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Article

Complexation of Metal Ions of Higher Charge by the Highly Preorganized Tetradentate Ligand 2,9-Bis(hydroxymethyl)-1,10-Phenanthroline. A Crystallographic and Thermodynamic Study

Raymond T. Gephart III,[†] Neil J. Williams,[†] Joseph H. Reibenspies,[‡] Alvaro S. De Sousa,[§] and Robert D. Hancock*,[†]

[†]*Department of Chemistry and Biochemistry, University of North Carolina at Wilmington, Wilmington, North Carolina 28403,* [‡]*Department of Chemistry, Texas A&M University, College Station, Texas 77843, and* [§]*Department of Chemistry, University of the Witwatersrand, Johannesburg 2050, South Africa*

The metal ion selectivity for M(III) (M = metal) ions exhibited by the highly preorganized ligand PDALC is investigated (PDALC = 2,9-bis(hydroxymethyl)-1,10-phenanthroline). The structures are reported of $[Bi(PDALC)(H_2O)_2(ClO_4)_3] \cdot H_2O$ (**1**), monoclinic, $P2_1/c$, $a = 12.8140(17)$, $b = 19.242(3)$, $c = 9.2917(12)$ Å, $\beta = 91.763(2)°$, $V = 2289.9(5)$ Å^3, $Z = 4$, $R = 0.0428$; $[Th(PDALC)(NO_3)_4] \cdot 3H_2O$ (**2**), monoclinic, $P2_1/n$, $a = 7.876(3)$, $b = 22.827(9)$, $c = 12.324(5)$ Å, $\beta = 94.651(6)°$, $V = 2208.4(15)$ Å^3, $Z = 4$, $R = 0.0669$; $[Cd(PDALC)_2](ClO_4)_2$ (**3**),), triclinic, $P\bar{1}$, $a = 7.5871(16)$, $b = 13.884(3)$, $c = 14.618(3)$ Å, $\alpha = 74.081(2)°$, $\beta = 88.422(2)°$, $\gamma = 78.454(2)°$, $V = 1450.2(5)$ Å^3, $Z = 2$, $R = 0.0267$. The Bi in **1** is best regarded as 9-coordinate, with four short bonds to the PDALC, and two short bonds to the coordinated water molecules, with three long bonds to perchlorate oxygens. The Bi−N bonds at 2.35 Å are by a considerable margin the shortest Bi−N bonds to 1,10-phenanthroline (phen) type ligands, which is suggested to be due to the Bi adapting to the metal ion size requirements of PDALC. The Th(IV) in **2** is 12-coordinate, with four bonds to PDALC, and the four chelated nitrates, with close to normal bond lengths to the PDALC ligand. The Cd(II) in **3** is 8-coordinate, with Cd−N and Cd−O bonds that are similar to those found in other 8-coordinate Cd(II) complexes. The five known structures of PDALC complexes, including the three reported here, suggest that the M−N bonds to PDALC are quite easily varied in length in response to differing metal ion sizes, but that the M−O bonds are more constrained by the rigid ligand to be close to the ideal value of 2.50 Å. The formation constants (log K_1) for M(III) ions with PDALC show that for small metal ions such as Ga(III) and Fe(III), log K_1 is only slightly higher than for phen, suggesting that these metal ions are too small to coordinate to the alcoholic oxygen donors of PDALC. For larger metal ions such as Bi(III), Gd(III), Th(IV), and UO_2^{2+}, log K_1 for PDALC is higher than log K_1 for phen by more than 5 log units, which stabilization is attributed to the fact that PDALC is preorganized for complexation with large metal ions with an ionic radius of about 1.0 Å. The fluorescence of M(III) complexes of PDALC is discussed. PDALC free ligand gives fluorescence typical of phen ligands, with the protonated form giving a broad less intense band, and the non-protonated form of the ligand giving an intense structured set of bands. Large lanthanide ions without partially filled f-subshells, such as La(III), Lu(III), and also Y(III), give a fairly strong CHEF (chelation-enhanced fluorescence) effect, while those with partially filled f-subshells, such as Gd(III), Yb(III), and Tb(III), strongly quench the fluorescence of PDALC. A heavy element such as Bi(III) has strong spin−orbit coupling effects that act to quench the fluorescence of PDALC almost completely, which effect is enhanced by the covalence of the Bi−N bonds.

Introduction

Ligand preorganization[1] is of ongoing interest[2] because of the potential of improved complexing ability and enhanced metal ion selectivity that it affords. Prominent ligands of higher levels of preorganization are the familiar macrocycles[3,4] and cryptands.[5] Of interest are non-macrocyclic ligands of high levels of preorganization,[6] which offer advantages such as lower cost, greater ease of synthesis,

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*To whom correspondence should be addressed. E-mail: hancockr@uncw.edu.

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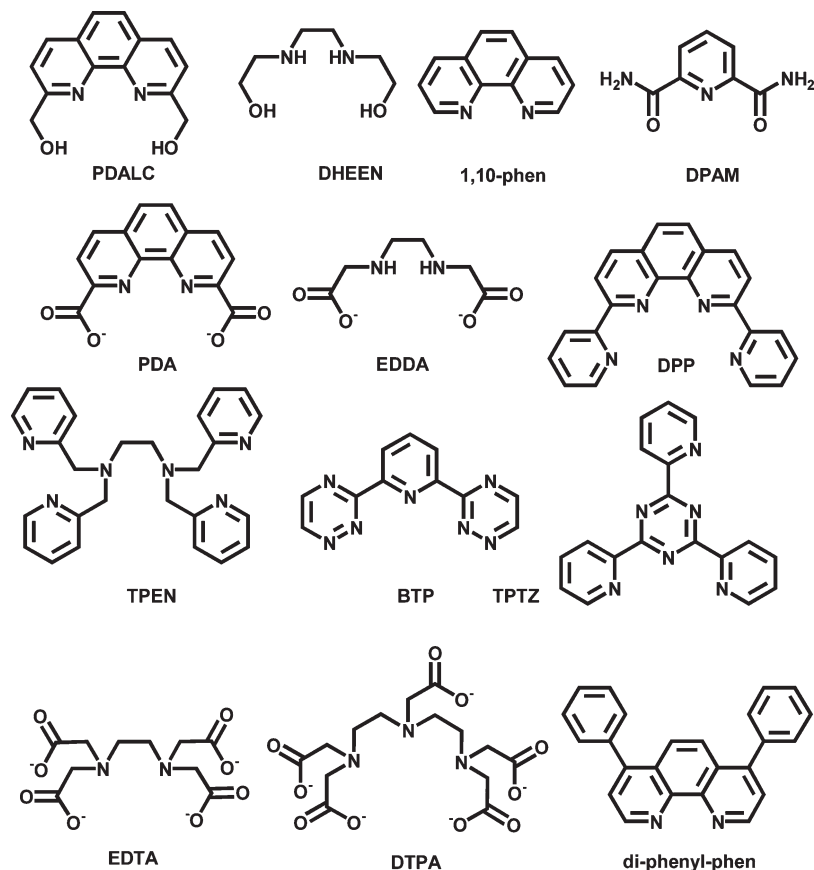
Figure 1. Ligands discussed in this paper.

and potentially rapid metalation and demetalation kinetics, which can be an advantage where metal ion separations are needed. Recent work on ligands such as PDA,[7,8] DPP,[9] and PDALC[10] (see Figure 1 for key to ligand abbreviations) has shown that non-macrocyclic ligands based on the rigid phen backbone, which have donor groups *ortho* to the N-donors (nitrogen donors) of phen, achieve levels of preorganization that rival or surpass those of macrocycles and cryptands, but have rapid metalation reactions. This is evidenced by log K_1 (formation constant) values for PDA of unprecedented levels[7-10] for a tetradentate ligand, that dwarf those of less preorganized analogues such as EDDA, and rival or exceed those even of hexadentate ligands such as EDTA.

Ligands such as PDALC,[10] or PDA[7,8] and DPP,[9] show metal ion size-based recognition that depends not on a cavity in the ligand, as is present in macrocycles, but on a fairly rigid cleft that shows selectivity for metal ions with an ionic radius[11] (r^+) of about 1.0 Å. The preference for larger metal ions with r^+ about 1.0 Å arises from the fact that these ligands form three 5-membered chelate rings. Chelate

ring-size is a dominant architectural feature in controlling metal ion size-based selectivity,[2] with 5-membered chelate rings promoting selectivity for large metal ions of r^+ about 1.0 Å (M−N bond lengths of ∼ 2.5 Å) while 6-membered chelate rings promote selectivity for very small metal ions with M−N ∼ 1.5 Å, as suggested in the following graphic:
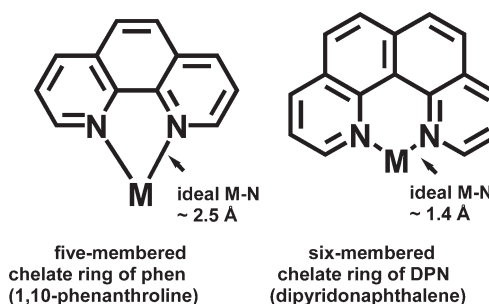
Metal ions such as Th(IV) show[8] greatly enhanced affinity for ligands such as PDA. Thus, while log K_1 for phen with Th(IV) is only[12,13] about 2, log K_1 with PDA is[8] 25.6. This represents an almost 24 log unit increase in log K_1 simply from adding two carboxylate groups to phen to give PDA.

The high log K_1 values of PDA with most metal ions are an advantage if one aims to complex metal ions so that they do not become lost from the ligand, as in biomedical

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applications such as Gd(III) complexes used as MRI agents.[15−17] If, however, one is interested in using a ligand as the basis for an extractant, where complexation should be reversible so that the ligand can be reused, then such strong complexation is undesirable. In a study of complexation of M(II) ions, PDALC has been found[10] to complex metal ions more weakly than PDA. This would be expected from the presence of two alcoholic oxygens on PDALC, which are much weaker bases than the carboxylates of PDA. However, PDALC shows[10] the expected selectivity toward larger metal ions with r^+ of about 1.0 Å, as found for PDA. PDALC has also shown[10] levels of preorganization much higher than for the analogue DHEEN, with low levels of preorganization because of free rotation about the bonds, as indicated in the graphic below:
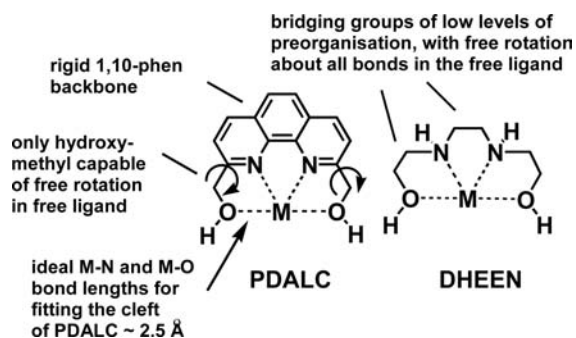
An application where selectivity toward larger metal ions might be of use is in the separation of Am^{3+} ($r^+ = 0.97$ Å[11]) and Cm^{3+} ($r^+ = 0.97$ Å[11]) from Ln^{3+} (Ln = lanthanide) ions, which is important in the treatment of nuclear waste.[18] The major difference between An(III) (An = actinide) and Ln(III) ions lies in the greater covalence[19,20] in the M−L (metal−ligand) bonding of the An(III) ions. Thus, PDALC with its N-donors should have considerable selectivity for An(III) ions over Ln(III) ions, as has been found for the N-donor ligands BIP,[21] TPEN,[22] 4,7-diphenyl-phen,[23] and TPTZ.[24−28] Ligands such as DPAM have also been reported[29] for the

extraction of Am^{3+}, as well as S-donor ligands.[30] Density functional theory (DFT) studies have been reported in relation to the differences in covalence between Ac(III) and Ln(III) metal−ligand bonding.[31] Thorium continues to be of interest in its potential application in breeder reactors,[32] where it would be used in the "thorium cycle" to produce the fissionable ^{233}U isotope. In this paper are reported log K_1 values for PDALC with metal ions of higher charge, including the Th(IV) and the UO_2^{2+} ions, as representatives of actinide chemistry. To examine the metal ion size-based selectivity of PDALC, log K_1 values for M(III) ions covering a range of sizes are included (metal ion radius[11] (r^+) followed by coordination number (C.N.) to which r^+ refers): Ga(III) (0.62 Å, 6), Fe(III) ($r^+ = 0.73$ Å, 7), In^{3+} ($r^+ = 0.86$ Å, 7), Lu(III) ($r^+ = 1.03$ Å, 9), and Bi^{3+} ($r^+ = 1.17$ Å, 8). The tetravalent Th(IV) has $r^+ = 1.09$ Å for C.N. = 9, and from typical U−O bonds in the plane of complexes of the UO_2^{2+} cation, it appears[8] to have an effective $r^+ \sim 1.1$ Å as applied to ligands binding in the plane. The structures of the PDALC complexes of Bi(III), Th(IV), and Cd(II) are reported here as examples of PDALC complexes of larger metal ions, to determine how well PDALC is preorganized for complexation with these larger metal ions. Phenanthroline-based ligands such as DPP have been found[9] to show a strong CHEF (chelation enhanced fluorescence) effect with suitably sized metal ions. The fluorescence properties of PDALC and a selection of its complexes with M(III) ions are also reported here.

Experimental Section

Materials and Methods. PDALC was synthesized by a literature method.[33] 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 [Bi(PDALC)(H₂O)₂(ClO₄)₃]·H₂O (1). 0.0222 g of PDALC (0.09240 mmol) was dissolved in *n*-butanol and placed in a 50 mL beaker. Then 7.043 mL of 0.01312 M Bi(NO₃)₃ in sufficient HClO₄ to give a pH of about 1.0 was added along with enough H₂O to make the two layers of equal volume. The beaker was covered with Parafilm with a few small holes punched in it to allow for slow evaporation. As the layers evaporated, the complex slowly crystallized out of solution. The crystals of **1** were separated and dried under vacuum. Elemental microanalysis: Calculated for C₁₄H₁₈BiCl₃N₂O₁₇: C, 21.71%; H, 2.34%; N, 3.62%. Found: C, 21.82%; H, 2.53%; N, 3.67%.

Synthesis of [Th(PDALC)(NO₃)₄]·3H₂O (2). A 0.0016 g portion of PDALC (0.002 mol) was dissolved in *n*-butanol (5 mL) and placed in a 50 mL beaker. Then 0.1 mL of 0.10 M Th(NO₃)₄ at in 1.0 M HNO₃ was added along with enough H₂O to make the two layers of equal volume. The beaker was covered with Parafilm with a few small holes punched in it to allow for slow evaporation. As the layers evaporated, the complex slowly crystallized out of solution. The crystals of **2** were separated and dried under vacuum. Elemental microanalysis: Calculated for C₁₄H₁₈ThN₆O₁₇: C, 21.71%; H, 2.34%; N, 10.85%. Found: C, 21.90%; H, 2.39%; N, 9.98%.

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Table 1. Crystallographic Details for [Bi(PDALC)(H$_2$O)$_2$(ClO$_4$)$_2$](ClO$_4$)·H$_2$O (**1**), [Th(PDALC)(NO$_3$)$_4$]·3H$_2$O (**2**), and [Cd(PDALC)$_2$](ClO$_4$)$_2$ (**3**)

	1	2	3
empirical formula	C$_{14}$H$_{18}$Cl$_3$N$_2$O$_{17}$Bi	C$_{14}$H$_{18}$N$_6$O$_{17}$Th	C$_{28}$H$_{24}$Cl$_2$N$_4$O$_{12}$Cd
formula weight	801.63	774.38	791.81
temperature	110(2) K	110(2) K	110(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Unit Cell Dimensions			
a (Å)	12.8140(17)	7.876(3)	7.5871(16)
b (Å)	19.242(3)	22.827(9)	13.884(3)
c (Å)	9.2917(12)	12.324(5)	14.618(3)
α (deg)	90	90	74.081(2)
β (deg)	91.763(2)	94.651(6)	88.422(2)
γ (deg)	90	90	78.454(2)
volume (Å^3)	2289.9(5)	2208.4(15)	1450.2(5)
Z	4	4	2
Final R indices			
[$I > 2\sigma(I)$]	R1 = 0.0428	R1 = 0.0669	R1 = 0.0267
	wR2 = 0.1020	wR2 = 0.1617	wR2 = 0.0701
R indices (all data)	R1 = 0.0497	R1 = 0.0812	R1 = 0.0281
	wR2 = 0.1099	wR2 = 0.1765	wR2 = 0.0711

Synthesis of [Cd(PDALC)$_2$](ClO$_4$)$_2$ (3). A 0.0204 g portion of PDALC (0.08491 mmol) dissolved in *n*-butanol was placed in a 50 mL beaker. A 835 μL portion of 0.1016 M Cd(NO$_3$)$_2$ was added along with enough H$_2$O to make the two layers of equal volume. The beaker was covered with parafilm with just the lip of the beaker uncovered. On evaporation, the complex slowly crystallized out as colorless crystals. Calculated for C$_{28}$H$_{24}$Cl$_2$-N$_4$O$_{12}$Cd: C, 43.43%; H, 3.12%; N, 7.24%. Found: C, 42.24%; H, 3.03%; N, 7.45%.

Molecular Structure Determination. A Bruker SMART 1K diffractometer using the omega scan mode, was employed for crystal screening, unit cell determination, and data collection at 110(2) K. The structures were solved by direct methods, and refined to convergence.[34] Absorption corrections were made using the SADABS program.[35] All hydrogens were located in difference Fourier maps (including those at ideal positions). The structure of **2** was non-merohedrally twinned and was refined with the HKLF 5 option from two rotationally related matrices. The nitrates in **2** were present as two 50% disordered sets. In one set the nitrates are all tilted in one direction, as seen in Figure 3b, while the other set is approximately a mirror image of the first. Some details of the structure determinations are given in Table 1, and crystal coordinates and details of the structure determinations of **1**, **2**, and **3** have been deposited with the CSD (Cambridge Structural Database).[36] A selection of bond lengths and angles that illustrate the coordination geometries around the metal ions in **1**, **2**, and **3** are given in Tables 2, 3, and 4, and the structures of **1**, **2**, and **3** are shown in Figures 2−4.

Formation Constant Determination. These were determined by UV−visible spectroscopy following procedures similar to those reported previously[7−10] 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 each titration, by means of titration of standard acid with

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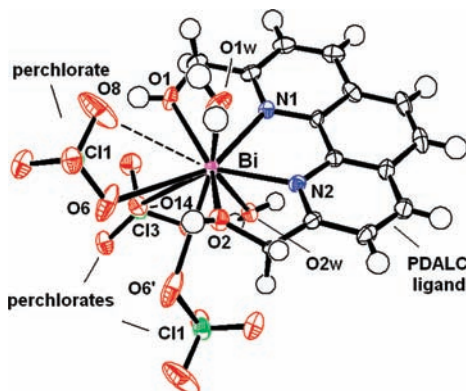(36) Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, United Kingdom.

Table 2. Bond Lengths and Angles of Interest in [Bi(PDALC)(H$_2$O)$_2$(ClO$_4$)$_2$]-(ClO$_4$)·H$_2$O (**1**)

Bond Lengths (Å)

Bi(1)−O(1W)	2.303(5)	Bi(1)−N(2)	2.350(5)
Bi(1)−N(1)	2.354(5)	Bi(1)−O(2W)	2.412(5)
Bi(1)−O(1)	2.450(4)	Bi(1)−O(2)	2.469(4)
Bi(1)−O(6)	3.019(4)	Bi(1)−O(14)	2.991(4)
Bi(1)−O(6')	3.306(4)		

Bond Angles (deg)

O(1W)−Bi(1)−N(2)	79.58(18)	O(1W)−Bi(1)−N(1)	77.50(18)
N(2)−Bi(1)−N(1)	70.00(18)	O(1W)−Bi(1)−O(2W)	148.26(18)
N(2)−Bi(1)−O(2W)	75.49(16)	N(1)−Bi(1)−O(2W)	75.73(16)
O(1W)−Bi(1)−O(1)	80.68(16)	N(2)−Bi(1)−O(1)	134.17(17)
N(1)−Bi(1)−O(1)	65.52(16)	O(2W)−Bi(1)−O(1)	103.09(15)
O(1W)−Bi(1)−O(2)	75.23(15)	N(2)−Bi(1)−O(2)	64.70(16)

Table 3. Bond Lengths and Angles of Interest in [Th(PDALC)(NO$_3$)$_4$]·3H$_2$O (**2**)[a]

Bond Lengths (Å)

Th(1)−N(1)	2.632(8)	Th(1)−N(2)	2.628(7)
Th(1)−O(1)	2.476(7)	Th(1)−O(2)	2.466(8)
Th(1)−O(11)	2.567(15)	Th(1)−(12)	2.641(16)
Th(1)−O(31)	2.621(15)	Th(1)−O(32)	2.640(16)
Th(1)−O(51)	2.513(15)	Th(1)−O(52)	2.575(15)
Th(1)−O(71)	2.527(16)	Th(1)−O(72)	2.591(16)

Bond Angles (deg)

O(1)−Th(1)−O(2)	176.7(3)	N(1)−Th(1)−N(2)	62.2(4)
O(1)−Th(1)−N(1)	61.2(4)	O(2)−Th(1)−N(2)	60.0(4)
O(1)−Th(1)−O(71)	65.3(4)	O(2)−Th(1)−O(71)	113.5(4)
O(71)−Th(1)−O(72)	49.8(4)	O(2)−Th(1)−O(72)	68.5(4)

[a] The nitrates were present as two disordered sets, and Bi−O bond lengths to one set only are given.

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 thermostatted 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 to 12 by additions to the external titration cell of small amounts of standard HClO$_4$

Figure 2. Structure of **1**, the complex [Bi(PDALC)(H$_2$O)$_2$(ClO$_4$)$_3$], showing the numbering scheme for donor atoms coordinated to the Bi. Thermal ellipsoids are shown at the 50% probability level. Drawing made with the Oak Ridge Thermal Ellipsoid Plot (ORTEP) program.[14]

Table 4. Bond Lengths and Angles of Interest in [Cd(PDALC)$_2$](ClO4)$_2$ (**3**)

Bond Lengths (Å)			
Cd(1)−N(2)	2.3421(17)	Cd(1)−N(1)	2.3497(16)
Cd(1)−N(4)	2.3498(16)	Cd(1)−N(3)	2.3517(16)
Cd(1)−O(2)	2.4601(16)	Cd(1)−O(3)	2.5074(15)
Cd(1)−O(4)	2.5090(15)	Cd(1)−O(1)	2.5211(16)

Bond Angles (deg)			
N(2)−Cd(1)−N(1)	70.56(5)	N(4)−Cd(1)−N(3)	70.68(6)
N(2)−Cd(1)−O(2)	65.95(6)	N(1)−Cd(1)−O(3)	77.16(5)
O(2)−Cd(1)−O(3)	92.70(6)	N(2)−Cd(1)−O(4)	79.12(5)
N(1)−Cd(1)−O(4)	81.51(5)	O(2)−Cd(1)−O(4)	96.01(6)
N(1)−Cd(1)−O(1)	65.82(5)	O(2)−Cd(1)−O(1)	157.96(6)
O(3)−Cd(1)−O(1)	90.37(5)	O(4)−Cd(1)−O(1)	89.65(5)

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.

PDALC is moderately water-soluble (∼10^{-3} M) but has intense bands in the UV that can be used to monitor complex-formation[10] in solution. Theoretical absorbance versus pH curves were fitted using the SOLVER module of EXCEL.[37] For a set of spectra for any one metal ion with PDA, SOLVER was used to fit protonation constants and molar absorbtivities for the species in solution involving PDA. For the M(III) ions studied here the approach[10] based on eq 1 was followed for the determination of log K_1, and the values obtained are given in Table 2. The standard deviations given for log K values in Table 2 were calculated using the SOLVSTAT macro provided with reference 37.

$$[M(PDALC)]^{n+} + H^+ \rightleftharpoons M^{n+} + (PDALC)H^+ \qquad (1)$$

Fluorescence measurements. Emission spectra (ES) fluorescence properties were determined on a Horiba Jobin Yvon Fluorolog-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 at 280 nm excitation wavelength. Scans were corrected for instrument configuration

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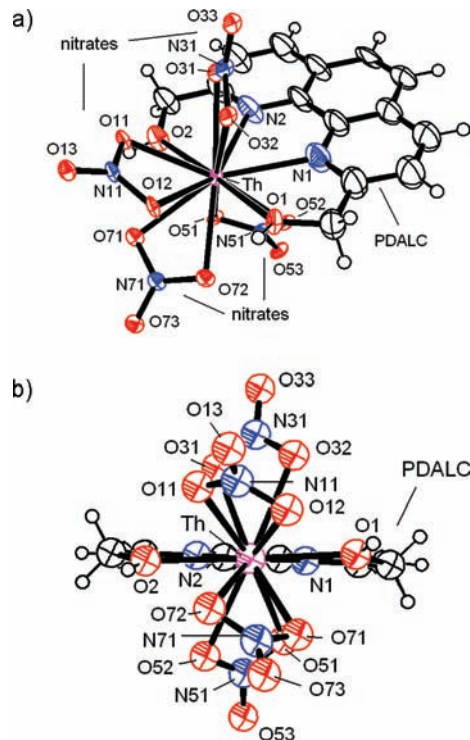(38) *FluorEssence program*, version 2.1; HORIBA Jobin Yvon, Inc.: Edison, NJ.

Figure 3. (a) Structure of **2**, the complex [Th(PDALC)(NO$_3$)$_4$]·3H$_2$O, showing the numbering scheme for nitrates and for donor atoms coordinated to the Bi. The nitrates are 50% disordered over two sets of orientations, and only one set of orientations is shown. The numbering scheme is such that the N and O atoms from the same nitrate have the same first digit. Thermal ellipsoids are shown at the 50% probability level. Drawing made with ORTEP.[14]. (b) View of the complex [Th(PDALC)-(NO$_3$)$_4$] down what is effectively a 2-fold rotational axis, showing one set of the two 50% occupancy disordered sets of nitrates, coordinated to the thorium, and all tilted in the same direction. The other set of nitrates is oriented in the opposite sense to those shown. Drawing made with ORTEP.[14]
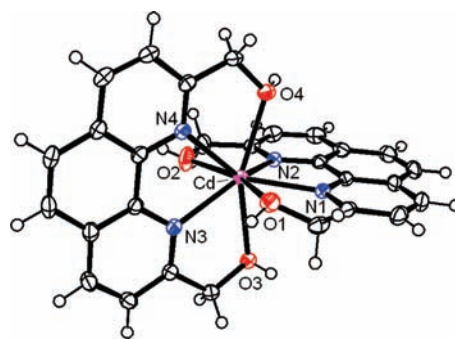

Figure 4. Structure of the complex cation [Cd(PDALC)$_2$]$^{2+}$ from **3**, showing the numbering scheme for donor atoms coordinated to the Cd. Thermal ellipsoids are shown at the 50% probability level. Drawing made with ORTEP.[14]

using factory supplied correction factors. Post processing of scans was performed using the FluorEssence program.[38] 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,

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Table 5. Metal−Nitrogen and Metal−Oxygen Bond Lengths to the PDALC Ligand in PDALC Complexes

metal ion:	Cd(II)	Th(IV)	Ca(II)	Bi(III)	Pb(II)
ionic radius (Å):[a]	0.96	1.09	1.12	1.17	1.29
M−N in PDALC (Å):[b]	2.35	2.63	2.50	2.35	2.49
M−O in PDALC (Å):[b]	2.50	2.47	2.42	2.46	2.63

[a] Ionic radii from ref 11. The radii refer to more usual coordination numbers for the metal ions Cd^{2+} (6), Th^{4+} (9), Ca^{2+} (8), Bi^{3+} (8), Pb^{2+} (8). [b] Bond lengths from structures of PDALC complexes from this work, or ref 10 (Ca^{2+} and Pb^{2+}).

data were normalized to a daily determined water Raman intensity (275ex/303em, 5 nm band-passes). Replicate scans were generally within 5% agreement in terms of intensity and within band-pass 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/water.

Results and Discussion

Formation Constant Studies. The log K_1 values measured for the metal ions studied here with PDALC are seen in Table 6. In all cases there was a clear transition from the spectrum of the M(III)/PDALC complex to that of the protonated form of PDALC as the pH was lowered, and from the equilibrium constants calculated for eq 1 in each case it was possible to calculate log K_1(PDALC) from a knowledge of the protonation constant of the ligand. Corrections were made for the fact that for some of the more acidic metal ions, the species present in solution where the PDALC complex was formed was actually a hydroxo complex such as $[Bi(OH)]^{2+}$. In Figure 5a are shown the spectra of 2×10^{-5} M Th(IV) and PDALC at a range of pH values from 1.77 to 8.26. In Figure 5b are shown the variation of absorbance with pH at six wavelengths for the same system. The solid lines are theoretical curves calculated using EXCEL,[37] and protonation equilibria with constants at the pH values shown. In Table 7 are shown the stabilization afforded the complexes of PDALC compared to the analogous complexes with phen. The structural change in the ligand that occurs in passing from phen to PDALC is the addition of two neutral alcoholic oxygen donors at the 2 and 9 positions of phen. It has been observed[2,42−45] that such addition of neutral oxygen donors to ligands shifts selectivity in the direction of larger metal ions, and Table 7 shows that for the M(III) ions studied, this holds true. Thus, for the small Ga(III) and Fe(III) ions, only a small increase in log K_1 for PDALC relative to phen is observed. As the metal ions increase in size, this increase in log K_1 becomes larger, and is at a maximum for Ln(III) ions, where the stabilization is as much as 5.5 log units. This is much larger than the stabilization produced by adding two hydroxyethyl groups to en to give DHEEN, for example, which for the large Ca(II) and Pb(II) ions results

in only about 1 log unit of stabilization.[10,13] For large M(III) ions, the stabilization of the PDALC relative to the phen complexes is generally above 5.2 log units, while for large M(II) ions, this stabilization is only about 2.8 log units. A possible explanation for this phenomenon may be that the M(III) ions are stronger Lewis acids toward the neutral alcoholic O-donors of PDALC than is the case for M(II) ions. For Th(IV), no structures of complexes with phen are known,[36] and calculation of species distribution diagrams shows that these should be hydrolyzed to give metal hydroxide. The high stability of its complexes with PDALC allows Th(IV) to produce complexes that can be crystallized from 0.1 M HNO$_3$, where hydrolysis is not a problem. The high affinity of the UO$_2^{2+}$ cation for PDALC is due to its effectively large size[8] with in-plane bonds that correspond to a metal ion with an ionic radius of about 1.1 Å.

Structural Studies; [Bi(PDALC)(H$_2$O)$_2$(ClO$_4$)$_3$]·H$_2$O (1). The structure of **1** is seen in Figure 2, and bond lengths and angles of interest in **1** are given in Table 2. The Bi in **1** is possibly 9-coordinate, depending on where one regards a Bi−L bond as being too long to count as a bond. In **1** there are four short bonds to the donor atoms of PDALC and a further two short bonds to water molecules. There are also three long bonds to ClO$_4^-$ oxygens: Bi−O(14), 2.99(4) Å; Bi−O(6), 3.019(4) Å; Bi−O(6′), 3.306(4) Å, with the latter two bonds representing an O(6) bridging between adjacent Bi atoms. There is a long Bi−O contact of 3.405(4) Å to O(8) from a ClO$_4^-$, which may be too long to be regarded as a bond. The structure is typical of those observed for Bi(III), or for Pb(II), where a stereochemically active lone pair is present.[46−57] One sees unusually short M−L bonds on the side of Bi(III) or Pb(II) away from the proposed site of the stereochemically active lone pair, while the M−L bonds become longer as one moves around the metal ion to the site of the lone pair. More covalently bound donor atoms tend to occupy the site opposite the lone pair. The lone pair on the Bi(III) in **1** must be near the very long bonds to the ionically bound ClO$_4^-$ oxygen donors, opposite the N-donors of the PDALC ligand.

What is of interest here is how well the Bi(III) fits into the cleft of PDALC. For Bi(III) structures with the phen

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Table 6. Formation Constants for PDALC Complexes in 0.1 M NaClO$_4$ at 25 °C

| metal ion	equilibrium	log K
H$^+$	H$^+$ + OH$^-$ ⇌ H$_2$O	13.78^a
	PDALC$^-$ + H$^+$ ⇌ PDALCH$^+$	4.70^b
Ga^{3+}	Ga^{3+} + PDALC ⇌ Ga(PDALC)$^{3+}$	6.5(1)
	Ga(PDA)$^+$ + OH$^-$ ⇌ Ga(PDA)(OH)	8.7(1)
	Ga(PDA)OH + OH$^-$ ⇌ Ga(PDA)(OH)$_2$$^-$	5.9(10)
In^{3+}	In^{3+} + PDALC ⇌ In(PDALC)$^{3+}$	9.1(1)
	In(PDA)$^{3+}$ + OH$^-$ ⇌ In(PDA)(OH)$^{2+}$	9.56(5)
Fe^{3+}	Fe^{3+} + PDALC ⇌ Fe(PDALC)$^{3+}$	6.9(1)
	Fe(PDALC)$^{3+}$ + OH$^-$ ⇌ Fe(PDALC)(OH)$^{2+}$	7.28(5)
	Fe(PDALC)(OH)$^{2+}$ + OH$^-$ ⇌ Fe(PDALC)(OH)$_2$$^+$	5.11(5)
Bi^{3+}	Bi^{3+} + PDALC ⇌ Bi(PDALC)$^{3+}$	8.3(1)
	Bi(PDALC)$^{3+}$ + OH$^-$ ⇌ Bi(PDALC)(OH)$^{2+}$	8.3(1)
	Bi(PDALC)(OH)$^{2+}$ + OH$^-$ ⇌ Bi(PDALC)(OH)$_2$$^+$	6.0(1)
	Bi(PDALC)(OH)$_2$$^+$ + OH$^-$ ⇌ Bi(PDALC)(OH)$_3$	4.0(1)
UO$_2$$^{2+}$	UO$_2$$^{2+}$ + PDALC ⇌ UO$_2$(PDALC)$^{2+}$	6.25(5)
	UO$_2$(PDALC)$^{2+}$ + OH$^-$ ⇌ UO$_2$(PDALC)(OH)$^+$	7.5(1)
	UO$_2$(PDALC)(OH)$^+$ + OH$^-$ ⇌ UO$_2$(PDALC)(OH)$_2$	4.4(1)
Th^{4+}	Th^{4+} + PDALC ⇌ Th(PDALC)$^{4+}$	7.2(1)
	Th(PDALC)$^{4+}$ + OH$^-$ ⇌ Th(PDALC)(OH)$^{3+}$	8.6(1)
	Th(PDALC)(OH)$^{3+}$ + OH$^-$ ⇌ Th(PDALC)(OH)$_2$$^{2+}$	5.2(1)
Lu^{3+}	Lu^{3+} + PDALC^{2-} ⇌ Lu(PDALC)$^+$	6.4(1)
	Lu(PDALC)$^{3+}$ + OH$^-$ ⇌ Lu(PDALC)(OH)$^{2+}$	8.61(5)
	Lu(PDALC)(OH)$^{2+}$ + OH$^-$ ⇌ Lu(PDALC)(OH)$_2$$^+$	6.72(5)

^{a} Reference 13. ^{b} Reference 10.
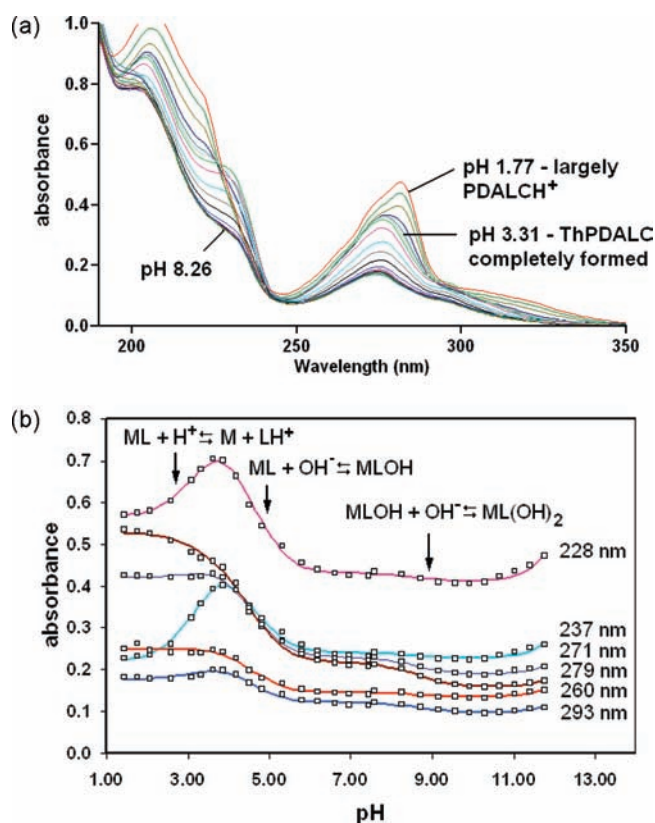
Figure 5. (a) Spectra of 2.00 × 10^{-5} M Th(IV)/PDALC solution in 0.1 M NaClO$_4$ in the pH range 1.77 to 8.26. (b) Variation of absorbance as a function of pH at the six wavelengths indicated for 2 × 10^{-5} M PDALC/Th(IV) in 0.1 M NaClO$_4$ at 25 °C. The points (□) are the experimental values of absorbance, while the solid lines are theoretical curves of absorbance versus pH calculated for pH-dependent equilibria corresponding to those indicated (M = Th(IV), L = PDALC).

ligand, the Bi—N bond lengths vary greatly depending on whether the phen is coordinated opposite the lone pair, or near to it. When very covalently bound anionic S-donor ligands are present, these occupy the site opposite the lone pair, and long Bi—N bonds to the phen averaging (6 structures in the CCD^{36}) 2.79 ± 0.05 Å result. When the phen N-donors occupy the site opposite the lone pair, short Bi—N bonds (21 structures in the CCD) are observed averaging 2.55 ± 0.08 Å. What is interesting in the structure of **1** is that the Bi—N bonds to PDALC at 2.350(5) and 2.354(5) Å are considerably shorter than any Bi—N bonds observed in the above phen complexes. It is difficult to assess the Bi—O bonds to the alcoholic groups, since these do not occupy the favored site opposite the lone pair. The Bi—O bonds at about 2.46 Å are somewhat longer than the Bi—N bonds to PDALC, but are shorter than Bi—O bonds to alcoholic oxygens in the CCD, which average about 2.67 Å (six structures). Bi(III) appears from its ionic radius (Table 7) to be too large for the cleft of PDALC. It adapts to this problem by producing a large distortion in response to the stereochemically active lone pair, which results in unusually short Bi—N and Bi—O bonds involving the PDALC, allowing it to coordinate with the PDALC more efficiently.

[Th(PDALC)(NO$_3$)$_4$]·3H$_2$O (2). The structure of [Th-(PDALC)(NO$_3$)$_4$]·3H$_2$O (**2**) is seen in Figure 3a, and bond lengths and angles of interest in **2** are given in Table 3. The Th in **2** is 12-coordinate, which C.N. for Th(IV) is largely limited to the [Th(NO$_3$)$_6$]$^{2-}$ anion (10 structures in the CCD^{36}), or structures containing NO$_3$$^-$ plus other small unidentate or bidentate ligands. The four nitrates coordinated to the Th are present as two disordered sets with 50% occupancy. The numbering scheme is such that N and O-atoms of the nitrates with the first digits as odd numbers (N11, O12, N32, N73, etc.) all belong to one set, and those starting with even numbers belong to the other. Atoms with the same first digit (e.g., N11, O11, O12, O13) all belong to the same nitrate. Steric crowding dictates that all four nitrates in one set are oriented in the same direction, as seen in Figure 3b, while the other set is oriented in the opposite

Table 7. Comparison of log K_1 for Some PDALC Complexes with log K_1 for the Corresponding phen Complexes

Metal ion:	Ga^{3+}	Fe^{3+}	In^{3+}	Lu^{3+}	Gd^{3+}	Th^{4+}	UO_2^{2+}	La^{3+}	Bi^{3+}
ionic radius[a] (Å):	0.62	0.73	0.86	1.03	1.11	1.09	1.1	1.22	1.17
log K_1(PDALC)[b]:	6.5	6.9	9.1	6.4	6.2	7.2	6.3	5.3	8.3
log K_1(phen)[c]:	(6.4)[d]	6.5	6.8[e]	(0.9)[f]	(0.9)[f]	(2)[g]		(0.9)[f]	(5.9)[h]
difference in log K_1: (log K_1(PDALC) −log K_1(phen))	0.1	0.4	2.3	5.5	5.5	5.2		5.3	2.4

[a] Ionic radii from ref 11. The radii refer to more usual coordination numbers for the metal ions in, e.g., the EDTA complexes: Ga^{3+} (6), Fe^{3+} (7), In^{3+} (7), Lu^{3+} (9), Gd^{3+} (9), La^{3+} (9), Bi^{3+} (8), Th^{4+} (9). The radius for UO_2^{2+} is derived from U−L bond lengths in the plane of the complex. [b] log K_1 values this work and ref 10. [c] Ref 13. [d] The literature value of log K_1 = 5.4 for Ga(III) with phen selected in ref 13 was determined[39] in sulfate medium. The value used here was corrected for the complexation of Ga(III) by sulfate, by comparison with log K_1 of phen for In(III), which has been determined in both sulfate,[39] and also[40] 0.1 M $NaClO_4$. [e] Ref 40. [f] A value of log K_1 = 2.6 for Nd(III)[41] with phen in 5 M NaCl has been accepted,[13] which indicates log $K_1 \sim$ 0.9 as a rough figure for Ln(III) ions with phen when corrected to ionic strength (μ) 0.1 by comparison with other neutral ligands where log K_1 is known both at both μ = 0.1 and 5.0. [g] Ref 41; in 5 M NaCl converted to μ = 0.1 as for Nd(III). [h] Ref 42 reports log K_1 for 2,2′-bipyridyl (bipy) with Bi(III) = 4.5, so that a value for the phen complex may be estimated from the observation[2] that log K_1(phen) for any one metal ion $\sim$ log K_1(bipy) + 1.4.

sense. The question of interest in **2** is how well the Th(IV) fits into the cleft of PDALC. Apart from the PDA complex of Th(IV),[8] there are no reported structures of phen or bipy type ligands coordinated to Th(IV) in the CCD. Six structures containing pyridines that are part of chelating ligands such as 8-hydroxyquinoline yield Th−N bonds that average 2.70 ± 0.11 Å, which suggests that the Th−N bonds in **2** averaging 2.63 Å might be slightly shorter than usual. The Th−O bonds to the alcoholic oxygen donors of the PDALC complex at 2.47(1) Å are considerably shorter than the Th−N bonds, which is normal for a "hard"[58,59] metal ion such as Th(IV).

[Cd(PDALC)₂](ClO₄)₂ (3). The structure of [Cd(PDALC)₂](ClO₄)₂ (**3**) is seen in Figure 4, and bond lengths and angles of interest for **3** are given in Table 4. The Cd in **3** is 8-coordinate, with Cd−N bonds that average 2.35 Å and Cd−O bonds that average 2.50 Å. The Cd−N bonds in **3** at 2.35 Å are somewhat shorter than found in the CCD (5 hits) for eight-coordinate Cd(II), where Cd−N averages 2.41 Å. It is difficult to be certain what the ideal Cd−O bond length is for 8-coordination with neutral O-donors, since most of such 8-coordinate structures refer to crown ethers which have steric constraints of their own. However, in the structure[60] of a polyglycol with 8-coordinate Cd(II) the Cd−O bonds to the alcoholic oxygens average 2.35 Å, suggesting that if anything the Cd−O bonds in **3** are a little long.

General Comments on PDALC Structures. The common feature of the PDALC structures reported here and elsewhere[10] are that the cleft of the ligand appears to constrain the M−O bond lengths to be fairly close to the ideal values of about 2.5 Å for coordination in the cleft, but the M−N bond lengths to the N-donors of the phen part of PDALC are much more variable, as seen in Table 5. This would be expected from the architecture of the cleft of PDALC, where there is little to constrain the variation of the M−N bond lengths, which can vary simply by the metal ion moving further in or out of the cleft. Variation of the M−O bond lengths is more constrained, however, with the hydroxymethyl groups of PDALC unable to move much to accommodate metal ions of differing sizes. Only for the very large Pb(II) ion are the Pb−O lengths considerably longer than the ideal
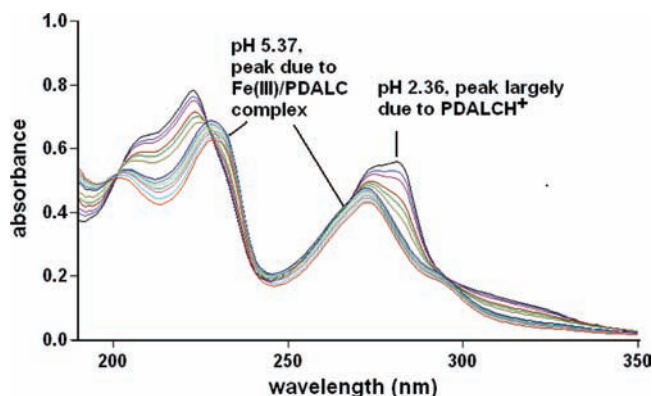
Figure 6. Spectra of 2.00×10^{-5} M Fe(III)/PDALC solution in 0.1 M $NaClO_4$ in the pH range 2.36 to 7.36.

length of 2.50 Å. One notes that the Pb(II) in its PDALC complex[10] lies somewhat above the plane containing the O-donors of the ligand, which appears to reflect the fact that Pb(II) is too large for the cleft.

Fluorescence of PDALC and its M(III) Complexes. In Figures 6 and 7a are seen fluorescence spectra of 2×10^{-5} M PDALC at a variety of pH values. As with PDA, the fluorescence spectrum of the protonated form of the ligand is a broad featureless band, and becomes more intense and structured as the pH is raised, and the non-protonated ligand is present. In Figure 7b are seen fluorescence spectra of 2×10^{-5} M M(III)/PDALC complexes, all recorded at pH 4.0 in 10% CH_3OH/H_2O. Ligands bearing fluorophores, and potentially capable of exhibiting a CHEF effect,[61,62] can be of the external type, where the metal ion does not bind to the fluorophore itself, or of the internal type, where the metal ion binds to donor atoms on the fluorophore. PDALC is of the internal type, which means that heavy metal ions are capable of quenching fluorescence via communication of spin−orbit coupling effects through M−L bonds to the π-system of the fluorophores. 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 fluorophore, which effects increase with atomic number

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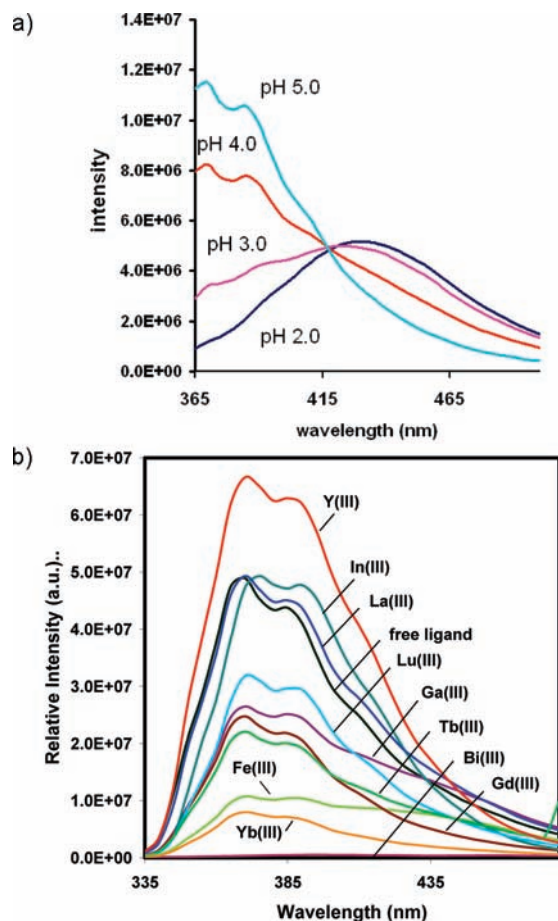
Figure 7. (a) Fluorescence spectra of 2×10^{-5} M PDALC in 50% CH_3OH/H_2O at the pH values indicated. Excitation wavelength = 300 nm. (b) Fluorescence of M(III) ions 1:1 with PDALC (2×10^{-5} M). Spectra recorded at pH 4.0 in 10% MeOH/water. Wavelength of excitation is 280 nm.

(Z), decreases fluorescence intensity.[61,62] One suggests that the order of the CHEF effect Y(III) > La(III) > Lu(III), which is the order of increasing Z, and is also found for PDA complexes,[63] reflects increasing spin−orbit coupling effects along the series, which increase intersystem crossing for the excited state, and weaken fluorescence. Bi(III) produces virtually total quenching of the fluorescence of PDALC. This is typical of heavy elements, exemplified most commonly by Hg(II), where strong spin−orbit coupling effects are present, which interact strongly with the π-system of the ligand because of the covalence of the M−N bonds. Unlike PDA,[63] the fluorescence of PDALC at pH 4.0 is quite intense, so that most metal ions do not produce an increase in fluorescence intensity on complex-formation. It appears that the non-complexed alcoholic oxygens are not as effective at quenching the fluorescence of PDALC as are the carboxylate groups of PDA. Metal ions with partly filled d-subshells (Fe(III)) or f-subshells (Gd(III), Tb(III), Yb(III)) quench the fluorescence of PDALC quite strongly, as

expected, by the ET (electron transfer) mechanism.[61,62] The fluorescence spectra of the Th(IV) and UO_2^{2+} complexes of PDALC are not shown, but are almost identical to that of Yb(III) shown in Figure 7b. Th(IV) acts to quench the fluorescence of PDALC strongly, which may be attributed to the strong spin−orbit coupling effects of such a heavy element. The UO_2^{2+} cation also strongly quenches the fluorescence of PDALC, in which effect it resembles its PDA complex,[8] which again may be due to large spin−orbit coupling effects.

Conclusions

The ligand PDALC shows considerable increases in log K_1 of as much as 5.5 log units compared to the analogous phen complexes, with large M(III) ions such as Lu^{3+}, Gd^{3+}, La^{3+}, Th^{4+}, UO_2^{2+}, and Bi^{3+}. Crystal structures of complexes of PDALC with large metal ions all show that the alcoholic oxygen-donors are coordinated to the metal ions, supporting the idea that it is coordination of these groups that greatly enhances the stability of these PDALC complexes relative to the phen complexes. These structures also suggest that the M−N bond lengths vary quite considerably with the size of the metal ion, since the architecture of PDALC does not constrain the M−N bond lengths. On the other hand, the M−O bond lengths of the PDALC complexes appear to be constrained to some degree toward the ideal M−O length of 2.5 Å for coordination in the cleft of PDALC. For a medium size metal ion such as In^{3+}, the stabilization of the PDALC complex relative to the phen complex is smaller at 2.3 log units, while the stabilization of the small Fe^{3+} and Ga^{3+} ions is negligible. This can be understood in terms of the metal ion size-based selectivity for large metal ions produced by the rigid cleft of PDALC. The fluorescence of PDALC complexes can be understood in terms of a CHEF effect produced by complex-formation with the metal ion, which ties up the lone pairs on the ligand which act to quench its fluorescence. Spin−orbit coupling effects of heavier elements quench fluorescence, which probably accounts for the low fluorescence of the Th(IV), and UO_2^{2+} PDALC complexes, and also the order of decreasing fluorescence intensity Y(III) > La(III) > Lu(III). Interaction of spin−orbit coupling effects of the heavy element with the π-system of PDALC appears to be enhanced by covalence in the M−N bond, accounting for the almost total quenching of fluorescence in the Bi(III)/PDALC complex. The PDALC complexes of metal ions with partially filled d-subshells (Fe(III)) or f-subshells (Gd(III), Yb(III), Tb(III)) undergo quenching by the ET (electron transfer) mechanism, so fluoresce only very weakly. The fact that PDALC can form complexes with metal ions such as Th(IV) and UO_2^{2+} in weak acid suggests that extractants based on PDALC as a functional group may have considerable usefulness in separations involving actinides and lanthanide ions.

(63) Williams, N. J.; Dean, N. E.; VanDerveer, D. G.; Luckay, R. C.; Hancock, R. D. *Inorg. Chem.* **2009**, *48*, 7853–7863.