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Article

Metal Ion Complexing Properties of the Highly Preorganized Ligand 2,9-bis(Hydroxymethyl)-1,10-phenanthroline: A Crystallographic and Thermodynamic Study

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Metal ion complexing properties of the ligand 2,9-bis(hydroxymethyl)-1,10-phenanthroline (PDALC) are reported. For PDALC, the rigid 1,10-phenanthroline backbone leads to high levels of preorganization and enhanced selectivity for larger metal ions with an ionic radius of about 1.0 Å that can fit well into the cleft of the ligand. Structures of PDALC complexes with two larger metal ions, Ca(II) and Pb(II), are reported. $[Ca(PDALC)_2](ClO_4)_2$ (**1**) is triclinic, $P\bar{1}$, $a = 7.646(3)$, $b = 13.927(4)$, $c = 14.859(5)$ (Å), $\alpha = 72.976(6)$, $\beta = 89.731(6)$, $\mu = 78.895(6)°$, $V = 1482.5(8)$ Å^3, $Z = 2$, $R = 0.0818$. $[Pb(PDALC)(ClO_4)_2]$ (**2**) is triclinic, $P\bar{1}$, $a = 8.84380(10)$, $b = 9.0751(15)$, $c = 12.178(2)$ (Å), $\alpha = 74.427(3)$, $\beta = 78.403(13)$, $\mu = 80.053(11)°$, $V = 915.0(2)$ Å^3, $Z = 2$, $R = 0.0665$. In **1**, the Ca(II) is eight-coordinate, with an average Ca−N of 2.501 Å and Ca−O of 2.422 Å. The structure of **1** suggests that Ca(II) is coordinated in a very low-strain manner in the two PDALC ligands. In **2**, Pb(II) appears to be eight-coordinate, with coordination of PDALC and four O donors from perchlorates bridging between neighboring Pb atoms. The Pb has very short Pb−N bonds averaging 2.486 Å and Pb−O bonds to the alcoholic groups of PDALC of 2.617 Å. It is suggested that the Pb(II) has a stereochemically active lone pair situated on the Pb(II) opposite the two N donors of the PDALC, and in line with this, the Pb−L bonds become longer as one moves around the Pb from the sites of the two N donors to the proposed position of the lone pair. There are two oxygen donors from two perchlorates, nearer the N donors, with shorter Pb−O lengths averaging 2.623 Å. Two oxygens from perchlorates nearer the proposed site of the lone pair form very long Pb−O bond lengths averaging 3.01 Å. The Pb(II) also appears to coordinate in the cleft of PDALC in a low-strain manner. Formation constants are reported for PDALC in 0.1 M $NaClO_4$ at 25.0 °C. These show that, relative to 1,10-phenanthroline, the hydroxymethyl groups of PDALC produce a significant stabilization for large metal ions such as Cd(II) or Pb(II) that are able to fit in the cleft of PDALC but destabilize the complexes of metal ions such as Ni(II) or Cu(II) that are too small for the cleft.

Introduction

Ligand design is of considerable importance[1] in areas such as biomedical applications,[2−4] detection and remediation of toxic metal ions in the environment,[5] and metal ion separations.[6] An aim of research into ligand design has been[1] to identify ligand structural features that can be used to reliably control selectivity of the ligand for metal ions. One such factor is the presence of neutral oxygen donors, whether as alcoholic,[7,8] ethereal,[7,8] or amide oxygens,[9−11] the addition of which to a ligand shifts selectivity in the direction of larger metal ions. Metal ion sizes are defined here in terms of ionic radii[12] (r^+) as follows: very large, $r^+ \geq 1.2$ Å; large, $1.2 > r^+ > 1.0$ Å; medium, $1.0 > r^+ > 0.8$ Å; medium-small, $0.8 > r^+ > 0.7$ Å; small, $0.7 > r^+ > 0.5$ Å; very small, $r^+ <$

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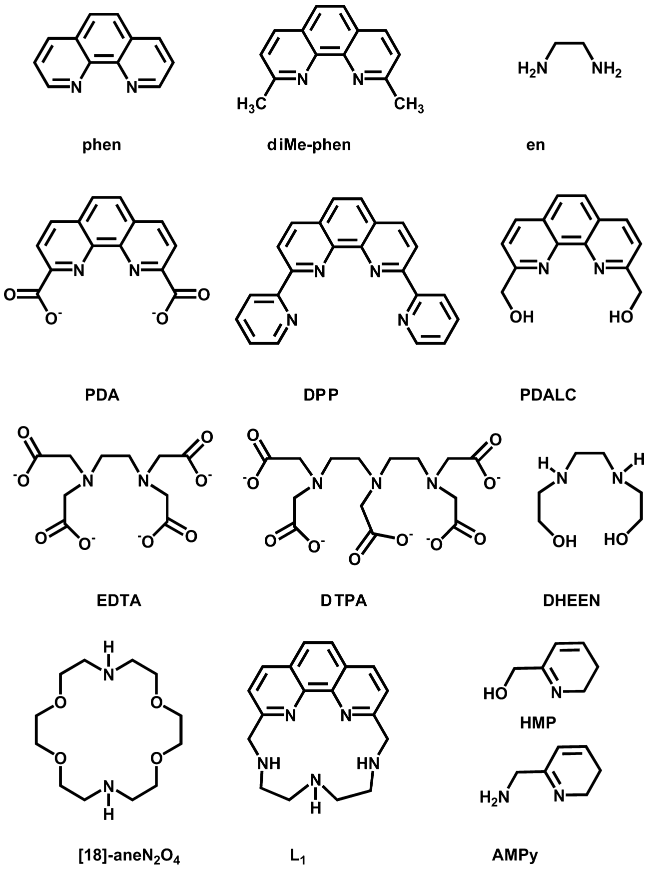
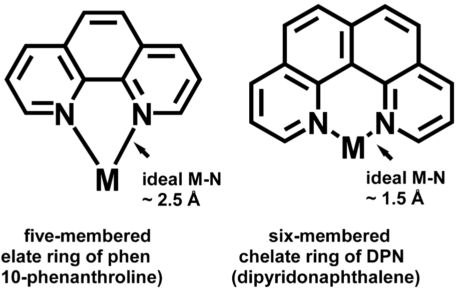


Figure 1. Ligands discussed in this paper.

0.5 Å. It has recently been shown that the levels of preorganization of ligands such as PDA[13,14] and DPP[15] (see Figure 1 for key to ligand abbreviations) are greatly increased by the presence of a rigid 1,10-phen backbone in the ligand. A ligand is more preorganized[16] the more it is constrained as the free ligand to be in the conformation required to complex the target metal ion. The metal ion complexing properties of the tetradentate PDA ligand are remarkable in that[13] it binds large metal ions of the right sizes ($r^+ \sim 1.0$ Å) nearly as strongly as, or in some cases better than, hexadentate EDTA, or even octadentate DTPA. This has been attributed[13] to the high levels of preorganization imparted to the ligand by the rigid phen backbone. The most common types of ligands with high levels of preorganization are those with macrocyclic structures, as found in crown ethers[17] or cryptands.[18] The rigidity of extended aromatic systems appears to offer a route to ligands of very high levels of preorganization without the necessity of a macrocyclic structure. Ligands such as PDA and DPP do not have a cavity as do macrocycles but should be regarded[13−15] as having a rigid cleft that best accommodates metal ions of an appropriate size. It is quite possible that the low levels of utilization of macrocycles, in applications where their use might seem to be dictated by the superior selectivity and thermodynamic stability that they impart to complexes with metal ions, lies in the more demanding syntheses, and associated higher costs, of macrocyclic ligands. The ligand PDA, and PDALC reported here, involve comparatively simple syntheses,[19] with accompanying high levels of preorganization.

It seemed of interest to investigate ligands of high levels of preorganization imparted by a rigid 1,10-phen backbone, which had neutral oxygen donor groups placed at the 2 and 9 positions, as is the case with the alcoholic groups of PDALC. Such a structure leads to the formation of three five-membered chelate rings. Numerous studies[1,20,21] have shown that five-membered chelate rings lead to a steric preference for coordination with large metal ions ($r^+ \sim 1.0$ Å), which accounts for the observation[1] that neutral oxygen donors, which are almost always part of five-membered chelate rings, lead to more stable complexes with large metal ions. The presence of six-membered chelate rings leads to a preference for small metal ions,[1,20,21] based on simple geometrical arguments that can be summarized in the following graphic for types of ligands based on extended aromatic systems such as are present in phen:



The formation constants (log K_1) of these ligands with a variety of metal ions are reported here, as well as the structures of the Ca(II) and Pb(II) complexes of PDALC. One should point out that the hydroxymethyl groups of PDALC might be capable of free rotation, so that the level of preorganization may be somewhat less than that of PDA, where the carboxylate group is quite strongly constrained to lie in the plane of the 1,10-phen backbone. However, one should expect the levels of preorganization of PDALC to be considerably higher than that of an analog such as

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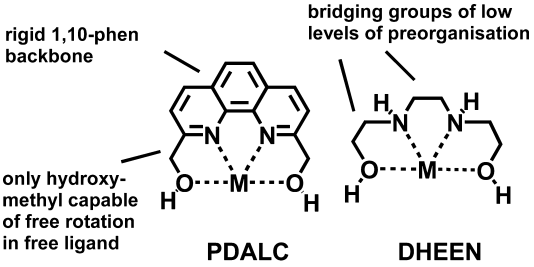
DHEEN, or even of macrocycles such as [18]-aneN_2O_4, and the interest here is the sharper selectivity patterns and enhanced thermodynamic stability expected for PDALC relative to a ligand such as DHEEN:



Experimental Section

Materials. The ligand PDALC was synthesized by a literature method[19] involving the oxidation of diMe-phen (Figure 1). Metal perchlorates were obtained in 99% purity or better from Aldrich and VWR.

Synthesis of [Ca(PDALC)$_2$](ClO$_4$)$_2$·H$_2$O (1). The synthesis of **1** was carried out by dissolving 0.0161 g of PDALC (0.06701 mmol) in *n*-butanol in a 50 mL beaker. Then, 2.00 mL of a 0.03335 M $Ca(ClO_4)_2$ stock solution (1.0373 g of $Ca(ClO_4)_2 \cdot 4H_2O$, Aldrich 99%, in 100 mL of deionized H_2O) was added, along with enough deionized H_2O to make the two layers approximately equal. The beaker was covered with parafilm, and the complex slowly crystallized out of solution upon standing. The colorless crystals of $[Ca(PDALC)_2](ClO_4)_2 \cdot H_2O$ were separated and dried under a vacuum. Elemental analysis calcd for $C_{28}H_{24}CaCl_2N_4O_{12}$: C, 46.74; H, 3.36; N, 7.79%. Found: C, 46.22; H, 2.98; N, 7.42%.

Synthesis of [Pb(PDALC)](ClO$_4$)$_2$·H$_2$O (2). The synthesis of **2** was carried out as described for **1** above, except that PDALC (0.06410 mmol) in *n*-butanol in a 50 mL beaker was used, and 1.933 mL of 0.03316 M $Pb(ClO_4)_2$ was added. Colorless crystals of $[Pb(PDALC)(ClO_4)_2] \cdot H_2O$ separated out upon standing and were dried under vacuum. Elemental analysis calcd for $C_{14}H_{12}Cl_2N_2O_{11}Pb$: C, 22.39; H, 1.83; N, 4.23%. Found: C, 22.62; H, 1.93; N, 4.42%.

Molecular Structure Determination. Mounted crystals of **1** and **2** were placed in a cold nitrogen stream maintained at −80 °C. A Rigaku AFC5 four-circle diffractometer was employed for crystal screening, unit cell determination, and data collection for all structures. The structures were solved by Patterson synthesis and refined to convergence.[22] Details of the structure determinations of **1** and **2** are shown in Table 1, and these together with the crystal coordinates have been deposited with the CSD.[23] Some more important bond lengths and angles for **1** and **2** are given in Tables 2 and 3. Structures of **1** and **2** are shown in Figures 2 and 3.

Table 1. Crystallographic Details for $[Ca(PDALC)_2](ClO_4)_2$ (**1**) and $[Pb(PDALC)(ClO_4)_2] \cdot H_2O$ (**2**)

compound	**1**	**2**
empirical formula	$C_{28}H_{24}CaCl_2N_4O_{12}$	$C_{14}H_{12}Cl_2N_2O_{11}Pb$
fw	719.49	662.35
temp	110(2) K	110(2) K
wavelength	0.71073 Å	1.54184
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimensions:		
a (Å)	7.646(3)	8.84380(10)
b (Å)	13.927(4)	9.0751(15)
c (Å)	14.859(5)	12.178(2)
α (deg)	72.976(6)	74.427(3)
β (deg)	89.731(6)	78.403(13)
γ (deg)	78.895(6)	80.053(11)
vol (Å^3)	1482.5(8)	915.0(2)
Z	2	2
final R indices		
[$I > 2\sigma(I)$]	R1 = 0.0818, wR2 = 0.1822	R1 = 0.0665 wR2 = 0.1729
R indices (all data)	R1 = 0.1068, wR2 = 0.1955	R1 = 0.0776 wR2 = 0.1944

Table 2. Bond Lengths (Å) and Angles (deg) of Interest in $[Ca(PDALC)_2](ClO_4)_2$ (**1**)

Ca(1)−O(1)	2.401(4)	Ca(1)−O(4)	2.419(4)
Ca(1)−O(2)	2.445(4)	Ca(1)−N(1)	2.495(4)
Ca(1)−N(4)	2.505(5)	Ca(1)−N(2)	2.505(5)
Ca(1)−O(3)	2.423(4)	Ca(1)−N(3)	2.498(4)
O(1)−Ca(1)−O(4)	91.91(15)	O(1)−Ca(1)−O(3)	92.19(16)
O(4)−Ca(1)−O(2)	93.55(15)	O(3)−Ca(1)−O(2)	85.62(15)
O(1)−Ca(1)−N(1)	64.24(14)	O(4)−Ca(1)−N(1)	79.75(14)
O(3)−Ca(1)−N(1)	89.73(14)	O(2)−Ca(1)−N(1)	129.62(15)
O(1)−Ca(1)−N(3)	81.57(15)	O(4)−Ca(1)−N(3)	129.62(15)
O(3)−Ca(1)−N(3)	64.58(15)	O(2)−Ca(1)−N(3)	85.13(15)
N(1)−Ca(1)−N(2)	65.65(15)	N(3)−Ca(1)−N(4)	65.46(15)

Table 3. Bond Lengths (Å) and Angles (deg) of Interest[a] in $Pb(PDALC)(ClO_4)_2] \cdot H_2O$ (**2**)

Pb(1)−N(2)	2.473(15)	Pb(1)−N(1)	2.498(17)
Pb(1)−O(1)	2.566(13)	Pb(1)−O(2)	2.688(12)
Pb(1)−O(4)	2.994(13)	Pb(1)−O(8)#	3.026(14)
Pb(1)−O(7)	2.538(12)	Pb(1)−O(6)#	2.708(12)
N(2)−Pb(1)−N(1)	67.3(5)	N(2)−Pb(1)−O(7)	76.4(5)
N(1)−Pb(1)−O(7)	78.1(5)	N(2)−Pb(1)−O(1)	130.4(5)
N(1)−Pb(1)−O(1)	63.6(5)	O(7)−Pb(1)−O(1)	87.3(4)
N(2)−Pb(1)−O(2)	62.5(5)	O(7)−Pb(1)−O(2)	74.4(4)
O(1)−Pb(1)−O(2)	154.8(4)	N(2)−Pb(1)−O(6)#	72.5(4)
N(1)−Pb(1)−O(6)#	67.2(5)	O(1)−Pb(1)−O(6)#	94.1(4)

[a] A # denotes that the oxygen atom is derived from a neighboring complex individual.

Formation Constant Determination. These were determined by UV−visible spectroscopy following procedures similar to those of Choppin et al.[25] for studying 1,10-phen 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 an acid−base titration where measured potentials were fitted to calculated pH values to yield a Nernstian slope and $E°$ for the cell. 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 2−7 by

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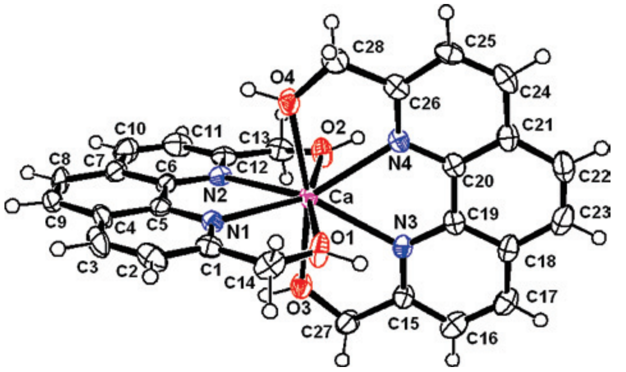

Figure 2. ORTEP[24] drawing of the complex cation $[Ca(PDALC)_2]^{2+}$ from **1** showing the numbering scheme. Thermal ellipsoids are shown at the 50% probability level.

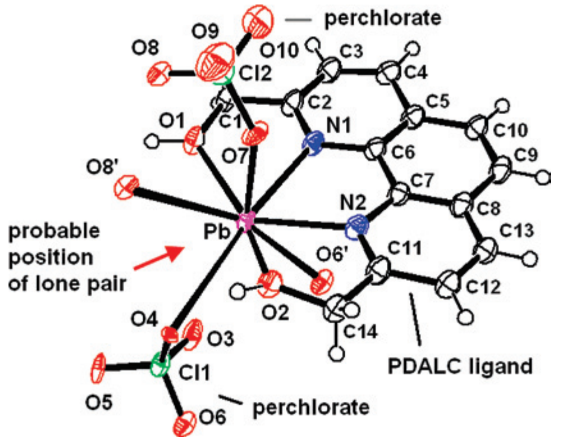

Figure 3. ORTEP[24] drawing of the complex $[Pb(PDALC)(ClO_4)_2]$ present in compound **2**, showing the numbering scheme. Also shown are two oxygens (O8′ and O6′) from perchlorates from neighboring $[Pb(PDALC)(ClO_4)_2]$ individuals that bridge between the Pb atoms. The arrow shows the probable position of the lone pair on Pb, as discussed in the text. Thermal ellipsoids are shown at the 50% probability level.

additions to the external titration cell of small amounts of $HClO_4$ or NaOH as required using a micropipette. 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.

PDALC is not very water soluble (~10^{-4} M) but has intense bands in the UV that can be used to monitor complex formation in solution. The variation of the spectra of PDALC solutions as a function of pH in 0.1 M $NaClO_4$ at 25 °C is seen in Figure 4. A single protonation constant for PDALC was determined from the variation in absorbance as a function of pH at five different wavelengths (Table 4). Fitting of theoretical absorbance versus pH curves was accomplished using the SOLVER module of EXCEL.[26] For a set of spectra for any one metal ion with PDALC, SOLVER[26] was used to fit protonation constants and molar absorbtivities for the species in solution involving PDALC. The standard deviations given in Table 4 were calculated using the SOLVSTAT macro provided with ref 26.

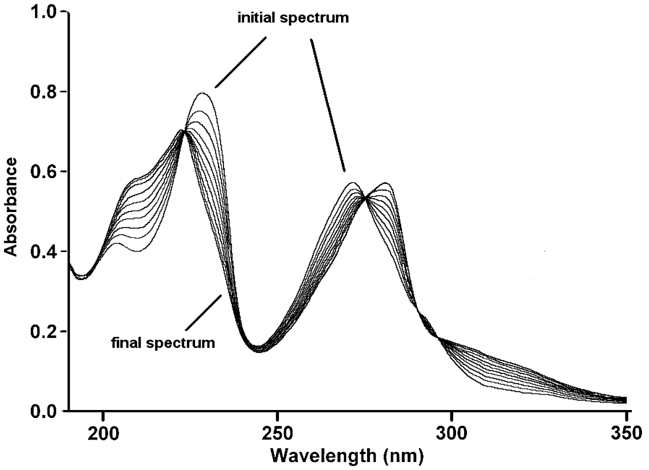

Figure 4. Absorption spectra of 2.00×10^{-5} M PDALC in 0.1 M $NaClO_4$ as a function of pH. The initial spectrum was recorded at pH 6.22, and the final pH was 1.30. The spectral changes can be modeled[26] as a single protonation equilibrium with p$K = 4.70$.

Table 4. Protonation and Formation Constants for PDALC Determined Here in 0.1 M $NaClO_4$ at 25 °C

equilibrium	log *K* (PDALC)	ref
$H^+ + OH^- \rightleftharpoons H_2O$	13.78	30
$L + H^+ \rightleftharpoons LH^+$	4.70(1)	this work
$Mg^{2+} + L \rightleftharpoons MgL^{2+}$	1.70(2)	this work
$Ca^{2+} + L \rightleftharpoons CaL^{2+}$	3.74(3)	this work
$Sr^{2+} + L \rightleftharpoons SrL^{2+}$	2.46(3)	this work
$Ba^{2+} + L \rightleftharpoons BaL^{2+}$	2.04(3)	this work
$La^{3+} + L \rightleftharpoons LaL^{3+}$	5.34(3)	this work
$Gd^{3+} + L \rightleftharpoons GdL^{3+}$	6.16(3)	this work
$Co^{2+} + L \rightleftharpoons CoL^{2+}$	6.36(3)	this work
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	7.42(6)	this work
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	7.56(3)	this work
$CuL(H_{-1})^+ + H^+ \rightleftharpoons CuL^{2+}$	7.50(2)	this work
$CuL(H_{-1})_2 + H^+ \rightleftharpoons CuL(H_{-1})^+$	11.15(4)	this work
$Zn^{2+} + L \rightleftharpoons ZnL^{2+}$	6.56(3)	this work
$Cd^{2+} + L \rightleftharpoons CdL^{2+}$	7.49(3)	this work
$CdL(H_{-1})^+ + H^+ \rightleftharpoons CdL^{2+}$	9.35(2)	this work
$Pb^{2+} + L \rightleftharpoons PbL^{2+}$	7.32(5)	this work
$PbL(H_{-1})^+ + H^+ \rightleftharpoons PbL^{2+}$	8.08(2)	this work
$PbL(H_{-1})_2 + H^+ \rightleftharpoons PbL(H_{-1})^+$	9.70(2)	this work

Results and Discussion

Structural Studies. The structure of the complex cation $[Ca(PDALC)_2]^{2+}$ in **1** is seen in Figure 2. The Ca in **1** is eight-coordinate, coordinating to the four N donors and four alcoholic O donors of the two PDALC ligands. What is important in relation to the relatively high thermodynamic stability (discussed below) of complexes of PDALC with metal ions such as Ca(II), which have appropriate ionic radii of about 1.0 Å, is the extent to which PDALC coordinates to Ca(II) in a low-strain manner in **1**. The Ca−N bond lengths (Table 2) involving the 1,10-phen moiety of the two PDALC ligands, which range from 2.495 to 2.505 Å, are quite similar to those found in eight structures for Ca(II) with 1,10-phen itself in the CSD,[23] which average 2.57 ± 0.04 Å. The N−Ca−N angles in **1** are 65.56 and 65.46°, compared to an average of 64.2 ± 1.0° for the 1,10-phen structures of Ca(II) in the CSD. The Ca−O bonds to the alcoholic O donors of PDALC in **1** average 2.42 Å, compared to alcoholic O donors in the CSD that are part of chelate rings, and coordinated to Ca, with Ca−O bonds averaging 2.46(4) Å. In addition, the Ca(II) lies almost exactly in the plane of the very nearly planar PDALC ligands. One can thus conclude that the structure of **1** suggests that the Ca(II) in the tetradentate PDALC ligand has as near as possible the same geometry as Ca(II) in structures of much less

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(26) Billo, E. J. *EXCEL for Chemists*; Wiley-VCH: New York, 2001.

sterically demanding ligands in the CSD which have the same donor groups, and therefore Ca(II) binds to PDA in a low-strain manner. Ca(II) has an ionic radius of 1.0 Å, which molecular mechanics calculations[20] suggest is an ideal size for coordination with PDALC.

The structure of **2** is shown in Figure 3, where it is seen that the Pb(II) has hemidirected[27] coordination geometry, typical of the presence of a sterically active lone pair on Pb(II).[28,29] There are thus short Pb−N bonds to the N donors of the PDALC ligand of 2.473 and 2.498 Å, which can be compared to an average of 2.59 Å for 80 structures of phen with Pb(II) found in the CSD. This is typical[28] of bond lengths for donors occupying the site at 180° to the proposed site of a stereochemically active lone pair, indicated for **2** by an arrow in Figure 3. Ordinarily, the site opposite the lone pair is occupied[27] by the most covalent of the donor atoms present, which for **2** are obviously the N donors of PDALC. As is typically found[27−29] for Pb(II) structures, the M−L bonds become longer as one moves away from the site opposite the lone pair, and so the Pb−O bonds to the alcoholic O donors of PDALC at 2.566 and 2.668 Å are somewhat longer than the Pb−N bonds, even though typically M−O bonds are shorter than M−N bonds because of the smaller radius of the O atom, as seen for Ca(II) in **1**. There are an additional four perchlorate O donors coordinated to the Pb. Two occupy positions which are further from the position of the lone pair and have somewhat shorter Pb−O bonds with Pb−O6′ = 2.708 Å and Pb−O7 = 2.538 Å. The other two perchlorate O donors are, as suggested in Figure 3, close to the position of the lone pair, so that these Pb−O bonds are very long, with Pb−O4 = 2.994 Å and Pb−O8′ = 3.026 Å. The hemidirected structure of **2** raises the question of what the ideal size of Pb(II) really is, and whether it fits PDALC well or not, since its ionic radius[12] of 1.19 Å is larger than the ideal size of 1.0 Å. However, the ionic radius refers to a sphere, and the hemidirected Pb(II) is not spherical.[29] In fact, the Pb−N bonds in **2** average 2.48 Å, rather similar to the Ca−N bonds of 2.50 Å in **1**, which suggests that Pb(II) may be a better fit for PDALC than indicated by its large ionic radius.

Formation Constants. The formation constants determined here are seen in Table 4. The presence of a single protonation constant (p*K*) for PDALC in the pH range 1.3−6.2 is strongly supported by the set of spectra for 2.00 × 10^{-5} M PDALC shown in Figure 4, with the persistence of four isosbestic points over the whole pH range, indicating that a single equilibrium is present. The p*K* of 4.70 for PDALC is typical of phen-type ligands and can be compared with p*K* values of[30] 4.92 for phen and 5.83 for diMe-phen at an ionic strength of 0.1. The somewhat lower p*K* for PDALC probably reflects the electron-withdrawing properties of the hydroxyl groups present.

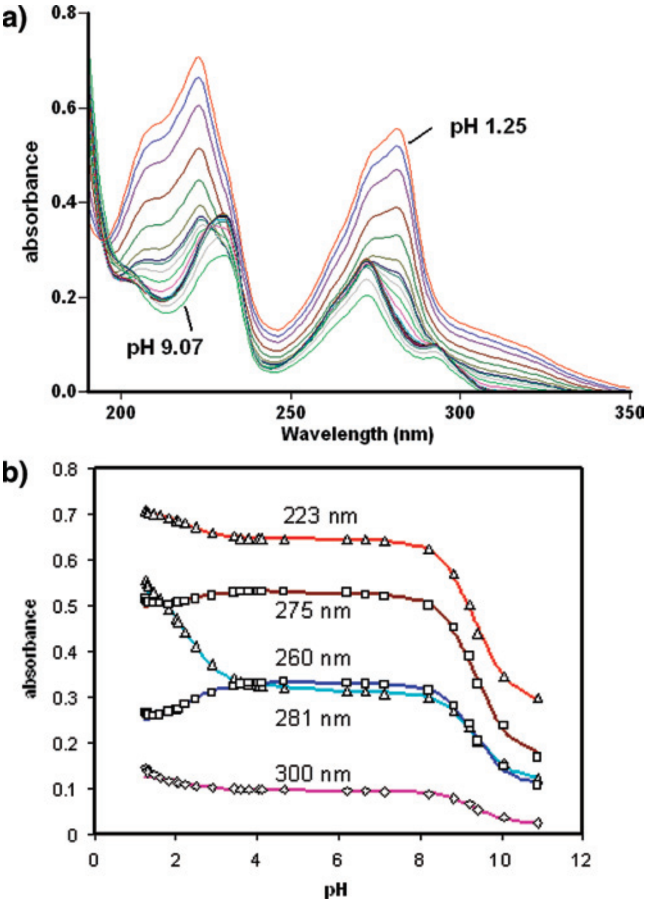

Figure 5. (a) Absorption spectra of 2.00 × 10^{-5} M PDALC plus 2.00 × 10^{-5} M Cd(II) in 0.1 M $NaClO_4$ as a function of pH. The spectrum at pH 1.25 corresponds largely to the monoprotonated PDALC ligand, with a small amount of the Cd(II)/PDALC complex still present, while those at higher pH values correspond to CdL and then CdLOH (L = PDALC). (b) Fitting of theoretical absorption vs pH curves (solid lines) to the experimental points at five wavelengths for 2 × 10^{-5} M Cd^{2+} plus PDALC in 0.1 M $NaClO_4$ at 25 °C. Theoretical curves were fitted using EXCEL[26] as described in the text. The changes in absorbance in the pH range 1−4 correspond to formation of the Cd(II)/PDALC complex (eq 1 in the text), while those between pH 8 and 11 correspond to deprotonation of the Cd(II)/PDALC complex (eq 2 in the text).

In Figure 5a is shown the set of spectra for 2 × 10^{-5} M PDALC and Cd(II) as a function of pH, which is typical of all the metal ions for which log *K* values are reported in Table 4. The presence of a complex in solution is evidenced by the very marked difference in the set of spectra with Cd(II) present, and that of the ligand alone (Figure 4). What is clear in Figure 5a is that at the lowest pH value of 1.25 the Cd(II)/PDALC spectrum is similar to that of the monoprotonated PDALC ligand in Figure 4, with a small quantity of the complex present, as evidenced by the shoulder on the peak, but as the pH is raised, other equilibria occur which are most reasonably interpreted as the formation of a complex ML according to

$$M^{2+} + \mathrm{PDALC} \rightarrow [\mathrm{M(PDALC)}]^{2+} \qquad (1)$$

For the less acidic metal ions in Table 4, only a single equilibrium involving PDALC and the metal ion is observed, which is reasonably interpreted as corresponding to equi-

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librium 1 above. For other, more acidic metal ions, further equilibria at higher pH are observed, which are most reasonably interpreted as involving deprotonation of the complex, as in the following equilibrium:[2]

$$[\mathrm{M(PDALC)}]^{2+} \leftrightarrow [\mathrm{M(PDALC)(H_{-1})}]^{+} + \mathrm{H}^{+} \qquad (2)$$

The variation in absorbance for the Cd(II)/PDALC system as a function of pH at five different wavelengths is shown in Figure 5b. The theoretical absorbance versus pH curves were fitted using EXCEL,[26] as described previously.[13−15] One cannot be sure whether the proton removed from the complex is from a coordinated alcoholic group of PDALC or a coordinated water molecule. However, it seems probable that the proton is lost from a coordinated alcoholic group, at least in the case of the larger metal ions, where such coordination usually leads to a considerable increase in acidity. This is supported by the large changes in absorbance seen in the pH range 8−11 in Figure 5b, which would seem less likely for a deprotonation equilibrium involving coordinated waters not part of the PDALC ligand, whose $\pi-\pi^*$ transitions are responsible for the spectra seen in Figure 5a. One might expect protons to be lost from the alcoholic groups of PDALC since the electron-withdrawing pyridyl groups should increase the acidity of the alcoholic groups as compared to water or other alcohols. The effect of pyridyl groups on acidity can be seen in that the first pK of ethylenediamine is[30] 9.92, whereas that of AMPy (2-aminomethylpyridine, Figure 1) is 8.65. A crystal structure of a PDALC complex with a deprotonated alcoholic group coordinated to the metal ion would be strong evidence for the idea that the proton lost in solution comes from the alcoholic group of PDALC rather than from a coordinated water. Some support along these lines is seen in the structures[31−33] of Mn(III) complexes of 2-hydroxymethylpyridine (HMP), which contain coordinated water molecules in addition to the HMP ligand. HMP is similar to PDALC in that it contains a hydroxymethyl group ortho to the nitrogen of a pyridine group, and the protons that have been lost from the complexes come from the coordinated alcoholic groups of the ligand, not from the coordinated waters. Similarly, in structures of Zn(II)[34] and Ni(II)[35] complexes of HMP, protons lost from the complex come from the coordinated alcoholic groups of the HMP ligand, rather than from other coordinated alcohols such as butanols.

In Table 5, the log K_1 values for PDALC are compared with those of other ligands in order to examine the effects of the high level of preorganization of the phen backbone of PDALC on thermodynamic complex stability and metal ion size-based selectivity. The metal ions in Table 5 are arranged in order of increasing ionic radius,[12] and it is apparent that there is a strong correlation between metal ion size and the stabilization produced by the hydroxymethyl groups of PDALC compared to phen. One notes the large increase in log K_1 of 2.1−2.8 log units that occurs in passing from phen to PDALC for large metal ions such as Ca(II), Cd(II), and Pb(II). In contrast, a small metal ion such as Cu(II) is considerably destabilized by the addition of hydroxymethyl groups to phen to give PDALC and reacts to these groups almost as if they were sterically hindering groups such as methyl groups, rather than donor groups. Thus, log K_1 for Cu(II) with diMe-phen[30] is 6.1, which is very much lower than that with phen (9.1) but only moderately lower than that with PDALC (7.6). A reviewer has queried whether the hydroxymethyl groups of PDALC could become sterically hindering even for a metal ion much too small to span the distance between the alcoholic groups of PDALC. The rigidity imparted to ligands of the PDALC type by the phen moiety means that small metal ions cannot span the distance between the donor atoms attached directly to the phen moiety. One notes that, for the similar ligand PDA, the complex with the small Ni(II) ion shows in its structure[36] that one carboxylate is left noncoordinated in $[\mathrm{Ni(PDA)(H_2O)_3}]$ and is H-bonded to a coordinated water molecule. In the Zn(II) complex of L1 (Figure 1), the saturated nitrogen donors adjacent to the phen moiety of the macrocycle are effectively not coordinated to the too-small Zn(II) ion,[37,38] which is too small to span the distance between these two donor atoms. The structure of $[\mathrm{Zn(PDALC)(H_2O)_3}]^{2+}$ has been generated (Figure 6) by semiempirical PM3 calculation[39,40] to illustrate what may happen to complexes of ligands such as PDALC with too-

Table 5. Comparison of log K_1 Values for PDALC (this work), with Those of phen and DHEEN (ref 30), Showing the Effect of Ionic Radius[12] on Changes in log K_1[a]

Metal ion	radius (Å)[b]	log K_1 PDALC	log K_1 phen	Δlog K_1 PDALC/phen[c]	log K_1 DHEEN	Δlog K_1 DHEEN/en[c]
Cu(II)	0.57	7.56	9.1	−1.6	9.68	−0.9
Ni(II)	0.69	7.42	8.7	−1.3	6.67	−0.6
Co(II)	0.72	6.36	7.1	−0.7	5.13	−0.4
Zn(II)	0.74	6.56	6.4	+0.2	4.79	−0.9
Mg(II)	0.74	1.7	1.5	+0.2	1.24[d]	+0.8
Cd(II)	0.96	7.49	5.4	+2.1	5.07	−0.3
Ca(II)	1.00	3.74	1.0	+2.7	1.08[d]	+1.0
Sr(II)	1.18	2.46	0.7	+1.8		
Pb(II)	1.19	7.32	4.5	+2.8	6.12	+1.0
Ba(II)	1.36	2.04	0.4	+1.6		

[a] See Figure 1 for ligand abbreviations. [b] The metal ions are arranged in order of increasing ionic radius.[12] Radii are for six-coordination, except for Cu(II), which is for four-coordination. [c] Δlog K_1 for PDALC/phen, for example, refers to log K_1(PDALC) − log K_1(phen). [d] Unpublished work by R. T. Gephart, III, and R. D. Hancock, glass electrode potentiometry, 25 °C 0.1 M $\mathrm{NaClO_4}$.

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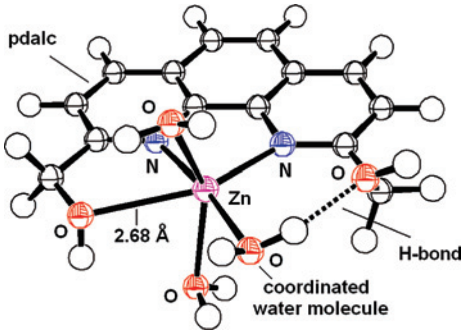

Figure 6. ORTEP[24] drawing of the complex of Zn(II) with PDALC as generated by PM3 semiempirical calculation.[39,40] The structure shows a H bond formed between a water coordinated to Zn(II), and the hydroxymethyl group of the PDALC ligand, as well as a very long Zn−O bond (2.68 Å) to the other hydroxymethyl group.

small metal ions. One sees that, as with the Ni(II)/PDA complex,[36] one hydroxymethyl of PDALC has, during energy minimization, become noncoordinating and is H-bonded to a water coordinated to the Zn(II). At the same time, the other Zn−O bond to the PDALC is very long. The steric effects that destabilize complexes of PDALC with small metal ions such as Zn(II) (or Cu(II)) may arise because (i) the long Zn−O bonds to the hydroxymethyl oxygen seen in Figure 6 must exist in place of a normal Zn−O bond to a coordinated water in the complex with phen itself and, (ii) even when the hydroxymethyl groups of PDALC is involved in a H bond with a coordinated water molecule on the Zn(II), this may be at less than ideal distances for the formation of a H bond, and so leads to destabilization.

Also shown in Table 5 are log K_1 values for the ligand DHEEN, which is an analog of PDALC insofar as it has two neutral N donors and two alcoholic O donors. As discussed in the introduction, DHEEN is much less preorganized than PDALC, and the consequence of this is that, for large metal ions that fit in the cleft of PDALC, log K_1 is considerably higher for PDALC than DHEEN. Conversely, for a small metal ion such as Cu(II), log K_1 for PDALC is considerably lower than for DHEEN. One also notes the greater metal ion size-based selectivity generated in passing from phen to PDALC, as evidenced by the Δlog K_1 (PDALC/phen) values compared to the Δlog K_1 (DHEEN/en) values in Table 1. Adding two hydroxymethyl groups to phen to give PDALC produces a much sharper response to metal ion size than does adding two hydroxyethyl groups to en to give DHEEN. One should also note the greater complex stability of PDALC complexes with large metal ions such as Cd(II) and Pb(II) as compared to those with the macrocycle [18]-aneN_2O_4, which has[30] log K_1 values of 5.1 and 6.7, respectively.

Conclusions

PDALC demonstrates a high level of preorganization for a nonmacrocyclic ligand as well as enhanced thermodynamic stability in its complexes with metal ions having an ionic radius of about 1.0 Å. The rigidity of the five-membered chelate rings formed by PDALC accounts for its selectivity for larger over smaller metal ions such as Ni(II) and Zn(II). PDALC is a member of a largely unrecognized class of ligands, including the previously reported[13,14] PDA and DPP,[15] that achieve levels of preorganization rivaling, or even exceeding, those of macrocyclic ligands, but which derive their high levels of preorganization from the rigidity provided by extended aromatic systems and not a cyclic structure.

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Supporting Information Available: CIF files of discussed complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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