

Complexes of the highly preorganized ligand PDALC (2,9-bis(hydroxymethyl)-1,10-phenanthroline) with trivalent lanthanides. A thermodynamic and crystallographic study

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ABSTRACT

Metal ion complexing properties of the highly preorganized tetradentate ligand PDALC (2,9-bis(hydroxymethyl)-1,10-phenanthroline) are presented. The structure of [Gd(PDALC)(NO₃)₃·H₂O (**1**) is reported: triclinic, $P\bar{1}$, $a = 7.545(12)$, $b = 10.811(17)$, $c = 11.909(18)$ Å, $\alpha = 97.71(2)^\circ$, $\beta = 91.56(2)^\circ$, $\gamma = 109.06(2)^\circ$, $V = 907(2)$ Å³, $Z = 2$, $R = 0.0354$. The Gd is 10-coordinate, with the coordination sphere comprising the four donor atoms of the PDALC plus the six O-donors of three chelated nitrates. Comparison with structures in the literature suggests that the Gd–L (L = ligand) bond lengths, particularly those to the alcoholic O-donors of PDALC, are a little short. It was suggested that the short Gd–L bond lengths in **1** were due to the efficiency of packing of the nitrates around the Gd, with the short 'bite' distances of the nitrate ligand. Formation constants ($\log K_1$) were measured spectroscopically in 0.1 M NaClO₄ at 25 °C by monitoring the variation of the π – π^* transitions of 2×10^{-5} M PDALC in the range 200–350 nm as a function of pH, in the presence of 1:1 concentrations of the lanthanide(III) (Ln(III)) metal ion. The measured $\log K_1$ values varied from 5.34 (La(III)) to 6.40 (Lu(III)), which is an unusually small variation across the series of Ln(III) ions. Values of $\log K_1$ with PDALC were also measured for Y(III) (5.85) and Sc(III) (6.02). The small amount of variation in $\log K_1$ for PDALC across the series of Ln(III) ions was rationalised in terms of the effect of neutral oxygen donors on complex stability, which promotes selectivity for larger metal ions such as La(III). It was discussed how the small amount of variation in $\log K_1$ across the Ln(III) series might lead to optimal selectivity for the Am(III) ion relative to the Ln(III) ions as a group.

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1. Introduction

The separation of Am³⁺ from the rather similarly sized Ln³⁺ (Ln = lanthanide) ions, particularly La(III) and Gd(III), is an application of continuing interest, because of its importance in the treatment of nuclear waste [1]. The main difference in ligand affinities between An(III) (An = actinide) and similarly-sized Ln(III) ions arises from the greater covalence [2,3] in the M–L (metal–ligand) bonding of the An(III) ions. Considerable selectivity for An(III) ions over Ln(III) ions has been found for the potentially more covalent N-donor ligands BIP [4], TPEN [5], 4,7-diphenyl-phen [6], and TPTZ (see Fig. 1 for key to ligand abbreviations) [7–11]. Ligands such as DPAM have also been reported [12] for the extraction of Am³⁺, as well as S-donor ligands [13]. DFT (density functional theory) studies have been reported in relation to the differences in covalence between Ac(III) and Ln(III) metal–ligand bonding [14]. DFT

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has been used [15,16] to predict formation constants ($\log K_1$) of ammonia complexes in aqueous solution. These studies support the greater covalence of Am(III) as compared to some Ln(III) ions in the predicted value of $\log K_1(\text{NH}_3)$ for Am(III) = 2.3 compared to La(III) = 0.3 and Lu(III) = 1.0.

Ligand preorganization [17] is of major importance in ligand design [18]. A ligand is preorganized when, as the free ligand, it is constrained to be in the conformation required to complex the metal ion. Classical examples of highly preorganized ligands are the crown ethers [19], N-donor macrocycles [20], and cryptands [21]. Recently, the metal ion complexing properties [22] of PDA [23–25], DPP [26], and PDALC [27], which are highly preorganized non-macrocyclic ligands based on the rigid phen ligand with donor groups at the 2 and 9 positions, have been presented. These ligands derive their high levels of preorganization not from a cavity, as is present in macrocycles [19,20] and cryptands [21], but from a rigid cleft that exercises strong metal ion size-based selectivity, with the advantage of rapid metalation and demetalation reactions, which is important if such ligands are to become the functional groups

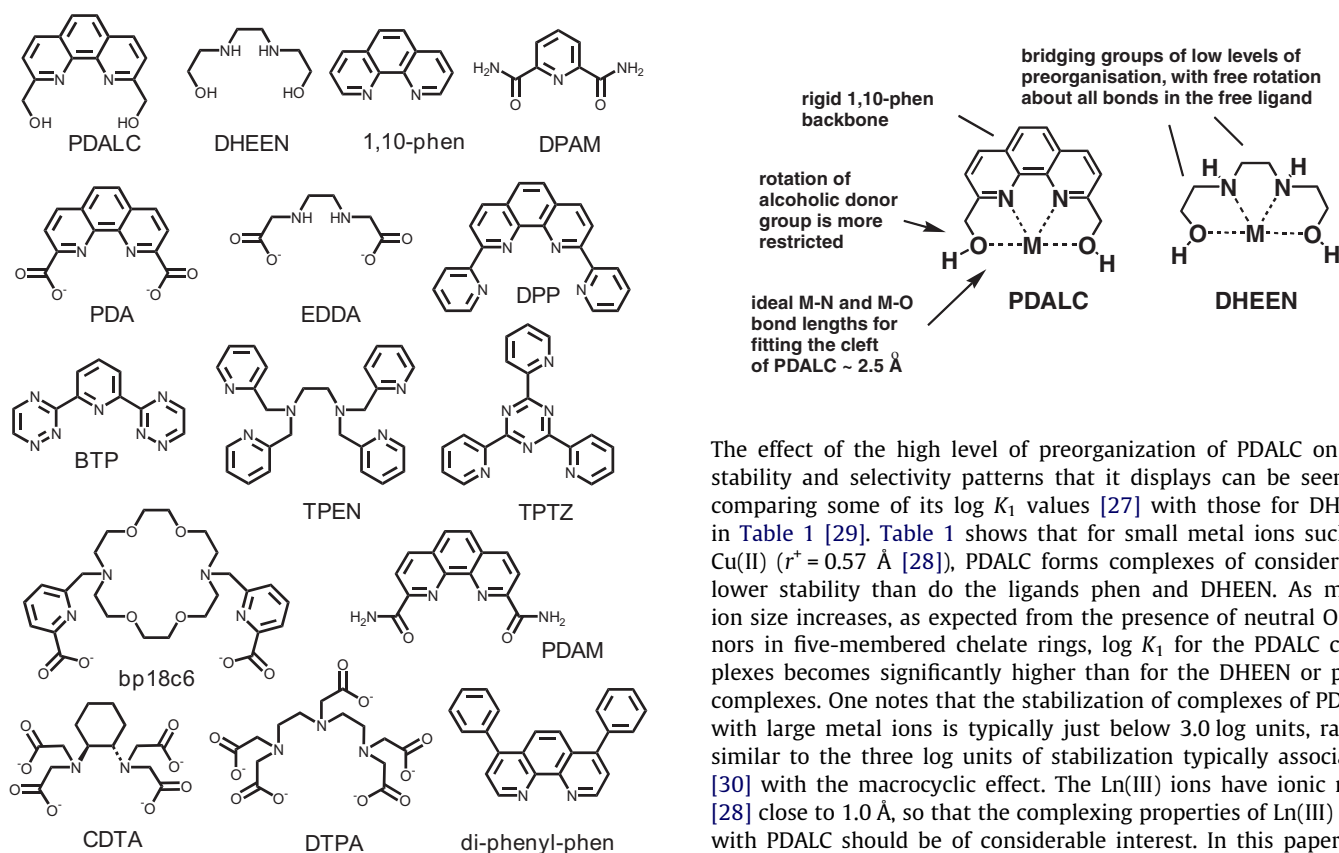


Fig. 1. Ligands discussed in this paper.

of solvent extractants for the separation of An(III) ions from Ln(III) ions.

The ligand PDALC is of especial interest in that it shows [27] strong selectivity towards larger metal ions of r^+ (ionic radius r^+) [28] of about 1.0 Å. It has been noted previously [18] that neutral O-donors (oxygen-donors) promote selectivity for large metal ions of r^+ of about 1.0 Å, so that neutral O-donors may also control the metal ion selectivities of crown ethers, as ligands that contain only neutral O-donors. PDALC has the interesting additional factor that its rigidity should enhance this factor as compared to analogues of low levels of preorganization such as DHEEN:

The effect of the high level of preorganization of PDALC on the stability and selectivity patterns that it displays can be seen by comparing some of its $\log K_1$ values [27] with those for DHEEN in Table 1 [29]. Table 1 shows that for small metal ions such as Cu(II) ($r^+ = 0.57$ Å [28]), PDALC forms complexes of considerably lower stability than do the ligands phen and DHEEN. As metal ion size increases, as expected from the presence of neutral O-donors in five-membered chelate rings, $\log K_1$ for the PDALC complexes becomes significantly higher than for the DHEEN or phen complexes. One notes that the stabilization of complexes of PDALC with large metal ions is typically just below 3.0 log units, rather similar to the three log units of stabilization typically associated [30] with the macrocyclic effect. The Ln(III) ions have ionic radii [28] close to 1.0 Å, so that the complexing properties of Ln(III) ions with PDALC should be of considerable interest. In this paper are reported the formation constants of PDALC complexes of the Ln(III) ions from La(III) to Lu(III), as well as with Y(III) and Sc(III). In addition, with the goal of better understanding the metal ion selectivities observed for PDALC, the structure of the complex $[\text{Gd}(\text{PDALC})(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ is reported.

2. Experimental

3.1. Materials and methods

PDALC was synthesised by a literature method [31]. 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 $>18 \text{ M}\Omega \text{ cm}^{-1}$ resistivity.

Table 1

Comparison of $\log K_1$ values for PDALC (this work), with those [29] of phen, and DHEEN, showing the effect of ionic radius [28] on changes in $\log K_1$. See Fig. 1 for ligand abbreviations.

Metal ion	Radius (Å) ^a	$\log K_1$ PDALC ^b	$\log K_1$ phen	$\Delta \log K_1$ PDALC/phen ^c	$\log K_1$ DHEEN	$\Delta \log K_1$ PDALC/DHEEN ^e
Cu(II)	0.57	7.56	9.1	−1.6	9.68	−2.1
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	+1.2
Zn(II)	0.74	6.56	6.4	+0.2	4.79	+1.8
Cd(II)	0.96	7.49	5.4	+2.1	5.07	+2.4
Ca(II)	1.00	3.74	1.0	+2.7	1.08 ^d	+2.6
La(III)	1.03	5.34	(2.8) ^e	2.5		
Pb(II)	1.19	7.32	4.5	+2.8	6.12	+1.2
Ba(II)	1.36	2.04	0.4	+1.6		

^a The metal ions are arranged in order of increasing ionic radius [28]. Radii are for 6-coordination, except for Cu(II) which is for 4-coordination.

^b Ref. [27].

^c $\Delta \log K_1$ for PDALC/phen, for example, refers to $\log K_1(\text{PDALC}) - \log K_1(\text{phen})$.

^d R.T. Gephart III, R.D. Hancock, unpublished work, glass electrode potentiometry, 25 °C 0.1 M NaClO₄.

^e Value refers to the Nd(III) complex [36] which should not be too different.

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