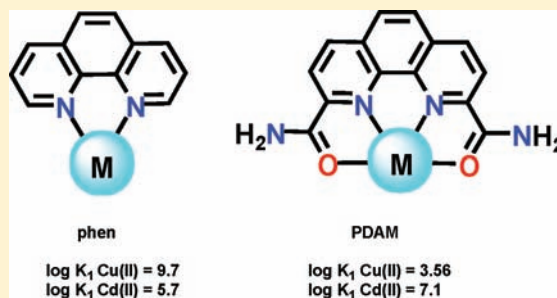


Unusual Metal Ion Selectivities of the Highly Preorganized Tetradentrate Ligand 1,10-Phenanthroline-2,9-dicarboxamide: A Thermodynamic and Fluorescence Study

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ABSTRACT: Some metal ion complexing properties of the ligand PDAM (1,10-phenanthroline-2,9-dicarboxamide) in aqueous solution are reported. Using UV–visible spectroscopy to follow the intense $\pi-\pi^*$ transitions of PDAM as a function of metal ion concentration, $\log K_1$ values in 0.1 M NaClO₄ and at 25 °C are, for Cu(II), 3.56(5); Ni(II), 3.06(5); Zn(II), 3.77(5); Co(II), 3.8(1); Mg(II), 0.1(1); Ca(II), 1.94(4); and Ba(II), 0.7(1). For more strongly bound metal ions, competition reactions between PDAM and EDTA (ethylenedinitrilotetraacetic acid) or tetren (1,4,7,10,13-pentaazatridecane), monitored following the UV spectrum of PDAM, gave the following $\log K_1$ values in 0.1 M NaClO₄ and at 25 °C: Cd(II), 7.1(1); Pb(II), 5.82(5); In(III), 9.4(1); and Bi(III), 9.4(1). The very low $\log K_1$ (PDAM) values for small metal ions such as Cu(II) or Zn(II) are unprecedented for a phen-based ligand (phen = 1,10-phenanthroline), which is rationalized in terms of the low basicity of the N donors of the ligand ($pK_a = 0.6$) and the fact that PDAM has a best-fit size corresponding to large metal ions of ionic radius ~ 1.0 Å. Large metal ions with ionic radius ≥ 1.0 Å show large increases in $\log K_1$ relative to their phen complexes, which in turn produces unparalleled selectivities, such as a 3.5 log units greater $\log K_1$ (PDAM) for Cd(II) than for Cu(II). PDAM shows strong fluorescence in aqueous solution, suggesting that its carboxamide groups do not produce a fluorescence-quenching photon-induced electron transfer (PET) effect. Only Ca(II) produces a weak CHEF (chelation enhanced fluorescence) effect with PDAM, while all other metal ions tested produce a decrease in fluorescence, a CHEQ (chelation enhanced quenching effect). The production of the CHEQ effect is rationalized in terms of the idea that coordination of metal ions to PDAM stabilizes a canonical form of the carboxamide groups that promotes a PET effect.



INTRODUCTION

Generation of ligand selectivity for one metal ion over another in aqueous solution is of interest in a range of applications,¹ including selective removal of Am(III) and Cm(III) from mixtures of Ln(III) ions in the treatment of nuclear waste,^{2,3} complexes of Gd(III) that are resistant to demetalation by Zn(II) in the development of MRI contrast agents,^{4–10} selective removal of toxic metal ions such as Pb(II) and Hg(II) from the body in cases of metal intoxication,¹¹ and designing fluorescence-based sensors for metal ions.^{12–15} Metal ion selectivity in solution is quantified¹ by the difference in $\log K_1$ values between metal ions of interest with the ligand being considered. Guides in ligand design include the HSAB principle of Pearson^{16–18} and features of ligand architecture such as chelate ring size,¹ where five-membered chelate rings promote selectivity for large metal ions and six-membered chelate rings promote selectivity for small metal ions. Ligand preorganization¹⁹ is also an important factor in ligand design. A preorganized ligand is one that has as its lowest energy conformation, or one of the lowest energy conformations, the conformation required to complex a target metal ion.¹⁹ Greater preorganization gives complexes of greater thermodynamic stability, and greater selectivity for target metal ions. Examples of preorganized ligands include crown

ethers,²⁰ cryptands,²¹ and aza-crowns.²² An approach to preorganized ligands has been ligands with polypyridyl groups reinforced by fused benzo rings, typified by phen¹ (see Figure 1 for a key to ligand abbreviations). This has led to ligands based on phen:^{23,24} PDA,^{25–29} PDALC,^{30,31} DPP,³² and DPA,³³ as well as macrocyclic ligands such as L1 in Figure 1, with a phen group as part of the macrocyclic ring.^{34–41} Other phen ligands with donor groups in the 2,9- position have been reported,^{42–46} including a phen group straddling a calixarene,⁴³ without sufficient accompanying thermodynamic data for evaluation of metal ion selectivity patterns.

The ligand PDAM⁴⁷ has two carboxamide donor groups, whose O donors lead to strong complexation of Ln(III) (Ln = lanthanide) ions, as well as Th(IV) and the UO₂²⁺ cation. Solvent extractants for Ln(III) and An(III) ions based on amide O donors have been extensively investigated.^{48–52} The presence of amide donor groups leads to lowered pK_1 values (pK_1 = first protonation constant) on ligands such as EDTAM (pK_1 = 4.36),^{53,54} NTAM (pK_1 = 2.6),⁵⁵ and DOTAM (pK_1 = 7.70),⁵⁶ as well as other amide-donor-containing ligands.⁵⁷ This is a

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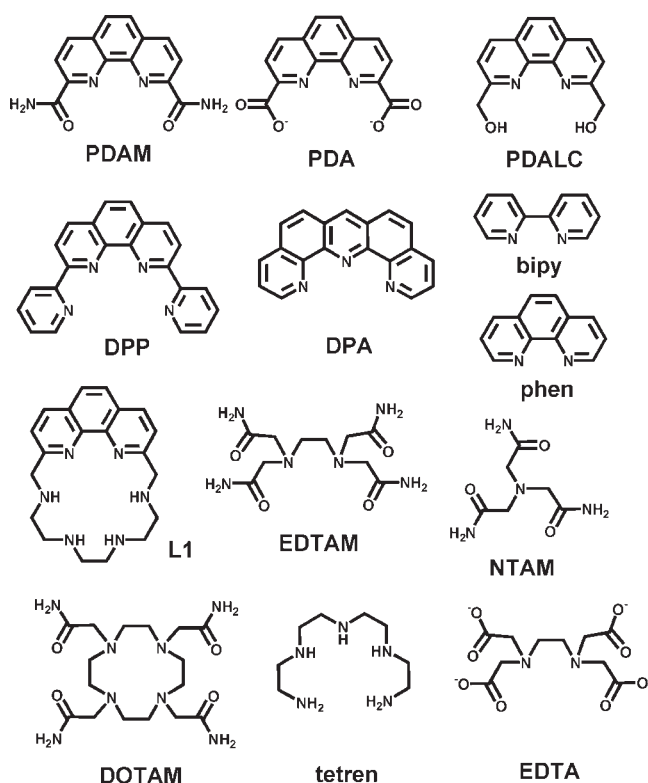


Figure 1. Ligands discussed in this paper.

considerable drop in the basicity of the saturated N donors (nitrogen donors) present, as compared to usual saturated amines such as CH_3NH_2 with $\text{p}K_1 = 10.65$.⁵⁷ As has also been found for picolinamide ($\text{p}K_1 = 1.8$),⁵⁸ where an amide is attached to a pyridyl group, the protonation constant of PDAM⁴⁷ ($\text{p}K_1 = 0.6$) is the lowest of any phen derivative,⁵⁷ so that its pyridyl N donors are nearly nonbasic. This suggests that the affinity of PDAM for metal ions such as Cu(II) or Ni(II) might be low, because the stability of their complexes with ligands based on phen depends on their high affinity for N donors. One might then have the interesting result of an N donor ligand such as PDAM that binds more strongly to large metal ions that have an affinity for the O donors of the ligand, which could lead to unusual selectivity patterns. In this paper, the study of PDAM is extended to include metal ions covering a range of sizes: the small Mg(II), Zn(II), Co(II), Ni(II), and Cu(II) ions, with $r^+ < 0.8 \text{ \AA}$; medium-sized metal ions such as Cd(II) and In(III) ($0.8 < r^+ < 1.0 \text{ \AA}$); and large metal ions such as Ca(II), Ba(II), Bi(III), and Pb(II) ($r^+ \geq 1.0 \text{ \AA}$). Ligands such as PDA and DPP have shown interesting fluorescence properties,^{27,32} so that a fluorescence study of metal ion complexes of PDAM is also reported here.

EXPERIMENTAL SECTION

Materials and Methods. PDAM was synthesized according to a literature method.⁶⁰ The metal perchlorates were obtained from VWR or Strem at 99% purity or better and used as received. All solutions were made up in deionized water (Milli-Q, Waters Corp.) of $>18 \text{ M}\Omega \text{ cm}^{-1}$ resistivity.

Stability Constant Determination. The solubility of PDAM in water is quite low, some $2 \times 10^{-5} \text{ M}$. PDAM has intense bands in the 200–350 nm region of the spectrum, so that a UV spectroscopic study of its protonation constants and metal ion complexation equilibria in 0.1 M

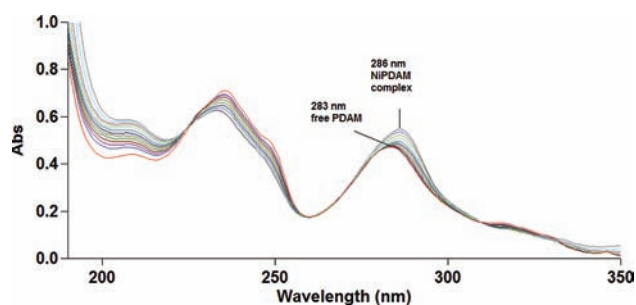


Figure 2. Variation of UV spectrum of $2 \times 10^{-5} \text{ M}$ PDAM in 0.1 M NaClO_4 at pH 5.36 titrated with 0.333 M $\text{Ni}(\text{ClO}_4)_2$.

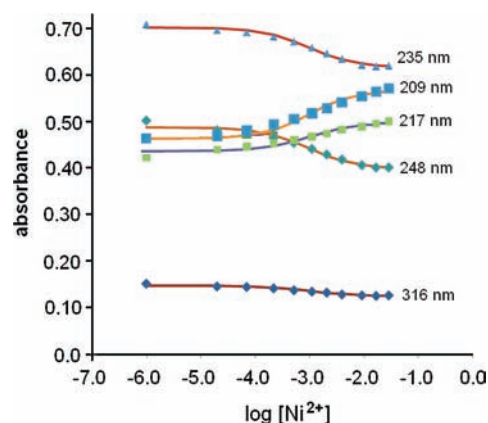


Figure 3. Variation of absorbance at a selection of wavelengths of $2 \times 10^{-5} \text{ M}$ PDAM in 0.1 M NaClO_4 as a function of $\log [\text{Ni}^{2+}]$. The points shown are the experimental points, while the solid lines are theoretical curves calculated using Solver,⁶¹ fitted values of molar absorptivities, and $\log K_1$ for the Ni(II)/PDAM system.

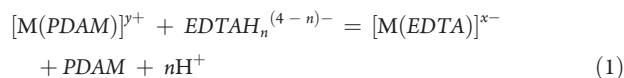
NaClO_4 was possible, as reported by the present workers on other phen-based ligands.^{25–27,30–33} The experiments were carried out with a 1.0 cm quartz flow cell (VWR) placed in a Varian 300 Cary 1E UV–visible spectrophotometer controlled by Cary Win UV Scan Application software, version 02.00(5). This was connected to an external titration cell thermostatted to $25.0 \pm 0.1 \text{ }^\circ\text{C}$, and the solution was continually circulated from the external cell to the flow cell in the spectrophotometer using a peristaltic pump. A VWR sympHony SR60IC pH meter with a VWR sympHony gel epoxy semimicro combination pH electrode was used for all pH readings, which were recorded in the external cell. For PDAM, the very low protonation constant⁴⁷ of 0.6 meant that the competition between the metal ion and the proton for coordination to the ligand could not be used for determining $\log K_1$. Instead, for metal ions with a $\log K_1$ with PDAM less than 5.0, which involved Ca(II), Ba(II), Mg(II), Co(II), Zn(II), Ni(II), and Cu(II), the variation of the absorbance of $2 \times 10^{-5} \text{ M}$ PDAM solutions as a function of metal ion concentration in titrations with solutions of metal perchlorate in 0.1 M NaClO_4 was used. For these titrations, the pH was maintained at about 2.5, which led to the PDAM being present entirely as the free ligand, but was low enough to avoid hydrolysis of the metal ions. The titration was carried out by adding aliquots of a solution containing both the metal ion and $2.0 \times 10^{-5} \text{ M}$ PDAM to a solution in the titration cell containing $2.0 \times 10^{-5} \text{ M}$ PDAM. This allowed the total PDAM concentration in the cell to remain constant during the course of the titration. Equilibration and mixing were allowed for by circulating the solution for 15 min before the next spectrum was recorded. The spectra for the Ni^{2+} titration of PDAM are shown in Figure 2, and Figure 3 shows the variation of absorbance at five

Table 1. Protonation and Formation Constants for PDAM (L) with a Selection of Metal Ions at 25 °C in 0.1 M NaClO₄

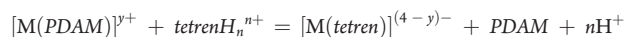
Lewis acid	equilibrium	log K	reference
H ⁺	H ⁺ + OH ⁻ ⇌ H ₂ O	13.78	57
H ⁺	L + H ⁺ ⇌ LH ⁺	0.6(1)	47
Mg ²⁺	Mg ²⁺ + L ⇌ MgL ²⁺	0.1(1)	this work
Ca ²⁺	Ca ²⁺ + L ⇌ CaL ²⁺	1.94(4)	this work
Ba ²⁺	Ba ²⁺ + L ⇌ BaL ²⁺	0.7(1)	this work
Zn ²⁺	Zn ²⁺ + L ⇌ ZnL ²⁺	3.77(5)	this work
Cd ²⁺	Cd ²⁺ + L ⇌ CdL ²⁺	7.1(1)	this work
Co ²⁺	Co ²⁺ + L ⇌ CoL ²⁺	3.8(1)	this work
Ni ²⁺	Ni ²⁺ + L ⇌ NiL ²⁺	3.06(5)	this work
Cu ²⁺	Cu ²⁺ + L ⇌ CuL ²⁺	3.56(5)	this work
Pb ²⁺	Pb ²⁺ + L ⇌ PbL ²⁺	5.82(5)	this work
In ³⁺	In ³⁺ + L ⇌ InL ³⁺	9.4(1)	this work
Bi ³⁺	Bi ³⁺ + L ⇌ BiL ³⁺	9.4(1)	this work
La ³⁺	La ³⁺ + L ⇌ LaL ³⁺	3.80(4)	47
Gd ³⁺	Gd ³⁺ + L ⇌ GdL ³⁺	4.30(3)	47
Lu ³⁺	Lu ³⁺ + L ⇌ LuL ³⁺	3.80(4)	47
Sc ³⁺	Sc ³⁺ + L ⇌ ScL ³⁺	4.57(4)	47
Th ⁴⁺	Th ⁴⁺ + L ⇌ ThL ³⁺	5.01(4)	47
UO ₂ ²⁺	UO ₂ ²⁺ + L ⇌ UO ₂ L ²⁺	4.33(4)	47

wavelengths for PDAM as a function of [Ni²⁺]. Fitting of theoretical absorbance versus pH or log [M] curves was accomplished using the Solver module of Excel.⁶¹ For a set of spectra for any one metal ion with PDAM, Solver was used to fit formation constants and molar absorbances for the species in solution involving PDAM. The standard deviations given for log K values in Table 1 were calculated using the SOLVSTAT macro provided with ref 61.

For metal ions with log K₁(PDAM) > 5.0, direct titration with a metal ion solution would not yield accurate log K₁ values: with 2 × 10⁻⁵ M PDAM present, formation of the PDAM complex would tend to be close to stoichiometric, making calculation of the free metal ion concentration by difference problematic. For such complexes, a competition reaction with a ligand such as EDTA or tetren was employed, as was done for the more stable complexes of the ligand PDA.^{25,28} One is thus spectroscopically determining the equilibrium quotient, Q, for the reactions, as in equilibrium 1:



As is the case with PDA complexes, log K₁(PDAM) is less than log K₁(EDTA) for any one metal ion, but the higher proton basicity of EDTA means that the PDAM complex is present at low pH, and the equilibrium moves to the right as the pH is raised. A similar approach was used with tetren as the competing ligand:



[2] Log K₁(PDAM) was determined using competition with EDTA for Cd(II) and with tetren for Cd(II), Pb(II), In(III), and Bi(III). The spectra of the 1:1:10 Bi(III)/PDAM/tetren system as a function of pH are shown in Figure 4.

Fluorescence Measurements. Emission spectra 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

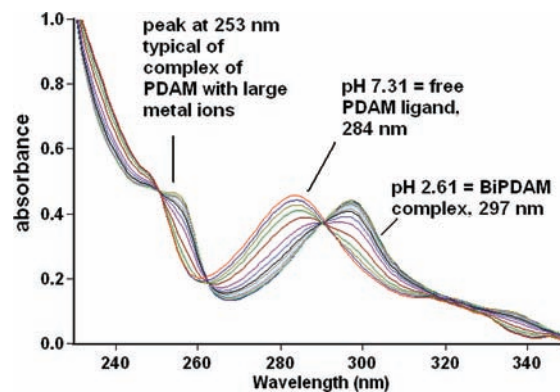


Figure 4. Spectra of 2.0 × 10⁻⁵ M (each) Bi³⁺ and PDAM and 2.0 × 10⁻⁴ M tetren, as a function of pH, at 25 °C in 0.1 M NaClO₄, in the pH range 2.07–7.31. The peak at 297 nm is that for the Bi(III)/PDAM complex, and that at 284 nm is for the free PDAM ligand, with the Bi(III) present as the tetren complex.

every 5 nm from 335 to 480 at a 280 nm excitation wavelength. Scans were corrected for instrument configuration using factory supplied correction factors. Post processing of scans was performed using the FluorEssence program.⁶² 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 the 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 PDAM plus a selection of PDAM complexes were recorded in water.

Density Functional Theory (DFT) Calculations. DFT calculations were carried out with the *ab initio* quantum chemistry package GAMESS.⁶³ Geometry optimization of [Zn(PDAM)(H₂O)₃]²⁺ was performed using the 6-31G* basis set⁶⁴ and B3LYP exchange-correlation functional.^{65,66} The optimized structure of [Zn(PDAM)(H₂O)₃]²⁺ generated by DFT calculation is seen in Figure 9.

RESULTS AND DISCUSSION

Formation Constants. Log K₁ values determined for some complexes of PDAM are given in Table 1. The response of the UV spectrum of PDAM to varying metal ion concentration is seen for the titration of 2 × 10⁻⁵ M PDAM with Ni(II) in Figure 2. In Figure 3 is shown the fitting of theoretical absorbance vs log [Ni²⁺] curves using Solver.⁶¹ Figure 4 shows the competition reaction between PDAM and a 10-fold excess of tetren for coordination to Bi(III) as a function of pH, and in Figure 5 is shown the fitting of this equilibrium with the known log K₁ for Bi(III) with tetren. The presence of several isosbestic points in Figure 4 supports the idea of a single equilibrium in the Bi(III)/PDAM/tetren system, which appears to be the pH-controlled transition from the PDAM complex at low pH to the tetren complex at higher pH. One has to bear in mind that metal ions such as Cu(II) have a deprotonation equilibrium^{54,57} with coordinated amides at about pH 6.1, where the deprotonated amide becomes bonded to the Cu(II) through the amide nitrogen, so that one might expect a similar equilibrium for Bi(III), and also In(III), but there is no evidence for this in the titrations carried out. It appears that in both cases the PDAM complex is displaced by the tetren at a pH below where deprotonation of coordinated amides would take place.

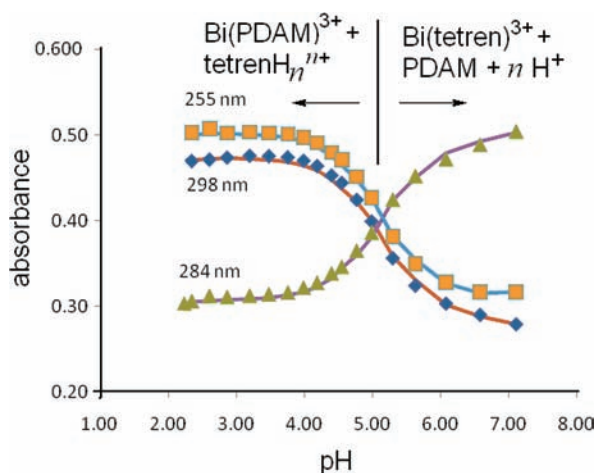


Figure 5. Absorbance versus pH for a solution containing 2×10^{-5} M (each) Bi(III) and PDAM and 2×10^{-4} M tetren, at 25 °C in 0.1 M NaClO₄. Points are experimental points. Solid lines are theoretical curves fitted using Solver⁶¹ and the midpoint of the equilibrium at pH = 5.01.

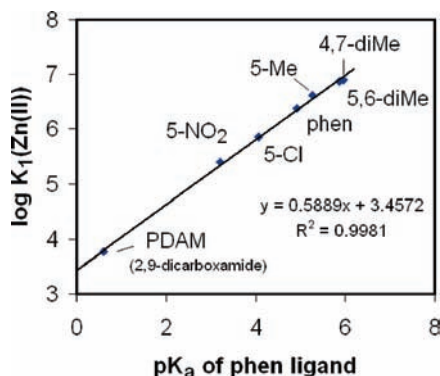


Figure 6. Relationship between $\log K_1$ for Zn(II) complexes of variously substituted phen ligands⁵⁷ and the pK_a values⁵⁷ for the same ligands. Apart from PDAM, phen ligands with 2,9-substituents have been omitted, as these may distort the relationship by steric hindrance. Abbreviations: PDAM and phen, see Figure 1. Other ligands are phen with substituents shown at the positions indicated, Me = methyl. The equation and coefficient of determination (R^2) for the least-squares best-fit line fitted to the points is shown on the diagram. pK_a and $\log K_1$ data, ref 57; PDAM, this work.

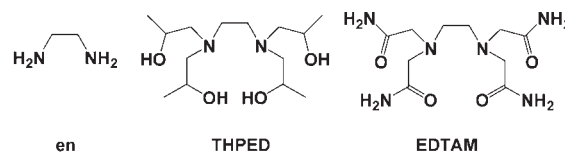
A striking feature of Table 1 is the very low $\log K_1$ values for small metal ions such as Cu(II), Ni(II), and Zn(II), particularly compared to the higher $\log K_1$ values for large metal ions such as Pb(II) or La(III). As might have been anticipated from the low pK_a for PDAM, metal ions such as Cu(II), Ni(II), and Zn(II), which depend on high affinity for N donors in general⁵⁷ to bind strongly with phen-type ligands, are most adversely affected by the low basicity of the N donors of PDAM. Figure 6 shows the relationship between $\log K_1$ for a selection of Zn(II) complexes of differently substituted phen ligands and ligand pK_a . The correlation excludes phen ligands with 2,9-substituted groups, as these substituents tend to produce steric hindrance (methyl or Cl groups) or else bind to the metal ion (PDALC or PDA), and in this correlation, one is focusing only on electronic effects on phen-based ligands. The linearity of the relationship suggests that the low $\log K_1$ for the Zn(II) complex of PDAM is as expected

Table 2. Comparison of $\log K_1$ Values for Complexes of Metal Ions of Different Ionic Radius with PDAM Compared to phen and PDALC

metal ion	ionic radius (Å) ^a	$\log K_1$		$\log K_1$		
		PDAM ^b	phen ^c	PDALC ^c	$\Delta \log K_1^f$	
Cu(II)	0.57	3.56	9.13	−5.57	7.56	−1.57
Ni(II)	0.69	3.06	8.70	−5.64	7.42	−1.3
Co(II)	0.72	3.8	7.1	−3.3	6.36	−0.7
Zn(II)	0.74	3.77	6.38	−2.61	6.56	+0.2
Mg(II)	0.74	~0.1	1.48	−1.4	1.70	+0.2
In(III)	0.80	9.4	6.81	+2.6	9.1	+2.3
Cd(II)	0.96	7.1	5.66	+1.4	7.5	+2.1
Ca(II)	1.00	1.94	1.00	+0.94	3.7	+2.7
La(III)	1.03	3.80	1.85	+1.95	5.3	+3.5
Bi(III)	1.03	9.4	(5.9)	+3.5	8.3	+2.4
Pb(II)	1.19	5.82	4.62	+1.20	7.3	+2.7
Ba(II)	1.36	0.7	0.4	+0.3	2.0	+1.6

^a Reference 59. ^b Reference 47 and this work. ^c Reference 57, La(III) and Bi(III) to be published. ^d Difference = $\log K_1(\text{PDAM}) - \log K_1(\text{phen})$. ^e References 30 and 31. ^f Difference = $\log K_1(\text{PDALC}) - \log K_1(\text{phen})$.

Scheme 1. Effect on Complex Stability of Complexes of a Small Metal Ion (Cu(II)) or of Large Metal Ions (Ca(II), La(III)), Produced by Adding Alcoholic O Donors (THPED) or Amide O Donors (EDTAM) to en



$\log K_1$:

Cu(II)	10.49	9.78	8.8
Ca(II)	0.11	1.63	3.29
La(III)	(1.4)	2.90	5.19

from the low basicity of PDAM, deriving from the electron-withdrawing nature of its carboxamide groups. For Cu(II) and Ni(II), similar relationships to those seen in Figure 6 occur, except that $\log K_1(\text{PDAM})$ is lower than expected from the correlation for the rest of the ligands. This suggests that the low stability of the complexes of Cu(II) and Ni(II) with PDAM may also be due to the carboxamide groups not only acting as electron-withdrawing groups but also sterically hindering the coordinated metal ion.

Large metal ions such as Ca(II), La(III), and Pb(II) show considerable stabilization in their PDAM compared to their phen complexes (Table 2). The amide O donor of the acetamide groups in ligands such as NTAM and EDTAM produces stabilizations of complexes of large metal ions that are greater than ligands such as THPED, which contains alcoholic oxygen donors (Scheme 1, $\log K_1$ data from refs 54 and 57).

In contrast to saturated amines such as en, where amide O donors produce greater metal ion size-related effects on complex stability than do alcoholic O donors, PDAM forms complexes of

Scheme 2. Resonance Structures of One Amide Group of PDAM Showing Placement of a Partial Negative Charge on the Amide Oxygen

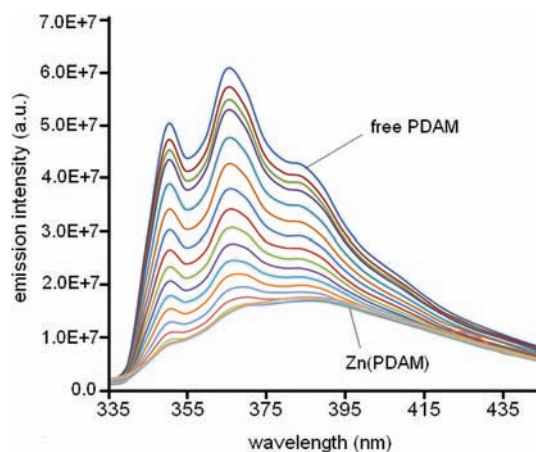
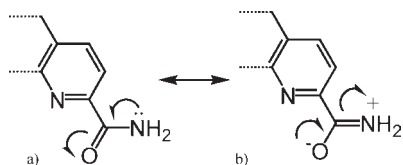
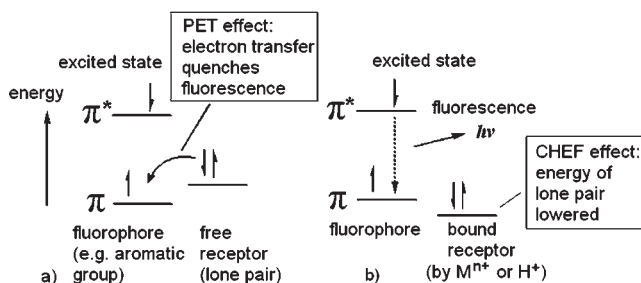


Figure 7. Fluorescence spectra of 2×10^{-5} M PDAM as a function of Zn(II) concentration, ranging from $[\text{Zn}^{2+}] = 0.0$ M for free PDAM (top spectrum) to $[\text{Zn}^{2+}] = 0.0446$ M for Zn(PDAM) (bottom spectrum). Excitation wavelength = 250 nm.

generally lower stability than does PDALC with its alcoholic O donors (Table 2). This may reflect the near nonbasicity of the N donors of PDAM, which lowers the affinity of even large metal ions such as La^{3+} for PDAM. The metal ions Bi(III) and In(III) are an exception and show a greater stabilization of their PDAM than PDALC complexes. These two ions are of higher acidity⁵⁷ than the other metal ions in Table 2: $\log K_1(\text{OH}^-) = 12.9$ for Bi(III) and 10.07 for In(III), compared with 5.5 for La(III). It is possible that the partial negative charge developed on the O donor of the amide groups of PDAM, as suggested by the canonical resonance structures in Scheme 2, leads to great stabilization of the PDAM complex with metal ions of high affinity for negatively charged O donors, of which OH^- is the archetypal representative.¹ This same effect could account for the higher $\log K_1(\text{PDAM})$ values (Table 1) for Sc(III) ($\log K_1(\text{OH}^-) = 9.7$) and Th(IV) ($\log K_1(\text{OH}^-) = 10.8$) than for the Ln(III) ions ($\log K_1(\text{OH}^-) = 5.5 - 6.7$).⁵⁷

Fluorescence Studies. In contrast to PDA and DPP, which show a strong positive CHEF (chelation enhanced fluorescence) effect^{27,32} with large metal ions such as Cd(II) or Ca(II), PDAM shows a weak (Ca(II) only) CHEF effect, or a strong CHEQ (chelation enhanced quenching) effect. Zinc(II) usually produces a large positive CHEF effect,¹² but Figure 7 shows how the fluorescence intensity of a 2×10^{-5} M PDAM solution drops with increasing Zn(II) concentration, a CHEQ effect. In phen-type ligands, fluorescence involves excitation of electrons from the π to the π^* level of the aromatic system, with light emitted as the excited electron falls back to the π level. For a ligand to have a positive CHEF effect, it should first have groups bearing lone

Scheme 3. Requirement for a Positive CHEF Effect^a



^a In the excited state of the fluorophore, at a, fluorescence is quenched by the PET effect, and at b, fluorescence is restored by the CHEF effect.

pairs that in the free ligand can quench the fluorescence by the PET (photoinduced electron transfer) effect (Scheme 3). The PET effect involves electrons dropping from a lone pair into the π level when an electron has been excited to the π^* level. In the case of PDA, the source of the quenching electrons would be the carboxylate groups. For a positive CHEF effect, a second requirement is that when a metal ion or the proton coordinates to the ligand, the energy of the electrons of the now bonded quenching lone pair drops below the energy of the π level of the fluorophore, and fluorescence is restored, as illustrated in Scheme 3.

Three metal ion related factors that appear¹² to control the CHEF effect can be summarized as follows: (1) *Spin-orbit coupling effects*: larger spin-orbit coupling constants for the metal ion promote intersystem crossing to the triplet state, where longer lifetimes for the excited state promote radiationless relaxation to the ground state. The usual order of ability to generate a CHEF effect that varies, $\text{Zn(II)} > \text{Cd(II)} \gg \text{Hg(II)}$, is thought to reflect increasing spin-orbit coupling constants with increasing Z (atomic weight). (2) *Paramagnetic metal ions*: Cu(II) and high-spin Ni(II), as well as paramagnetic Ln(III) ions such as Gd(III) or Tm(III), promote quenching. (3) *Nonparamagnetic metal ions of low Z* that bind to all of the potentially quenching lone pairs of the sensor cause enhanced fluorescence, typified by Zn(II) and Ca(II). It should be noted that higher Z metal ions such as La(III) and Lu(III) can also produce large CHEF effects, and it may be that covalent M-L bonding is required²⁷ to communicate spin-orbit coupling effects to the fluorophore. (4) A further effect is that^{67,68} *steric effects* may distort the bonding of the metal to the quenching lone pair, resulting in reduced overlap between metal orbitals and the lone pair. The latter thus does not drop lower in energy than the π level of the fluorophore, and the metal ion fails to produce a CHEF effect or produces a weakened CHEF effect.

In Figure 8 is shown the fluorescence of 2×10^{-5} M PDAM and of some of its complexes with metal ions. As noted above, virtually all metal ions except Ca(II) produce a CHEQ effect with PDAM. This might be understood as arising from the fact that the free carboxamide groups of PDAM are not effective at creating a PET effect but that the canonical form “b” of the carboxamide group in Scheme 2, promoted by binding to metal ions, is more able to do so. The more strongly a metal ion coordinates to the carboxamide group of PDAM, the more it promotes the canonical form “b”, and the more fluorescence is quenched. The ability to promote the formation of canonical structure “b” in Scheme 2 is possibly related to the affinity of the metal ion for negatively charged O donors, which can be

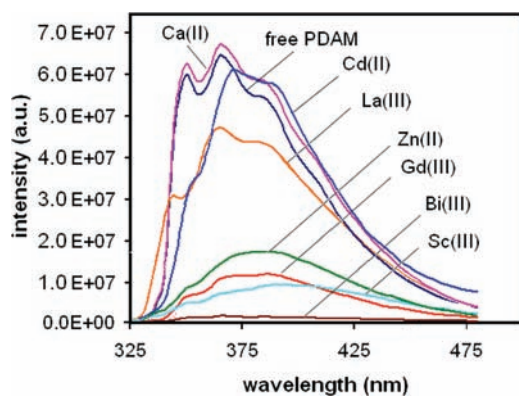


Figure 8. Fluorescence of PDAM and PDAM complexes, at 2.0×10^{-5} M in aqueous solution, excitation wavelength = 250 nm.

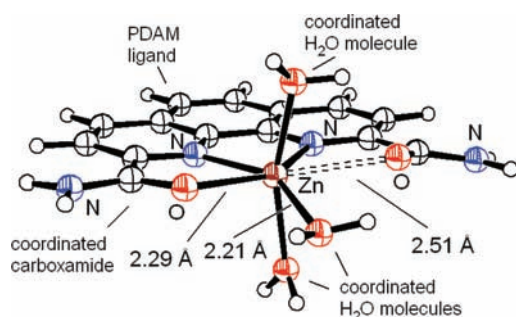


Figure 9. Structure of PDAM complex of Zn(II) generated using DFT calculation,⁶³ showing how Zn(II) achieves an approximately pentagonal bipyramidal coordination geometry with a normal Zn–O bond to one carboxamide oxygen of 2.29 Å, while the other carboxamide is at best weakly coordinated to the Zn(II) with a long Zn–O contact of 2.51 Å. Drawing made with ORTEP.⁷²

characterized¹ by the affinity for OH^- . Thus, weakly acidic Ca(II) ($\log K_1(\text{OH}^-)^{57} = 1.30$) produces a weak CHEF effect. Metal ions such as La(III) ($\log K_1(\text{OH}^-)^{57} = 5.5$) or Cd(II) ($\log K_1(\text{OH}^-)^{57} = 3.9$) of modest acidity produce a modest CHEQ effect, while a more acidic metal ion such as Sc(III) ($\log K_1(\text{OH}^-)^{57} = 9.7$) that does not have large spin–orbit coupling constants nor unpaired electrons nevertheless produces a large CHEQ effect. The large CHEQ effect for Gd(III), which is also observed for Cu(II) (not shown), is the usual CHEQ effect associated¹² with paramagnetism. Bi(III), and also Hg(II) (not shown), virtually eliminate the fluorescence of PDAM, which can be understood as arising from covalent M–L bonding coupled with large spin–orbit coupling constants.

The strong CHEQ effect for Zn(II) may reflect strong interaction of the Zn(II) with one of the two carboxamide groups. We were not able to grow crystals of PDAM complexes of any metal ions. The structure of $[\text{Zn}(\text{PDAM})(\text{H}_2\text{O})_3]^{2+}$ generated by DFT calculation⁶³ is seen in Figure 9. The structure is approximately pentagonal bipyramidal, with one very long Zn–O contact of 2.51 Å and one more normal Zn–O bond of 2.29 Å, to the carboxamide oxygens of PDAM. This supports the idea that Zn(II) causes a strong CHEQ effect in PDAM through one strongly bound carboxamide group. The structure generated for the Zn(II)/PDAM complex appears reasonable in terms of a search of the CSD⁶⁹ for seven-coordinate Zn(II) structures. The CSD contains some 12 000 structures of Zn(II) complexes,

of which (excluding π -bonded aromatic groups and metal–metal bonds) only some 57 contain nominally seven-coordinate Zn(II). Virtually all of these contain one or more long Zn–ligand contact, as found for the DFT-generated structure of the Zn(II)/PDAM complex in Figure 9. Examples include⁷⁰ one Zn–N bond of 2.37 Å in a seven-coordinate complex of Zn(II) with a ligand containing three pyridyl donors and two amide donors and one Zn–N bond of 2.50 Å in a complex⁷¹ containing three N donors and two chelating nitrate groups.

The high thermodynamic selectivity for Cd(II) over Zn(II) of 3.3 log units, coupled with the much greater intensity of fluorescence of the Cd(II)/PDAM complex than the Zn(II)/PDAM complex seen in Figure 8, which is a factor of 3.3 at 375 nm, means that PDAM could be used to detect Cd(II) in a fairly large excess of Zn(II), which would largely quench the fluorescence of PDAM, so that PDAM could be a turn-on sensor for Cd(II) in the presence of excess Zn(II).

CONCLUSIONS

PDAM has, for a phen-based ligand, unusually low affinity for Cu(II), Ni(II), Co(II), Zn(II), and Mg(II), which are small metal ions with $r^+ < 0.8$. Two factors appear to contribute to this: (1) MM calculations show⁴⁷ that PDAM fits best with large metal ions with an ionic radius of about 1.0 Å, so that part of the problem is steric. (2) The low $\text{p}K_a$ of PDAM of 0.6 suggests that its N donors are of very low basicity, which disadvantages metal ions such as Cu(II) and Ni(II) that rely on high affinity for N donors to stabilize their complexes. The O donors of the carboxamide groups of PDAM stabilize complexes of larger metal ions such as Cd(II) or La(III) to the extent that Cd(II) shows selectivity over Cu(II) of 3.5 log units and over Zn(II) of 3.3 log units, larger than for any other N-donor-containing ligand, including cryptands.⁵⁷ The stabilization produced by the amide O donors of PDAM appears to have a component relating to metal ion acidity ($\log K_1(\text{OH}^-)$), so that more acidic large metal ions such as Bi(III) or In(III) produce complexes with PDAM of the highest stability. The free PDAM ligand fluoresces strongly, suggesting that the carboxamide groups do not possess a lone pair of electrons capable of producing a PET effect. Only Ca(II) produces a modest CHEF effect, while all other metal ions produce a CHEQ effect, with a drop in fluorescence intensity. This appears to be due to the metal ions stabilizing the canonical form of the carboxamide with a negative charge on the oxygen, which is then capable of producing a PET effect. The extent to which metal ions produce a CHEQ effect appears to be governed by large spin–orbit coupling effects (high Z), paramagnetism, and the extent to which heavy metal ions such as Bi(III) or Hg(II) form covalent bonds to the N donors of PDAM.

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REFERENCES

- (1) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875.
- (2) Nash, K. L.; Madic, C.; Mathur, J. N.; Lacquement, J. *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Netherlands, 2006; Vol. 4, p 2622.
- (3) Kolarik, Z. *Chem. Rev.* **2008**, *108*, 4208.
- (4) Aime, S.; Delli Castelli, D.; Geninatti Crich, S.; Gianolio, E.; Terreno, E. *Acc. Chem. Res.* **2009**, *42*, 822.
- (5) Datta, A.; Raymond, K. N. *Acc. Chem. Res.* **2009**, *42*, 938.
- (6) Caravan, P. *Acc. Chem. Res.* **2009**, *42*, 851.
- (7) Sherry, A. D.; Woods, M. *Ann. Rev. Biomed. Eng.* **2008**, *10*, 391.
- (8) Port, M.; Idee, J.-M.; Medina, C.; Robic, C.; Sabatou, M.; Corot, C. *BioMetals* **2008**, *21*, 469.
- (9) Caravan, P.; Ellison, J. J.; McMurry, T. J.; Lauffer, R. B. *Chem. Rev.* **1999**, *99*, 2293.
- (10) Maiocchi, A. *Mimi Rev. Med. Chem.* **2003**, *3*, 845.
- (11) Andersen, O. *Chem. Rev.* **1999**, *99*, 2683.
- (12) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.
- (13) Burdette, S. C.; Walkup, G. K.; Spingler, B.; Tsieng, R. Y.; Lippard, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 7831.
- (14) Goldsmith, C. R.; Lippard, S. J. *Inorg. Chem.* **2006**, *45*, 555.
- (15) Bazzicalupi, C.; Bencini, A.; Berni, E.; Bianchi, A.; Fornasari, P.; Giorgi, C.; Valtancoli, B. *Eur. J. Inorg. Chem.* **2003**, 1974.
- (16) Pearson, R. G.; Mawby, R. J. *Halogen. Chem.* **1967**, *3*, 55.
- (17) Pearson, R. G. *Coord. Chem. Rev.* **1990**, *100*, 403.
- (18) Pearson, R. G. *Chemical Hardness*; Wiley-VCH: Weinheim, Germany, 1997.
- (19) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8.
- (20) Pederson, C. J. *J. Am. Chem. Soc.* **1967**, *89* (2495), 7017.
- (21) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49.
- (22) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540.
- (23) Hancock, R. D.; Melton, D. L.; Harrington, J. M.; McDonald, F. C.; Gephart, R. T.; Boone, L. L.; Jones, S. B.; Dean, N. E.; Whitehead, J. R.; Cockrell, G. M. *Coord. Chem. Rev.* **2007**, *251*, 1678.
- (24) Bencini, A.; Lippolis, V. *Coord. Chem. Rev.* **2010**, *254*, 2096.
- (25) Melton, D. L.; VanDerveer, D. G.; Hancock, R. D. *Inorg. Chem.* **2006**, *45*, 9306.
- (26) Dean, N. E.; Hancock, R. D.; Cahill, C. L.; Frisch, M. *Inorg. Chem.* **2008**, *47*, 2000.
- (27) Williams, N. J.; Dean, N. E.; VanDerveer, D. G.; Luckay, R. C.; Hancock, R. D. *Inorg. Chem.* **2009**, *48*, 7853.
- (28) Moghimi, A.; Alizadeh, R.; Shokrollahi, A.; Aghabozorg, H.; Shamsipur, M.; Shokravi, A. *Inorg. Chem.* **2003**, *42*, 1616.
- (29) Fan, L.-L.; Li, C.-J.; Meng, Z.-S.; Tong, M.-L. *Eur. J. Inorg. Chem.* **2008**, 3905.
- (30) Gephart, R. T., III; Williams, N. J.; Reibenspies, J. H.; De Sousa, A. S.; Hancock, R. D. *Inorg. Chem.* **2008**, *47*, 10342.
- (31) Gephart, R. T., III; Williams, N. J.; Reibenspies, J. H.; De Sousa, A. S.; Hancock, R. D. *Inorg. Chem.* **2009**, *48*, 8201.
- (32) Cockrell, G. M.; Zhang, G.; VanDerveer, D. G.; Thummel, R. P.; Hancock, R. D. *J. Am. Chem. Soc.* **2008**, *130*, 1420.
- (33) Hamilton, J. M.; Whitehead, J. R.; Williams, N. J.; El Ojaimi, M.; Thummel, R. P.; Hancock, R. D. *Inorg. Chem.* **2011**, *50*, 3785.
- (34) Bencini, A.; Berni, E.; Bianchi, A.; Fornasari, P.; Giorgi, C.; Lima, J. C.; Lodeiro, C.; Melo, M. J.; Seixas de Melo, J.; Parola, A. J.; Pina, F.; Pina, J.; Valtancoli, B. *Dalton Trans.* **2004**, 2180.
- (35) Bazzicalupi, C.; Bencini, A.; Fusi, V.; Giorgi, C.; Paoletti, P.; Valtancoli, B. *J. Chem. Soc., Dalton Trans.* **1999**, 393.
- (36) Bazzicalupi, C.; Bencini, A.; Bianchi, A.; Giorgi, C.; Fusi, V.; Valtancoli, B.; Bernado, M. A.; Pina, F. *Inorg. Chem.* **1999**, *38*, 3806.
- (37) Arca, M.; Blake, A. J.; Casabo, J.; Demartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lippolis, V.; Kivekas, R.; Muns, V.; Schroder, M.; Verani, G. *J. Chem. Soc., Dalton Trans.* **2001**, 1180.
- (38) Blake, A. J.; Devillanova, F. A.; Garau, A.; Harrison, A.; Isaia, F.; Lippolis, V.; Tiwary, S. K.; Schroder, M.; Verani, G.; Whittaker, G. *J. Chem. Soc., Dalton Trans.* **2002**, 4389.
- (39) Arca, M.; Azimi, G.; Demartin, F.; Devillanova, F. A.; Escriche, L.; Garau, A.; Isaia, F.; Kivekas, R.; Lippolis, V.; Muns, V.; Perra, A.; Shamsipur, M.; Sportelli, L.; Yari, A. *Inorg. Chim. Acta* **2005**, *358*, 2403.
- (40) Blake, A. J.; Casabo, J.; Devillanova, F. A.; Escriche, L.; Garau, A.; Isaia, F.; Lippolis, V.; Kivekas, R.; Muns, V.; Schroder, M.; Sillanpaa, R.; Verani, G. *J. Chem. Soc., Dalton Trans.* **1999**, 1085.
- (41) Aragoni, M. C.; Arca, M.; Bencini, A.; Biagini, S.; Blake, A. J.; Caltagirone, C.; Demartin, F.; De Filippo, G.; Devillanova, F. A.; Garau, A.; Gloe, K.; Isaia, F.; Lippolis, V.; Valtancoli, B.; Wenzel, M. *Inorg. Chem.* **2008**, *47*, 8391.
- (42) Ambrosi, G.; Formica, M.; Fusi, V.; Giorgi, L.; Guerri, A.; Micheloni, M.; Paoli, P.; Pontellini, R.; Rossi, P. *Inorg. Chem.* **2007**, *46*, 4737.
- (43) Eggert, J. P. W.; Harrowfield, J. M.; Luning, U.; Skelton, B. W.; White, A. H. *Polyhedron* **2006**, *25*, 910.
- (44) Newkome, G. R.; Puckett, W. E.; Kiefer, G. E.; Gupta, V. K.; Fronczek, F. R.; Pantaleo, D. C.; McClure, G. L.; Simpson, J. B.; Deutsch, W. A. *Inorg. Chem.* **1985**, *24*, 811.
- (45) Bazzicalupi, C.; Bencini, A.; Ciattini, S.; Giorgi, C.; Masotti, A.; Paoletti, P.; Valtancoli, B.; Navon, N.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **2000**, 2383.
- (46) Liu, T.-F.; Lin, H.-K.; Zhu, S.-R.; Wang, Z.-M.; Wang, H.-G.; Leng, X.-B.; Chen, Y.-T. *J. Mol. Struct.* **2001**, *597*, 199.
- (47) Merrill, D.; Hancock, R. D. *Radiochim. Acta* **2011**, *99*, 161.
- (48) Mathur, J. N.; Murali, M. S.; Nash, K. L. *Solvent Extr. Ion Exch.* **2001**, *19*, 357.
- (49) Charbonnel, M. C.; Flandin, J. L.; Giroux, S.; Presson, M. T.; Madic, C.; Morel, J. P. In *Proceedings of the International Solvent Extraction Conference, ISEC-2002*; South African Institute of Mining and Metallurgy: Johannesburg, 2002; p 1154.
- (50) Spjuth, L.; Liljenzin, J. O.; Skalberg, M.; Hudson, M. J.; Chan, G. Y. S.; Drew, M. G. B.; Feaviour, M.; Iveson, P. B.; Madic, C. *Radiochim. Acta* **1997**, *78*, 39–46.
- (51) Sasaki, Y.; Tachimori, S. *Solvent Extr. Ion Exch.* **2002**, *20*, 21.
- (52) Sinkov, S. I.; Rapko, B. M.; Lumetta, G. J.; Hay, B. P.; Hutchison, J. E.; Parks, B. W. *Inorg. Chem.* **2004**, *43*, 8404.
- (53) Siddons, C. J.; Hancock, R. D. *J. Chem. Soc., Chem. Commun.* **2004**, 1632.
- (54) Clapp, L. M.; Siddons, C. J.; Vanderveer, D. J.; Rogers, R. D.; Griffin, S. F.; Whitehead, J. M.; Jones, S. B.; Hancock, R. D. *Inorg. Chem.* **2005**, *44*, 8945.
- (55) Clapp, L. M.; VanDerveer, D. J.; Jones, S. B.; Hancock, R. D. *Dalton Trans.* **2006**, 2001.
- (56) Maumela, H.; Hancock, R. D.; Carlton, L.; Reibenspies, J.; Wainwright, K. P. *J. Am. Chem. Soc.* **1995**, *117*, 6698.
- (57) Martell, A. E.; Smith, R. M. *Critical Stability Constant Database*; National Institute of Science and Technology (NIST): Gaithersburg, MD, 2003; Vol. 46.
- (58) Conley, H. L.; Martin, R. B. *J. Phys. Chem.* **1965**, *69*, 2914.
- (59) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.
- (60) Makela, M.; Marita, Z.; Zhang, L.; Zetterberg, K.; Hansson, S. *Synth. Commun.* **1992**, *22*, 2811.
- (61) Billo, E. J. *EXCEL for Chemists*; Wiley-VCH: New York, 2001.
- (62) *FluorEssence*, version 2.1; HORIBA Jobin Yvon, Inc.: Edison, NJ.
- (63) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
- (64) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
- (65) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (66) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (67) Gan, W.; Jones, S. B.; Reibenspies, J. H.; Hancock, R. D. *Inorg. Chim. Acta* **2005**, *358*, 3958.

- (68) Williams, N. J.; Gan, W.; Reibenspies, J. H.; Hancock, R. D. *Inorg. Chem.* **2009**, *48*, 1407.
- (69) Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *B58*, 380. Cambridge Structure Database, Version 5.3, 2011.
- (70) Petitjean, A.; Khoury, R. G.; Kyritsakas, N.; Lehn, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 6637.
- (71) Maheswari, P. U.; Modec, B.; Pevec, A.; Kozlevcar, B.; Massera, C.; Gamez, P.; Reedijk, J. *Inorg. Chem.* **2006**, *45*, 6637.
- (72) ORTEP-3 for Windows, Version 1.08: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.