Coordination Behavior of 1,4-Disubstituted Cyclen Endowed with Phosphonate, Phosphonate Monoethylester, and H-Phosphinate Pendant Arms

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Content:

Synthesis of 1,4-dibenzyl-1,4,7,10-tetraazacyclododecane (1) Figure S1. Hydrogen bond network found in the crystal structure of 1,4-H₄do2p·4H₂O. Table S1. Geometric parameters of hydrogen bond network found in the crystal structure of 1,4-H₄do2p·4H₂O. Table S2. Experimental values of overall protonation/stability constants (log β_{hlm}) of the ligands 1,4-H₄do2p, 1,4-H₂do2p^{OEt} and 1,4-H₂Bn₂do2p^H and their complexes with metal ions. Figure S2. Distribution diagram of differently protonated species of studied ligands. Figure S3. Distribution diagram of species present in Cu(II)–studied ligand mixtures. Figure S4. Distribution diagram of species present in Zn(II)–studied ligand mixtures. Figure S5. ¹H NMRD profiles of Mn(II)–1,4-H₂do2p^{OEt} and Mn(II)–1,4-H₂Bn₂do2p^H complexes. Figure S6. Temperature dependence of ⁵D₀ \leftarrow ⁷F₀ transition in absorption spectra of Eu(III)–1,4-H₄do2p complex.

Synthesis of 1,4-dibenzyl-1,4,7,10-tetraazacyclododecane (1)

Cyclen was obtained from Chematech and was used as received. Oxalyl-protected cyclen and its dibenzyl derivative were obtained according to ref.^[1]. The 1,4-dibenzylcyclen was obtained by slightly modified literature method:^[1]

Dibenzyl-oxalyl-cyclen (9.0 g, 22 mmol) was dissolved in a mixture 30% aq. NaOH (100 ml) and EtOH (20 ml). The solution was stirred and heated to 95 °C overnight. The reaction mixture was cooled and the volatiles were evaporated in vacuum. The solid was dissolved in water (70 ml) and washed by CH₂Cl₂ (100 ml) three times. The CH₂Cl₂ phases were combined, the solution was dried by anhydrous Na₂SO₄ and volatiles were evaporated in vacuum. The oily residue solidified in fridge. The white solid was dried in vacuo (7.0 g, 90 %). Spectral data were consistent with those reported in literature.^[1]

[1] Bellouard, F.; Chuburu, F.; Kervarec, N.; Toupet, L.; Triki, S.; Le Mest, Y.; Handel, H. *cis*-Diprotected cyclams and cyclens: a new route to symmetrically or asymmetrically 1,4disubstituted tetraazamacrocycles and to asymmetrically tetrasubstituted derivatives. *J. Chem. Soc., Perkin Trans.* 1 **1999**, 3499–3505.



Figure S1. Hydrogen bond network found in the crystal structure of 1,4-H₄do2p·4H₂O. Carbonbound hydrogen atoms are omitted for clarity.

D-H	d(D–H) [Å]	d(H…A) [Å]	<d-h…a [°]<="" th=""><th>d(D…A) [Å]</th><th>Α</th></d-h…a>	d(D…A) [Å]	Α
N1-H11	0.86(3)	2.64(3)	110(2)	3.040(1)	N4
N1-H11	0.86(3)	2.30(3)	118(2)	2.808(2)	N10
N7-H71	0.88(2)	2.65(5)	107(1)	3.030(2)	N4
N7-H71	0.88(2)	2.75(2)	97(1)	2.989(2)	N10
N7-H71	0.88(2)	2.03(2)	153(2)	2.847(2)	O1W
N7-H72	0.91(2)	1.82(2)	162(2)	2.704(2)	O4W [<i>x</i> -1, <i>y</i> -1, <i>z</i>]
N10-H101	0.88(2)	1.99(2)	161(2)	2.839(2)	O13 [- <i>x</i> +1, - <i>y</i> +1, - <i>z</i> +1]
O11-H11O	0.72(2)	1.89(2)	170(3)	2.603(1)	O22
O21-H221	0.78(2)	1.83(2)	178(2)	2.608(1)	O23 [- <i>x</i> +1, - <i>y</i> , - <i>z</i>]
O1W-H11W	0.86(2)	1.83(3)	168(2)	2.684(2)	O13
O1W-H12W	0.83(2)	1.99(2)	160(2)	2.785(1)	O22
O2W-H21W	0.86(2)	1.92(2)	172(2)	2.779(2)	O12 [- <i>x</i> +1, - <i>y</i> +1, - <i>z</i> +1]
O2W-H22W	0.83(2)	2.00(2)	178(2)	2.825(1)	O23 [- <i>x</i> +1, - <i>y</i> , - <i>z</i> +1]
O3W-H31W	0.87(3)	1.92(3)	164(2)	2.772(2)	O2W
O3W-H32W	0.87(3)	1.90(3)	166(2)	2.748(2)	O1W
O4W-H41W	0.87(3)	1.81(3)	165(2)	2.666(2)	O3W [- <i>x</i> +2, - <i>y</i> +1, - <i>z</i> +1]
O4W-H42W	0.82(2)	1.89(2)	174(2)	2.704(2)	O12

Table S1. Geometric parameters of hydrogen bond network found in the crystal structure of 1,4-H4do2p-4H2O.

Table S2. Experimental values of overall protonation/stability constants $(\log \beta_{hlm})^a$ of 1,4-H₄do2p, 1,4-H₂do2p^{OEt} and 1,4-H₂Bn₂do2p^H and their complexes with metal ions. Conditions: 25 °C, *I* = 0.1 M (NMe₄)Cl. Standard deviations in parenthesis as calculated by OPIUM.

Ion	Equilibrium ^b	h	1	m	1,4-H4do2p	1,4-H2do2pOEt	1,4-H2Bn2do2p ^H
H+	$L^{n-} + H^+ \iff HL^{1-n}$	0	1	0	12.84(2)	11.377(6)	11.249(9)
	$L^{n-} + 2 H^+ \Longrightarrow H_2 L^{2-n}$	1	1	0	24.04(2)	19.95(1)	18.08(2)
	$L^{n-} + 3 H^+ \implies H_3 L^{3-n}$	2	1	0	31.79(2)	21.24(2)	-
	$L^{n-} + 4 H^+ \Longrightarrow H_4 L^{4-n}$	3	1	0	36.73(2)	-	-
	L^{n-} + 5 H ⁺ \Longrightarrow H ₅ L ⁵⁻ⁿ	4	1	0	38.13(2)	-	-
Mg ²⁺	$L^{n-} + Mg^{2+} \iff [Mg(L)]^{2-n}$	0	1	0	7.36(1)	-	-
	$L^{n-} + Mg^{2+} + H^+ \implies [Mg(HL)]^{3-n}$	1	1	0	17.07(2)	-	-
	$L^{n-} + Mg^{2+} + 2 H^{+} \Longrightarrow [Mg(H_2L)]^{4-n}$	2	1	0	26.31(3)	-	-
Ca ²⁺	$L^{n-} + Ca^{2+} \iff [Ca(L)]^{2-n}$	0	1	1	9.29(2)	5.90(2)	3.96(3)
	$L^{n-} + Ca^{2+} + H^+ \implies [Ca(HL)]^{3-n}$	1	1	1	18.31(2)	-	-
	$L^{n-} + Ca^{2+} + H_2O \implies [Ca(OH)(L)]^{1-n} + H^+$	-1	1	1	-	-	-8.32(4)
Mn ²⁺	$L^{n-} + Mn^{2+} \iff [Mn(L)]^{2-n}$	0	1	1	15.41(1)	11.420(9)	9.39(2)
	$L^{n-} + Mn^{2+} + H^+ \implies [Mn(HL)]^{3-n}$	1	1	1	23.513(4)	-	-
	$L^{n-} + Mn^{2+} + 2 H^{+} \rightleftharpoons [Mn(H_2L)]^{4-n}$	2	1	1	28.74(2)	-	-
	$L^{n-} + Mn^{2+} + H_2O \implies [Mn(OH)(L)]^{1-n} + H^+$	-1	1	1	-	-0.78(2)	-1.74(2)
Cu ²⁺	$L^{n-} + Cu^{2+} \iff [Cu(L)]^{2-n}$	0	1	1	26.45(4)	19.95(3)	-
	$L^{n-} + Cu^{2+} + H^+ \implies [Cu(HL)]^{3-n}$	1	1	1	33.13(4)	-	-
	$L^{n-} + Cu^{2+} + 2 H^+ \implies [Cu(H_2L)]^{4-n}$	2	1	1	37.80(3)	-	-
	$L^{n-} + Cu^{2+} + H_2O \implies [Cu(OH)(L)]^{1-n} + H^+$	-1	1	1	-	7.24(7)	-
Zn^{2+}	$L^{n-} + Zn^{2+} \Longrightarrow [Zn(L)]^{2-n}$	0	1	1	21.111(9)	15.416(6)	13.26(2)
	$L^{n-} + Zn^{2+} + H^+ \implies [Zn(HL)]^{3-n}$	1	1	1	27.998(5)	-	-
	$L^{n-} + Zn^{2+} + 2 H^{+} \Longrightarrow [Zn(H_2L)]^{4-n}$	2	1	1	32.110(6)	-	-
	$L^{n-} + Zn^{2+} + H_2O \implies [Zn(OH)(L)]^{1-n} + H^+$	-1	1	1	8.30(2)	5.91(1)	4.14(4)
	$L^{n-} + Zn^{2+} + 2 H_2O \implies [Zn(OH)_2(L)]^{-n} + 2 H^+$	-2	1	1	-	-	-8.17(5)
Gd ³⁺	$L^{n-} + Gd^{3+} \iff [Gd(L)]^{3-n}$	0	1	1	19.15(5)	-	-
	$L^{n-} + Gd^{3+} + H^+ \rightleftharpoons [Gd(HL)]^{4-n}$	1	1	1	26.20(5)	-	-
	$L^{n-} + Gd^{3+} + 2 H^{+} \stackrel{\longrightarrow}{=} [Gd(H_2L)]^{5-n}$	2	1	1	32.22(3)	-	-
	$L^{n-} + Gd^{3+} + 3 H^{+} = [Gd(H_3L)]^{6-n}$	3	1	1	36.08(4)	-	-

 ${}^{a}\beta_{hlm} = [H_{h}L_{l}M_{m}]/([H]^{h}\cdot[L]^{l}\cdot[M]^{m}). {}^{b}n = 4 \text{ for } 1,4-H_{4}do2p, \text{ and } n = 2 \text{ for } 1,4-H_{2}do2p^{OEt} \text{ and } 1,4-H_{2}Bn_{2}do2p^{H}.$



Figure S2. Distribution diagram of differently protonated species of **A**: 1,4-H₄do2p; **B**: 1,4-H₂do2p^{OEt}; and **C**: 1,4-H₂Bn₂do2p^H (c_L = 5 mM, I = 0.1 M NMe₄Cl, 25 °C).



 $\label{eq:Figure S3.} \ensuremath{\text{Distribution diagram of species present in (A): Cu(II)-1,4-H_4do2p system; and (B): Cu(II)-1,4-H_2do2p^{OEt} system. Stoichiometric coefficients: H-L-M. }$



Figure S4. Distribution diagram of species present in (A): Zn(II)–1,4-H₄do2p system; (B): Zn(II)–1,4-H₂do2p^{OEt} system; and (C): Zn(II)–1,4-H₂Bn₂do2p^H system ($c_L = c_{Zn} = 5 \text{ mM}$, I = 0.1 M NMe₄Cl, 25 °C). Stoichiometric coefficients: H-L-M.



Figure S5. ¹H NMRD profiles of **A**: Mn(II)–1,4-H₂do2p^{OEt} (pH 9.0, ~100% [Mn(1,4-do2p^{OEt})]); and **B**: Mn(II)–1,4-H₂Bn₂do2p^H (pH 9.0, ~100% [Mn(Bn₂do2p^H)]) systems.



Figure S6. Temperature dependence of ${}^5D_0 \leftarrow {}^7F_0$ transition in absorption spectrum of Eu(III)–1,4-H4do2p complex.