (average of r^+ for six- and eight-coordinate); Bi^{3+}, eight-coordinate; Gd^{3+}, La^{3+}, nine-coordinate. [c] Estimated by comparison with log K_1 for other aminocarboxylate ligands such as EDTA. [d] A value of log K_1 = 19.2 for EDDA with Ga(III) is suggested in ref [20], but this clearly cannot be correct in comparison with log K_1 for Ga(III) with other aminocarboxylates, such as log K_1 = 20.4 with EDTA, so that a more realistic estimate for log K_1 with EDDA is used here. [e] For ethylenediamine-*N*,*N*-diacetate rather than ethylenediamine-*N*,*N*′-diacetate.

has yielded very different p*K* values of 6.96, 3.42, 3.26, and 2.56, compared to those reported by us previously.[13] Protonation constants in 50% ethanol can be very different from those in pure water. We have now obtained preliminary values (single titration) for the protonation constants for PDA in 50% ethanol by UV−visible spectroscopy and obtained a pK_1 of 6.92, in reasonable agreement with the value of 6.96 reported by Moghimi et al. We obtained a pK_2 value of 3.86, somewhat higher than the value of 3.42 of Moghimi et al. This difference may reflect the fact that our study was carried out in 0.1 M $NaClO_4$, while that of Moghimi et al. was carried out in 0.1 M $NaNO_3$. A pK_3 value of ~1.4 in 50% ethanol was obtained by us. A reviewer expected us also to obtain four p*K* values in water for PDA, as was reported by Moghimi et al. in 50% ethanol. To show that it is likely that only two protonation equilibria are present for PDA in the pH range 2−9 studied in water, for the UV spectra for PDA in the pH range 3.36−9.02 four isosbestic points are observed in Figure 2a, so that no additional equilibria should be present. Similarly, in the pH range 2.3−3.36 in Figure 2b, two isosbestic points are observed, supporting the idea that only one protonation equilibrium is present in this pH range. To understand why PDA in water shows only two p*K* values above 2.0, one should consider the p*K* values in the graphic below (all data except PDA are from ref 20, ionic strength 0.1, 25 °C).



The graphic shows that addition of a carboxylate to pyridine to give PIC has very little effect on pK_1, and addition of a second carboxylate to give DIPIC actually lowers pK_1; thus, it is hard to rationalize a pK_1 value for PDA that is significantly higher than that for phen. One might ask why pK_2 for DIPIC is higher than pK_2 for PIC. The answer is indicated by structures in the CSD[26] (57 hits) which show that the diprotonated form of DIPIC has both protons attached to the carboxylates; this type of structure is clearly not possible for PIC. One sees for PIC that once one proton has been placed on the ligand, addition of a second proton in close juxtaposition to the first is very difficult. The same effect should be true for PDA once it has been diprotonated; i.e., addition of a third and fourth proton in close juxtaposition to the first two protons should be very difficult. This presents a powerful argument that pK_3 and pK_4 for PDA in water should be low (< 2.0), as found for pK_2 for PIC, and also QUIN. One notes also that QUIN has a lower first p*K* value than does PIC, which one attributes to the electron-withdrawing effect of the benzo group, also present in PDA.

A further comment by a reviewer is that the protonation constants of the M(III)/PDA complexes to yield M/PDAH complexes at about 2.6 (Table 2) might be unusually large. This behavior is also found for EDTA complexes, where protonation constants[20] for formation of $M(EDTA)H^+$ complexes are also about 2.6, and so is not particularly unusual.

Aluminum(III). The spectrophotometric titration for the Al(III)/PDA complex in Figure 2c shows that, at pH values less than 4, the spectrum is that of the protonated

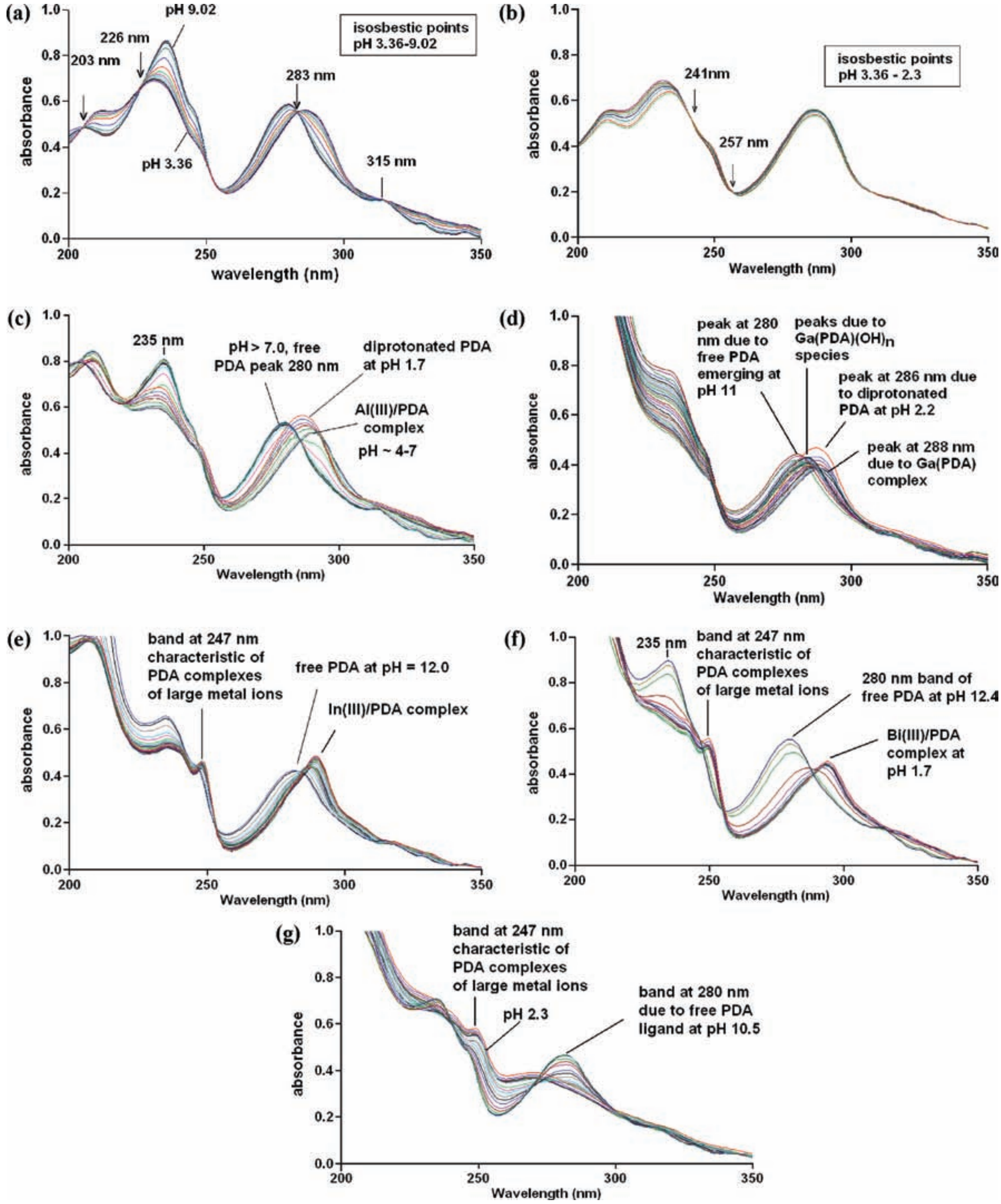


Figure 2. (a) UV spectroscopic titration of 2.00×10^{-5} M PDA in 0.1 M $NaClO_4$ between pH 3.36 and 9.02. The presence of four isosbestic points (at 203, 226, 283, and 315 nm) strongly supports the conclusion that there is but a single protonation equilibrium in this pH range. (b) UV spectroscopic titration of 2.00×10^{-5} M PDA in 0.1 M $NaClO_4$ between pH 2.3 and 3.36. The presence of two isosbestic points (at 241 and 257 nm) strongly supports the conclusion that there is but a single protonation equilibrium in this pH range. The small changes in the spectra with changing pH suggest that the protonation is occurring on a carboxylate rather than an N donor that is part of the chromophore. (c) UV spectrophotometric titration of 2.00×10^{-5} M PDA plus 2.00×10^{-5} M Al^{3+} in 0.1 M $NaClO_4$ between pH 1.7 and 12.0. Note the absence of a sharp band at 247 nm. (d) UV spectrophotometric titration of 2.00×10^{-5} M PDA plus 2.00×10^{-5} M Ga^{3+} in 0.1 M $NaClO_4$ between pH 1.7 and 11.0. Note the absence of a sharp band at 247 nm. (e) UV spectrophotometric titration of 2.00×10^{-5} M PDA plus 2.00×10^{-5} M In^{3+} in 0.1 M $NaClO_4$ between pH 1.7 and 12.0. Note the sharp band at 247 nm, which appears to be indicative of binding of the In(III) to all four donor groups of PDA. (f) UV spectrophotometric titration of 2.00×10^{-5} M PDA plus 2.00×10^{-5} M Bi^{3+} in 0.1 M $NaClO_4$ between pH 1.7 and 12.0. Note the sharp band at 247 nm,which appears to be indicative of binding of the Bi(III) to all four donor groups of PDA. (g) UV pectrophotometric titration of 2.00×10^{-5} M PDA plus 2.00×10^{-5} M Fe^{3+} in 0.1 M $NaClO_4$ between pH 1.7 and 10.5. Note the sharp band at 247 nm, which appears to be indicative of binding of the Fe(III) to all four donor groups of PDA.

PDA ligand. That this is the spectrum of the protonated PDA ligand ($PDAH_2$) is confirmed by the fluorescence spectra, as discussed below. The fluorescence spectra are a great aid to interpretation of the speciation, as the fluorescence spectrum of the $PDAH_2$ species is very different from that of the PDAH or PDA species. The UV spectra suggest that over a narrow pH range the Al(III)/PDA complex is present, until at pH >7 the

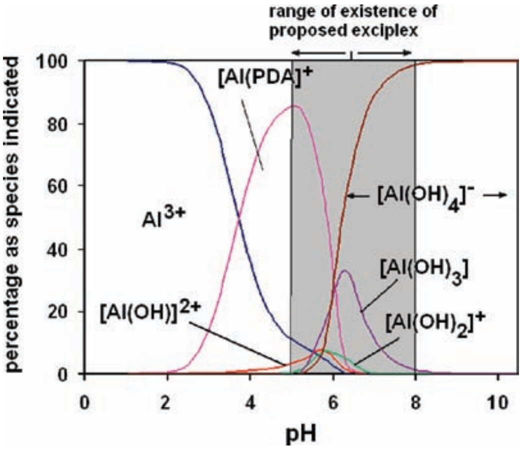


Figure 3. Species distribution diagram as a function of pH calculated for a 1:1 mixture of PDA and Al(III) at 2×10^{-5} M. The shaded area is the pH range over which fluorescence (see Figure 6) suggests the possible presence of an exciplex. Constants used refer (this work and ref [20] for Al(III) hydroxy species) to ionic strength 0.1 and 25.0 °C.

spectrum of the free nonprotonated PDA dianion is observed, characterized by bands at 280 and 235 nm. This breakdown of the Al(III) complex at higher pH, where the equilibrium is marked by an isosbestic point at 285 nm, is interpreted as the formation of the $[Al(OH)_4]^-$ anion.

One can calculate a constant for the equilibrium where the protons are displaced from PDA as the pH is raised, corresponding to eq 4, of log $K = 6.9$.

$$Al(PDA)^+ + 2H^+ \leftrightarrows Al^{3+} + PDAH_2 \qquad (4)$$

The Al(III)/PDA complex breaks up to produce the $[Al(OH)_4]^-$ ions and the PDA^{2-} ion, as in eq 3, at pH 5.92. From this and log $\beta_4 = 33.3$ at ionic strength 0 for the $[Al(OH)_4]^-$ ion, one can calculate a log K_1 value of 6.8 for the Al(III)/PDA complex. This is in reasonable agreement with the value obtained from eq 4, but since no value of log β_4 for the $[Al(OH)_4]^-$ anion at an ionic strength of 0.1 has been accepted,[20] the value of log K_1 from eq 4 is preferred. A species distribution diagram for the Al(III)/PDA system between pH 2 and 10 is seen in Figure 3. At higher pH the Al(III)/PDA complex is calculated to break down to the $[Al(OH)_4]^-$ anion.

Gallium(III). The spectra for the Ga(III)/PDA complex system at different pH values from 2 to 11 are seen in Figure 2d. The spectrophotometric titration for the Ga(III)/PDA system resembles that for Al(III)/PDA but is more complicated, due to the formation of what must be regarded as hydrolyzed $[Ga(PDA(OH)_n]$ species as the pH is raised. The pH-dependent equilibrium at about pH 2 is interpreted as corresponding to the equilibrium between $PDAH_2$ and the Ga(III)/PDA complex, as shown in eq 5. That this interpretation is correct is supported by the fluorescence spectra, as discussed below.

$$Ga(PDA)^+ + 2H^+ \leftrightarrows Ga^{3+} + PDAH_2 \qquad (5)$$

From eq 5, one is able to calculate log $K_1 = 9.7$ for the Ga(III)/PDA complex. Other pH-dependent equilibria are observed as the pH is raised, which are interpreted as hydrolysis of the Ga(III)/PDA complex, until at pH 11 the spectrum of the PDA dianion appears. The constants for the hydrolysis equilibria of the Ga(III)/PDA complex are given in Table 2.

Indium(III). The spectra for the In(III)/PDA complex system at different pH values from 2 to 11 are seen in Figure 2e. The appearance of the spectra for the In(III)/PDA complex is typical[13,14] of those of a large metal ion. Quite diagnostic is the sharp band at 247 nm, which is absent for the spectra of metal ions that are too small to bind all four donor atoms of PDA simultaneously, as seen for the small Al(III) and Ga(III) ions in Figure 2c,d. The sharp band at 247 nm is a $\pi-\pi^*$ transition, which in the free ligand is coupled to vibrations of the ligand that broaden the band. On formation of a complex with a large metal ion, the rigidity of the PDA in its complex with the metal ion increases greatly, and these vibrations are no longer coupled to the electronic transition, greatly sharpening the appearance of the band. This phenomenon is much more marked for complexes of DPP,[16] where several $\pi-\pi^*$ bands simultaneously undergo dramatic sharpening on formation of a complex with a large metal ion, but not a small metal ion. Figure 2e shows that the In(III)/PDA complex persists down to pH 2 and is only broken up by formation of $[In(OH)_4]^-$ at pH 12. The equilibrium constants for the In(III)/PDA system are given in Table 2, along with[20] log β_4 for formation of the $[In(OH)_4]^-$ complex used in calculating log K_1 for the PDA complex. It should be noted that with log $K_1 = 19.7$ for In(III) with PDA compared to 9.7 for Ga(III), PDA has produced the largest selectivity ($= 19.7 - 9.7 = 10.0$ log units) for In(III) relative to Ga(III) for any known[20] ligand. Usually the difference in log K_1 between In(III) and Ga(III) with any given ligand is 5 log units or less and is typically as large as 5 log units only with a ligand such as DTPA, with[20] log K_1 = 29.5 and 24.3, respectively, where presumably the larger In(III) is better at adapting to the octadenticity of the ligand.

Bismuth(III). The spectra for the Bi(III)/PDA complex system at different pH values from 2 to 11 are seen in Figure 2f. The system is quite similar to that for In(III)/PDA, with a sharp band at 247 nm typical of large metal ions. The pH-dependent equilibria in Figure 2f lead to the log K values given in Table 2, with log K_1 being calculated according to eq 3.

Iron(III). The spectra for the Fe(III)/PDA complex system at different pH values from 2 to 11 are seen in Figure 2g. The pH-dependent equilibria in Figure 2g, as well as equilibria in the presence of EDTA, lead to the log K values given in Table 2. One notes that at the lowest pH the Fe(III)/PDA spectrum has the peak at 247 nm typical of coordination to a large metal ion. This raises the interesting point of how a metal ion such as Fe(III), with an ionic radius[17] of only 0.72 Å even for seven-coordination, can span the gap between the two carboxylates of PDA.

General Considerations. The values of r^+ used in Table 5 for purposes of discussion refer to the more likely CN values of the metal ions involved, rather than a constant CN of 6 as used in previous discussions.[13,14] Use of r^+ values that refer to more appropriate CN values is more accurate, in that it gives a more realistic measure of metal ion size than does an r^+ value referring to a constant CN

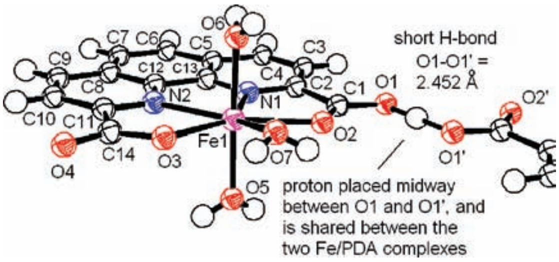


Figure 4. The $[Fe(PDA(H)_{1/2})(H_2O)_3]^{1.5+}$ complex cation in **1** showing the seven-coordinate Fe(III). The carboxylate from a second $[Fe(PDA(H)_{1/2})(H_2O)_3]^{1.5+}$ complex cation is shown on the right to indicate the proton that lies in the short H bond formed between O(1) and O(1)′. Thermal ellipsoids are not shown. The drawing was made with ORTEP.[43]

of 6. A reviewer has questioned the use of r^+ appropriate to CN = 4 for Cu(II). The rationale for CN = 4 for Cu(II) is that it is Jahn−Teller distorted, and its appropriate size is that relating to a square-planar metal ion lying within the plane of a single planar tetradentate ligand. In Table 5 is shown the selectivity (differences in log K_1) between the PDA complexes and the complexes of its less preorganized analogue EDDA. One notes from Table 5 the very large metal ion selectivity generated by the cleft of PDA against the too-small metal ions Al(III) and Ga(III). Also shown in Table 5 are log K_1 values for the macrocycle DOTA, which shows typical variation in log K_1 with metal ion size for this class of N-donor macrocycles with pendant acetate groups on the N-donors. PDA produces a better metal ion size based selectivity, In(III) > Ga(III) > Al(III), than does DOTA. This better selectivity occurs in spite of the fact that DOTA is octadentate and so might be expected to generate for In(III) superior metal ion size based selectivity against Al(III) and Ga(III), which seldom have[26] a CN value exceeding 6 with ligands that might provide water-stable complexes.

Structure of $[Fe(PDA(H)_{1/2})(H_2O)_3](ClO_4)_2 \cdot 3H_2O \cdot {}^1/_2H_5O_2$ (1). The structure of the complex cation of $[Fe(PDA(H)_{1/2})(H_2O)_3]^{1.5+}$ is displayed in Figure 4, and bond lengths and angles involving the Fe are given in Table 4. The proton necessary to balance the charge of a second perchlorate, if one has Fe(III) plus the formally dianionic PDA ligand, was located as two half-protons. The very short O(1)−O(1)′ distance of 2.452 Å shown in Figure 4 suggested a short H bond, and a single proton was placed halfway between O(1) (a carbonyl oxygen of PDA) and O(1)′ of a neighboring Fe(III)/PDA complex cation. This gives a half-proton per Fe(III)/PDA complex cation. The charge balance is completed by a half-proton bound between O(19) and O(20), the oxygens of the water molecules in the $H_5O_2^+$ cation, which is disordered over two positions and which forms an H-bond with O(19)- - -O(20) = 2.39 Å. The latter O- - -O separation is close to the average O- - -O separation in $H_5O_2^+$ cations found in the CSD of 2.43 ± 0.04 Å (40 hits). The presence of two half-protons per Fe(III)/PDA cation, one in the H bond between O(1) and O(1)′ and the other as part of half of a $H_5O_2^+$ cation, balances the charge on **1**. The short O(1)−O(1)′ H bonding distance of 2.453 Å is of interest because of the proposed role of such short H bonds in biology.[29] Many instances of such short H bonds involving oxygens from coordinated ligands have been observed.[30−32]

The Fe(III) in **1** is seven-coordinate, being almost a regular pentagonal bipyramid. It has been noted[33] that some metal ions expand their coordination number (CN), and hence M−L bond lengths, when coordinated to ligands that would fit better with a larger metal ion. This is seen in the structures[26] of the complexes of the small metal ions Mg(II) and Fe(III) with EDTA, where all chelate rings formed are five-membered, favoring larger metal ions. The Mg(II) and Fe(III) in their EDTA complexes are, like the Fe in **1** or the Mg(II) in its PDA complex,[34] seven-coordinate, with a coordinated water molecule, which increases their ionic radii. For the TMDTA complexes, the presence of a six-membered chelate ring shifts the size preference toward smaller metal ions, and so the Fe(III)/TMDTA complex[35,36] and Mg(II)/TMDTA complex[37,38] are six-coordinate. Thus, the Fe(III) in its PDA complex, and also Mg(II) in its PDA complex,[34] adopt a higher CN than usual, to accommodate the size preferences of the ligand for larger metal ions. There are four structures[39−42] of Fe(III) with CN = 7, where there is a coordinated phen or phen-like ligand, and these give an average Fe−N length to the phen-type nitrogens of 2.173 ± 0.044 Å, so that the Fe−N bond lengths in **1** of 2.188(2) and 2.216(2) Å appear normal. The Fe−O(2) bond in **1**, which is to the protonated carboxylate, as might be expected, is somewhat longer than Fe−O(3) to the nonprotonated carboxylate. The Fe−O bonds to carboxylates in **1**, even Fe−O(3) at 2.12 Å, are considerably longer than those in seven-coordinate Fe(III)/EDTA complexes, which average (11 structures[26]) 2.035 ± 0.064 Å. The Fe−O lengths to the carboxylates of PDA thus provide evidence of Fe−O bond stretching in the Fe(III)/PDA complex. MM (molecular mechanics) calculations suggest[13] that the strain-free O- - -O distance between the two carboxylates in PDA is 4.8 Å, giving low-strain M−O distances to the carboxylates of PDA complexes of half this distance, or 2.4 Å. For large metal ions coordinated to PDA the M−O

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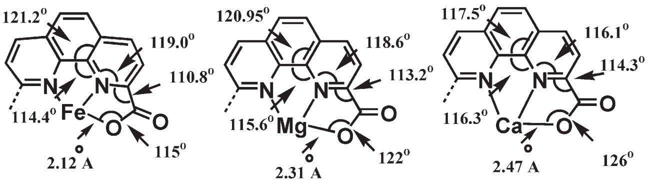
distances to the carboxylates of PDA are as follows: for Ca(II),[13] Ca−O = 2.47 and 2.46 Å; for[14] Th(IV), Th−O = 2.40 and 2.44 Å; for[14] UO_2^{2+}, U−O = 2.42 and 2.28 Å. The short Fe−O bond lengths in the Fe(III)/PDA complex are accompanied by numerous small distortions of the bond angles of the PDA ligand. A comparison of some bond angles in the coordinated PDA ligand for the Fe(III) complex and the much less sterically strained Ca(II) complex[13] is shown in the following graphic. Also included are the corresponding angles and lengths for the Mg(II)/PDA complex:[34]



The structure of **1** supports the idea that a sharp band[13,14] at 247 nm in the electronic spectrum of a PDA complex is an indication that the metal ion is able to bind to all four donor atoms of the ligand simultaneously. In response to a query from a reviewer, the spectrum of Mg(II)/PDA also shows a sharp band at 247 nm, in line with its solid-state structure[34] that shows all four donor atoms of PDA to be coordinated to the Mg. One sees that the dimensions given in the above graphic for the medium-small Mg(II) (r^+ = 0.81 Å, CN = 7) are all intermediate between those for the small Fe(III) (r^+ = 0.72 Å, CN = 7) and the large Ca(II) (r^+ = 1.12 Å, CN = 8) ions. A reviewer has pointed out that with a half-proton coordinated to a carboxylate per complex cation, the structure of **1** does not correspond exactly to any solution species present in the Fe(III)/PDA system, but one does not expect the presence of the proton to greatly alter the conclusions drawn from the structure of the complex. For metal ions such as Al(III) and Ga(III), which appear to be too small to contact all four donor atoms of the PDA simultaneously, no band is present at 247 nm, and accompanying this is a very low complex stability with PDA (Table 5).

Fluorescence Studies. The fluorescence spectra for 2 × 10^{-5} M PDA in 10% methanol/90% water at a variety of pH values ranging from 1.14 to 8.19 are shown in Figure 5a. The methanol was found to reduce the amount of Rayleigh scattering observed quite considerably. At the lowest pH values the species present must be the diprotonated $PDAH_2$ species, and it is noted that the fluorescence of this species is rather weak. In contrast, the $PDAH^-$ species, which is at a maximum at about pH 3.0, fluoresces the most strongly. This difference is important in confirming that at pH values down toward pH 2, the equilibrium being observed with a metal ion present does indeed involve formation of the $PDAH_2$ species as the pH is lowered. At higher pH values above 5 the fluorescence is constant and must be due to the nonprotonated dianion PDA^{2-}.

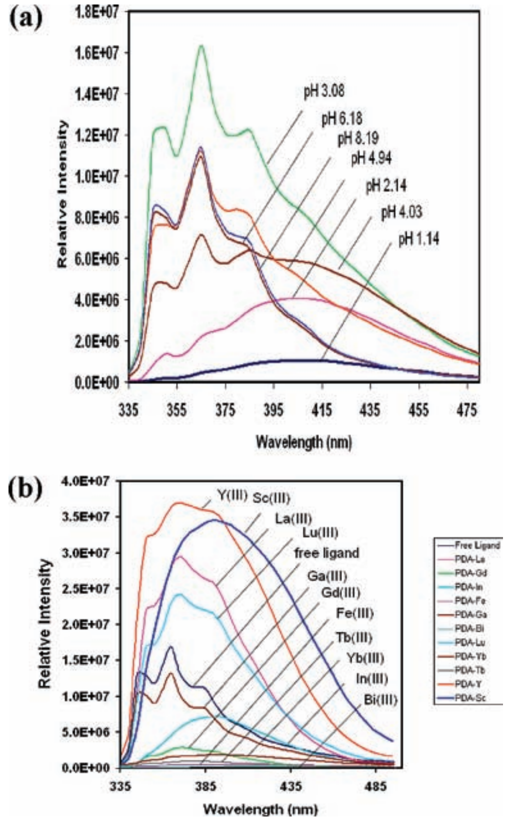


Figure 5. (a) Fluorescence spectra of 2 × 10^{-5} M PDA, in 10% methanol/90% water, at pH values ranging from 1.14 to 8.19. Excitation was with 280 nm radiation. (b) Fluorescence spectra of PDA and of some PDA complexes of trivalent metal ions in 10% methanol/90% water, all close to pH 4.0, at 2 × 10^{-5} M. Excitation was with 280 nm radiation.

The fluorescence spectra of a variety of M(III)/PDA complex ions, all at 2 × 10^{-5} M and pH 4.0, are seen in Figure 5b. At this pH all the complexes should be fully formed, except for the Al(III) complex discussed below, but without $M(PDA)OH_n$ species present. One notes that the Y(III) complex produces the largest CHEF effect, followed by La(III) and then Lu(III). The presence of large spin−orbit coupling effects, on atoms that are part of the fluorescent species, which effects increase with atomic number (Z), decreases fluorescence intensity.[44,45] One suggests that the order of the CHEF effect Y(III) > La(III) > Lu(III) reflects increasing spin−orbit coupling effects along the series, which increase intersystem crossing for the excited state and weaken fluorescence. The lighter Sc(III) ion (r^+ = 0.87 Å, CN 8), with its expected small spin−orbit coupliing effects, produces a CHEF effect nearly as strong as that due to Y(III), but, like In(III), which is also borderline for being large enough to coordinate in a strain-free manner with PDA, the peak is broadened and shifted to longer wavelength, with a loss of structure. It has been suggested[46] that M−N bond length distortion involving nitrogens on the fluorophore decreases the CHEF effect, and this may be the case here

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for the Sc(III) complex. All other M(III) ions studied produce a decrease in fluorescence intensity relative to the free PDA ligand. The lanthanide(III) ions Gd(III), Tb(III), and Yb(III) all have partly filled f subshells, and Fe(III) has a partly filled d subshell, which can accept electrons from the excited state and so quench fluorescence by the ET (electron transfer) mechanism.[44] Finally, heavy-metal ions such as Bi(III) have large spin−orbit coupling effects, which are more effectively linked to the fluorophore by the covalence of the Bi−N bonds, so that fluorescence in the Bi(III)/PDA complex is totally quenched. In this Bi(III) resembles Pb(II) and Hg(II), which are excellent quenchers of fluorescence when coordinated to the fluorophore. The lighter In(III) has smaller spin−orbit coupling effects, and probably also lesser covalence in the M−N bond, and so is not as effective as Bi(III) at quenching fluorescence.

Fluorescence of Al(III)/PDA. The fluorescence of the Al(III)/PDA complex at 2×10^{-5} M in 10% methanol/90% water is seen in Figure 6a. The fluorescence spectra of PDA at pH values from 2 to 4 resemble strongly those of the protonated forms of PDA ligand in Figure 5a, supporting the interpretation that the UV absorption spectra in this pH range in Figure 2c correspond to $PDAH_2$ and PDAH species produced by breakdown of the Al(III)/PDA complex at low pH. The fluorescence spectra for the Ga(III)/PDA system (not shown) confirm also the interpretation that the equilibrium centered on pH 2.0 corresponds to breakdown of the Ga(III)/PDA complex at low pH to give $PDAH_2$ and Ga^{3+}.

What is of interest in Figure 6a is the large emission peak at 435 nm that is at a maximum at pH 6.03. It is not present in the free ligand, in the PDA complexes of other metal ions, or even in 2×10^{-5} M Al^{3+} at various pH values with no PDA present. The Al^{3+} on its own was run in case the peak is simply light scattering by small amounts of colloidal $Al(OH)_3$ precipitate. The pH of its appearance does not correspond to any Al(III)/PDA species evident in the absorption spectra for the Al(III)/PDA system in Figure 2a. This type of behavior resembles the exciplex postulated for the Zn(II) complex of L1 (Figure 1) by Bianchi et al.[47] An exciplex is a complex formed[48] between a ground-state species and an excited-state species, and in the case of the Zn(II) complex of L1 it is suggested[47] that in solution the excited state of the anthracenyl group of L1 π-stacks on the phen portion of the ligand. The spectrum at pH 6.03 of the proposed exciplex in Figure 6 strongly resembles that found by Bianchi et al., in that the π*−π emissions of the fluorophore are still apparent, but a broad emission band at longer wavelength appears.

Following the approach of Bianchi et al.,[47] the appearance of the exciplex emission band may be obtained by subtracting the emission band of the free PDA ligand from the emission spectrum of the Al(III)/PDA complex at pH 6.0, where the exciplex is at a maximum. The rationale for this approach is that the π*−π emissions in the free PDA and in the Al(III)/PDA complex should be similar, with any differences being due to the exciplex.

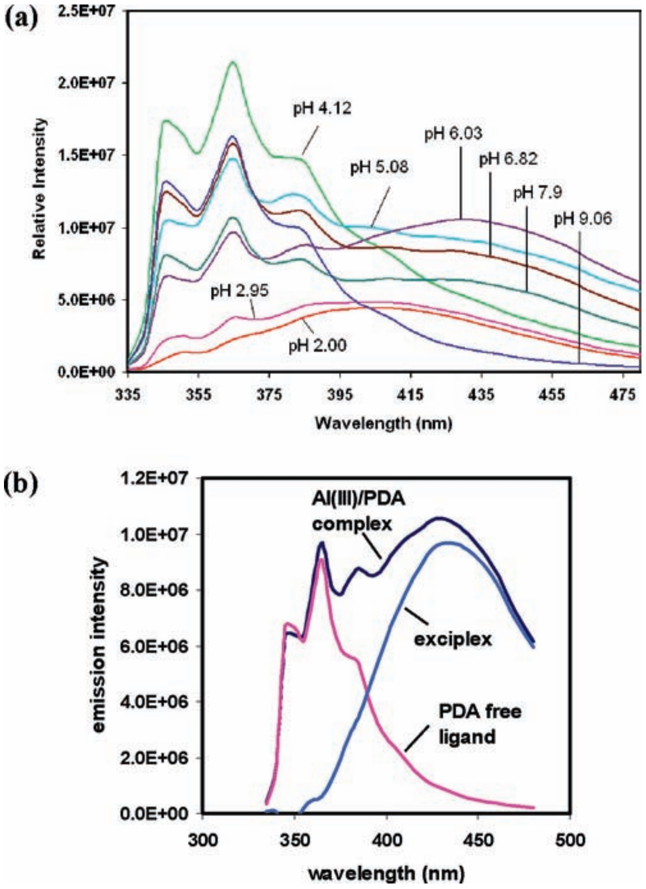

Figure 6. (a) Fluorescence spectra of 2×10^{-5} M Al^{3+} and PDA (1:1) at different pH values in 10% methanol/90% water. The wavelength of excitation is 280 nm. As discussed in the text, it is suggested that the peak at 435 nm, which is at a maximum at pH 6.03, may be an exciplex involving one Al(III) and two PDA ligands. (b) Emission spectrum of the proposed exciplex formed in 2×10^{-5} M PDA and Al^{3+} at pH 6.0. Following the report of Bianchi et al., the emission spectrum of the exciplex is generated by subtracting the emission spectrum of 2×10^{-5} M PDA free ligand at pH 6.0 from the emission spectrum of the Al(III)/PDA complex at pH 6.0.

The emission intensity of the two π*−π bands of the free PDA ligand at shortest wavelength was normalized on that of the same two bands in the Al(III)/PDA complex to obtain the best result. The resulting band in Figure 6b is the typical broad featureless band associated[47,48] with an exciplex.

It is not clear what form an exciplex of the Al(III)/PDA system might take. One notes from the species distribution diagram in Figure 3 that the band due to the proposed exciplex is at a maximum at pH ∼6, where the Al(III)/PDA complex would be about 50% of the PDA present, together with about 50% as the free PDA^{2-} anion, as seen in eq 6. The other half of the Al(III) would be present at pH ∼6 as the $[Al(OH)_4]^-$ anion.

$$Al(PDA)^{+} + 4OH^{-} \leftrightharpoons [Al(OH)_4]^{-} + PDA^{2-} \qquad (6)$$

The exciplex might involve an excited state of a second PDA^{2-} anion π-stacking on the PDA coordinated to the

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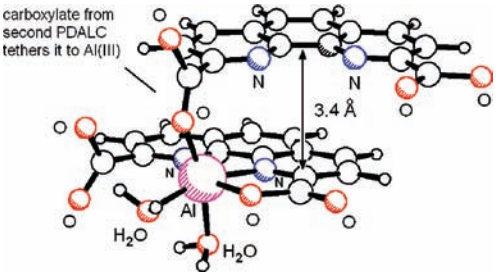

Figure 7. Possible structure for the exciplex postulated here to explain the emission spectra of the Al(III)/PDA system in Figure 6. The structure is an energy-minimized molecular mechanics model of an Al(III) complex with two PDA ligands, where the first PDA coordinates in a more normal, albeit tridentate, mode, and the second is tethered to the Al(III) by a single carboxylate. A reasonable interplanar distance of 3.4 Å for face-to-face π stacking of aromatic systems results. The upper PDA can swivel on the Al(III)−O pivot, to alter the overlap of the two PDA ligands and maximize the π-stacking interaction, which is not included in the MM model, so that the relative alignment of the two PDA ligands may not be exactly as shown. The structure was generated using HyperChem,[48] and the drawing was made with ORTEP.[43]

Al(III). Modeling this with HyperChem[49] by a simple MM calculation, using the default MM parameters in the program, suggests a structure of the type shown in Figure 7. The role of the Al(III) in this model would be to tether the second PDA ligand via a coordinated carboxylate oxygen, to bring it close to the PDA coordinated to the Al(III), and also to perturb the electron density in the π system of the coordinated PDA.

Conclusions

The ligand PDA shows strong size-based selectivity in that the log K_1 values of the PDA complexes of the too small Al(III) and Ga(III) ions are very low. Somewhat larger metal ions such as In(III) and Fe(III) appear able to adapt and coordinate to all four donor atoms of PDA and have higher log K_1 values, while a very large metal ion such as Bi(III) has very high log K_1 values. The sharp band at 247 nm in the electronic spectra of the PDA complexes appears to be a good indicator of whether the metal ion is able to coordinate with all four donor atoms of PDA simultaneously. The band at 247 nm is absent for the PDA complexes of the very small Al(III) and Ga(III) ions but present for all the larger M(III) ions studied, including the theoretically somewhat too small Fe(III) and In(III) cations. The structure of the Fe(III)/PDA complex confirms that the somewhat too small Fe(III) is able to coordinate to all four donor atoms of PDA by (a) expanding its coordination number to 7 instead of the more common 6 and (b) inducing numerous small bond angle distortions in the PDA ligand. Accompanying the ability to coordinate in a tetradentate fashion with PDA, one sees that log K_1 is high for the medium-sized In(III) and very high for the large Bi(III). The ability of metal ions to induce a CHEF effect in the PDA complexes follows current thinking on factors that control the fluorescence of metal ion complexes. Thus the CHEF effect varies in the order Y(III) > La(III) > Lu(III), the order of increase in atomic weight Y(III) < La(III) < Lu(III), and hence of spin−orbit coupling,[44] that weakens fluorescence by promoting intersystem crossing. For metal ions with partially filled d orbitals (Fe(III)) or f orbitals (Gd(III), Tb(III), Yb(III)) fluorescence is almost completely quenched by the photoinduced electron transfer mechanism.[44] For heavy metal ions such as In(III), and particularly the heavy Bi(III) ion, fluorescence of the PDA complexes is strongly quenched by the covalence of the M−N bonds, which acts to increase the interaction between the π system of the fluorophore and the spin−orbit coupling effects on the metal ion. For Al(III), a strong broad peak at 435 nm, which is at a maximum at pH 6.0, is tentatively interpreted as being due to the presence of an exciplex in solution.

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(49) *Hyperchem program, version 7.5*; Hypercube, Inc., 419 Philip Street, Waterloo, Ontario N2L 3X2, Canada.