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Metal Ion-Dependent Molecular Inclusion Chemistry: Inclusion of Aromatic Anions by Coordinated 1,4,7,10-Tetrakis((*S*)-2-hydroxy-3-phenoxypropyl)-1,4,7,10-tetraazacyclododecane

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The ability of the pendant donor macrocyclic ligand 1,4,7,10-tetrakis((*S*)-2-hydroxy-3-phenoxypropyl)-1,4,7,10-tetraazacyclododecane((*S*)-thphpc12) (or [Cd((*S*)-thphpc12)]$^{2+}$) to act as a metal ion-dependent receptor for aromatic anions has been investigated in solution and in the solid state. [Cd((*S*)-thphpc12)]$^{2+}$ adopts a stable conical conformation with a large hydrophobic cavity, which has been shown to contain, via complementary multiple hydrogen bonding, *p*-nitrophenolate, aromatic carboxylates, *p*-toluenesulfonate, certain aromatic amino acid anions, phenoxyacetate, and acetate. In the case of *p*-nitrophenolate only, one or two anions can be contained within the receptor cavity. The crystal structure of [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$] shows a coplanar arrangement of the *p*-nitrophenolates, where each is retained in the cavity by a pair of hydrogen bonds to cis hydroxyl groups. The crystal structure of the *p*-aminobenzoate inclusion complex indicates retention of the guest via a pair of hydrogen bonds to each oxygen atom of the carboxylate moiety. The crystal structure of the (L)-phenylalaninate inclusion complex indicates that the amino acid is retained by five hydrogen bonds, two involving the nitrogen atom and three to the oxygen atoms of the carboxylate moiety. Binding constants (10^3–10^5 M^{-1}) for the inclusion of some of the aforementioned anions in [Cd((*S*)-thphpc12)]$^{2+}$ and related receptors were measured by ^{1}H NMR titration in DMSO-d_6 at 298 K.

Introduction

Recently, we demonstrated the practicality of constructing metal ion-dependent molecular receptor complexes.[1] These are ternary complexes that are formed from pendant donor macrocyclic ligands that assemble into an extended conical conformation in response to octadentate coordination with an appropriate metal ion. The resulting binary complex can then act as a receptor for smaller guest molecules, thus generating a ternary complex. While this mechanism has been noted serendipitously on at least one previous occasion,[2] the objective of our work was to systematize the process and thereby initiate a means by which the well-established phenomenon seen in biology, whereby a protein (the ligand), a metal ion, and a substrate (the guest) come together in an assembly that subsequently functions as a metalloenzyme, could be simulated. We found that the ligand 1,4,7,10-tetrakis((*S*)-2-hydroxy-3-phenoxypropyl)-1,4,7,10-tetraazacyclododecane (hereafter (*S*)-thphpc12) (See Chart 1 ; the eight bonds to each Cd^{2+} have been omitted, for clarity.) provided a convenient starting point for this work. We demonstrated by X-ray crystallography, ^{13}C NMR spectroscopy, and conductivity measurements the capacity of the Cd(II) and Pb(II) diperchlorate complexes of (*S*)-thphpc12) to include the aromatic anions *p*-toluenesulfonate and *p*-nitrophenolate in its binding cavity, at the expense of one of the two nonincluded perchlorate ions. From conductivity studies, it was clear that *p*-nitrophenolate binds more strongly than *p*-toluenesulfonate and that the retention of either guest is stronger in the Cd(II) than in the Pb(II) complex of the ligand. The binary complexes formed in this way are inherently chiral, not only because of the four stereogenic

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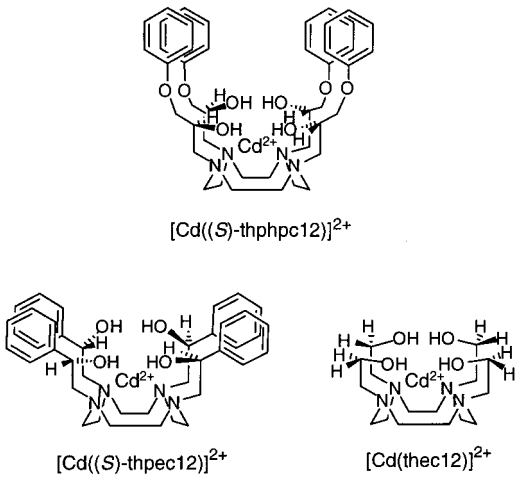
Chart 1



centers contained within the pendant arms but also because of the unidirectional spiralling of the arms that is induced by the proclivity of the eight-coordinate metal ions to assume square antiprismatic (rather than cubic) geometry.

The purpose of this work was to explore more fully the potential of [Cd((*S*)-thphpc12)]$^{2+}$ as a receptor for aromatic anions through isolation and structural characterization of other ternary receptor complexes and through in situ binding-constant measurements for various receptor−guest combinations. In particular, we wished to examine quantitatively the selectivity of the guest-binding, discover whether multiple guest retention could be achieved, and look for indications of chiral discrimination between the enantiomers of aromatic amino acid anions.

Experimental Section

General. ^{13}C and ^{1}H NMR spectra were recorded at 75.46 and 300.08 MHz, respectively, using a Varian Gemini 300 spectrometer at 295 K. ^{13}C chemical shifts are quoted with respect to the central resonance of the solvent multiplet for which the resonance position was taken, δ 77.00 for $CDCl_3$ and δ 39.60 for DMSO-d_6. Elemental analyses were performed at the University of Otago, New Zealand. Conductivity measurements were made on 10^{-3} M solutions in dimethylformamide at 293 K using a TPC LC 84 conductivity bridge. Established conductivity (Λ_M) ranges for 10^{-3} M 1:1 and 2:1 electrolytes in DMF are 65−90 and 130−170 Ω^{-1} cm^2 mol^{-1}, respectively.[3] [Cd((*S*)-thphpc12]$(ClO_4)_2$ **1** and [Cd(thec12)]$(ClO_4)_2$ **4** were prepared by previously reported procedures. Sodium salts of the various guest anions were prepared by reacting stoichiometric quantities of the acidic component with sodium hydroxide in water, followed by removal of the water and recrystallization of the solid residue from ethanol or a similar solvent. All solvents were purified before use by established methods.[5] Reactions were carried out under an atmosphere of dry nitrogen.

Synthesis of [Cd((*S*)-thphpc12)(*p*-Nitrophenolate)$_2$]. Sodium *p*-nitrophenolate (74 mg, 0.46 mmol) was added to a solution of [Cd((*S*)-thphpc12]$(ClO_4)_2$ (248 mg, 0.23 mmol) in dry acetonitrile (15 cm^3) at ambient temperature. The salt dissolved, and a fine yellow precipitate formed after about 1 min. The suspension was boiled under reflux for 1 h and then cooled, and the product was filtered off and dried under high vacuum. Yield: 184 mg, 70%. ^{13}C NMR (DMSO-d_6): δ 175.64, 158.44, 132.02, 129.53, 126.93, 120.80, 118.30, 114.53, 70.30, 64.46, 56.49, 50.09, 48.51. Anal. Calcd for $C_{56}H_{68}CdN_6O_{14}$: C, 57.91; H, 5.90; N, 7.23. Found: C, 57.92; H, 5.91; N, 7.23. Λ_M = 61 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M, DMF) (1:1).

Synthesis of [Cd((*S*)-thphpc12)(*p*-Nitrophenolate)]-*p*-toluenesulfonate·3H$_2$O. Sodium *p*-nitrophenolate (30 mg, 0.18 mmol) was added to a suspension of [Cd((*S*)-thphpc12)(*p*-toluenesulfonate)]ClO_4 **1** (212 mg, 0.18 mmol) in acetonitrile (15 cm^3). The suspension was heated under reflux for 1 h, whereupon the host had not completely dissolved. DMF (1 cm^3) was added to dissolve the host, and the solution was heated under reflux for another hour. On cooling to room temperature, the solvent was removed by rotary evaporation, leaving an oily residue. Water (10 cm^3) was added, and the oily dispersion was heated to boiling. DMF was added to the dispersion dropwise until a clear solution was obtained. Slow cooling of the solution resulted in small yellow crystals that were filtered off and washed with cold water (5 cm^3). Yield: 183 mg, 78%. ^{13}C NMR (DMSO-d_6): δ 172.84, 158.38, 145.57, 137.88, 134.34, 129.62, 128.21, 126.61, 125.62, 120.95, 117.91, 114.57, 69.98, 64.48, 55.57, 50.03, 48.28, 20.89. Anal. Calcd for $C_{57}H_{77}CdN_5O_{17}S$: C, 54.83; H, 6.22; N, 5.61. Found: C, 54.67; H, 6.06; N, 5.78. Λ_M = 94 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M, DMF) (high 1:1).

Synthesis of [Cd((*S*)-thphpc12)(Benzoate)]ClO$_4$. [Cd((*S*)-thphpc12)]$(ClO_4)_2$ (394 mg, 0.36 mmol) was dissolved in dry methanol (20 cm^3). The solution was heated to reflux, and a solution of sodium benzoate (52 mg, 0.36 mmol) in dry methanol (4 cm^3) was added. The solution was heated under reflux for 2 h and then cooled to room temperature. The solvent was removed, and ether (20 cm^3) was added to the residue. A white solid formed that was filtered off and recrystallized from ethanol (50 cm^3). Small white plates formed that were isolated by filtration. Yield: 275 mg, 69%. ^{13}C NMR (DMSO-d_6): δ 172.61 (C═O), 158.66, 136.89, 130.62, 129.75, 129.55, 127.76, 121.05, 114.79, 70.09, 63.88, 55.89, 50.96, 47.62. Anal. Calcd for $C_{51}H_{65}CdClN_4O_{14}$: C, 55.39; H, 5.92; N, 5.07. Found: C, 55.18; H, 6.10; N, 5.24. Λ_M = 67 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M, DMF) (1:1).

Synthesis of [Cd((*S*)-thphpc12)(Salicylate)]ClO$_4$. A solution of sodium salicylate (33 mg, 0.20 mmol) in dry methanol (2 cm^3) was added to a boiling solution of [Cd((*S*)-thphpc12](ClO$_4$)$_2$ (222 mg, 0.20 mmol) in dry methanol (15 cm^3). The clear solution was heated under reflux for 2 h and cooled to ambient temperature. The solution was then cooled in the refrigerator overnight, whereupon small white crystals formed. These were filtered off and vacuum-dried. Yield: 144 mg, 63%. ^{13}C NMR (DMSO-d_6): δ 173.52 (C═O), 161.84, 158.60, 132.82, 130.81, 129.77, 121.12, 119.13, 117.43, 116.29, 114.76, 69.90, 64.21, 55.27, 50.46, 47.90. Anal. Calcd for $C_{51}H_{65}CdClN_4O_{15}$: C, 54.60; H, 5.84; N, 4.99. Found: C, 54.63; H, 5.89; N, 5.15. Λ_M = 77 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M, DMF) (1:1).

Synthesis of [Cd((*S*)-thphpc12)(*p*-Aminobenzoate)]ClO$_4$. Sodium *p*-aminobenzoate (35 mg, 0.23 mmol) was added to a solution of [Cd((*S*)-thphpc12](ClO$_4$)$_2$ (241 mg, 0.23 mmol) in dry acetonitrile (15 cm^3). The sodium salt dissolved on heating the solution at reflux for 2 h. After the solution cooled to room temperature, the solvent was removed to give a solid residue that was suspended in water (5 cm^3). The residue became oily and sticky and was heated to boiling. Acetonitrile was added slowly until the oily sludge dissolved, and the clear solution was cooled slowly over several

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days. Large colorless prisms formed and were filtered off. Yield: 124 mg, 50%. ^{13}C NMR (DMSO-d_6): δ 173.43 (C═O), 158.64, 151.49, 131.31, 129.70, 123.43, 120.98, 114.79, 112.47, 70.13, 63.88, 56.05, 50.96, 47.71. Anal. Calcd for $C_{51}H_{66}CdClN_5O_{14}$: C, 54.84; H, 5.59; N, 6.27. Found: C, 54.67; H, 5.87; N, 6.45. Λ_M = 62 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M, DMF) (1:1).

Synthesis of [Cd((*S*)-thphpc12)(1-Naphthalene carboxylate)]-$ClO_4 \cdot H_2O$. Method 1: [Cd((*S*)-thphpc12)]$(ClO_4)_2$ (232 mg, 0.21 mmol) was dissolved in dry acetonitrile (15 cm^3). Sodium 1-naphthalene carboxylate (39 mg, 0.21 mmol) was added and the solution was heated under reflux for 2 h. The solvent was removed under reduced pressure, and the residue was triturated with ether (20 cm^3) to afford a white solid. The solid was stirred in the ether solution for 1 h and then filtered off and suspended in water (10 cm^3). The suspension was heated to boiling, and acetonitrile (ca. 7 cm^3) was added slowly until the suspended material dissolved. Slow cooling of the solution resulted in the formation of fine white needles that were collected by filtration and dried in vacuo. Yield: 146 mg, 58%. ^{13}C NMR (DMSO-d_6): δ 174.31 (C═O), 158.63, 135.44, 133.64, 131.18, 130.15, 129.71, 128.51, 128.17, 127.35, 126.09, 125.52, 124.89, 121.02, 114.76, 70.05, 64.01, 55.79, 50.88, 47.71. Anal. Calcd for $C_{55}H_{69}CdClN_4O_{15}$: C, 56.27; H, 5.92; N, 4.77. Found: C, 56.45; H, 5.71; N, 4.94. Λ_M = 71 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M, DMF) (1:1). Method 2: [Cd((*S*)-thphpc12)]$(ClO_4)_2$ (218 mg, 0.20 mmol) was dissolved in dry methanol (15 cm^3) under reflux. Sodium 1-naphthalene carboxylate (37 mg, 0.20 mmol) was added, and the solid dissolved. A white precipitate formed after 5 min. The suspension was heated under reflux for 2 h without dissolution of the suspended material. The suspension was cooled to ambient temperature, and the precipitated material was filtered off and dried under vacuum. Yield: 144 mg, 61%.

Synthesis of [Cd((*S*)-thphpc12)(2-Naphthalene carboxylate)]-ClO_4. Sodium 2-naphthalene carboxylate (36 mg, 0.19 mmol) was added to a solution of [Cd((*S*)-thphpc12)]$(ClO_4)_2$ (212 mg, 0.19 mmol) in dry acetonitrile (15 cm^3). The solution was heated under reflux for 2 h and then cooled. The solvent was evaporated, and ether (20 cm^3) was added to precipitate a white solid. The solid was filtered off and recrystallized from aqueous acetonitrile to afford white needles of the pure product (154 mg, 68%). ^{13}C NMR (DMSO-d_6): δ 172.56 (C═O), 158.64, 134.44, 134.29, 132.52, 129.69, 129.02, 127.65, 127.17(2C), 126.74, 126.21, 121.01, 114.78, 70.09, 63.90, 55.87, 50.96, 47.62. Anal. Calcd for $C_{55}H_{67}CdClN_4O_{14}$: C, 57.15; H, 5.84; N, 4.85. Found: C, 57.34; H, 5.79; N, 4.78. Λ_M = 64 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M, DMF) (1:1).

Synthesis of [Cd((*S*)-thphpc12)((L)-Phenylalaninate)]ClO_4. Method 1: Sodium (L)-phenylalaninate (39 mg, 0.21 mmol) was added to a solution of [Cd((*S*)-thphpc12)]$(ClO_4)_2$ (227 mg, 0.21 mmol) in dry acetonitrile (15 cm^3), and the suspension was heated under reflux for 2 h. The solvent was removed under reduced pressure, leaving a semisolid residue that was taken up in hot methanol (15 cm^3). Small colorless crystals were deposited on cooling of the solution. Yield: 110 mg, 46%. Method 2: The same procedure was used, except that the initial solution was left standing for several days at room temperature. Large prisms that were suitable for X-ray structural analysis crystallized. ^{13}C NMR (DMSO-d_6): δ 179.19 (C═O), 158.41, 139.56, 129.55, 129.16, 128.06, 125.85, 120.86, 114.61, 70.09, 63.99, 57.37, 56.21, 50.74, 47.96, 40.95. Anal. Calcd for $C_{53}H_{70}CdClN_5O_{14}$: C, 55.40; H, 6.14; N, 6.10. Found: C, 55.09; H, 5.92; N, 6.13. Λ_M = 63 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M, DMF) (1:1).

Synthesis of [Cd((*S*)-thpec12)]$(ClO_4)_2$. A solution of cadmium perchlorate hexahydrate (622 mg, 1.47 mmol) in dry ethanol (5 cm^3) was added over 5 min to a boiling solution of (*S*)-thpec12[6,7] (646 mg, 0.98 mmol) in dry ethanol (60 cm^3). The product precipitated as a white powder during the addition, and the suspension was heated under reflux for another hour to ensure complete reaction. After cooling to ambient temperature, the product was filtered off and dried under high vacuum. Yield: 0.95 g, 99%. ^{13}C NMR (DMSO-d_6): δ 141.98, 128.67, 128.37, 127.04, 68.44, 60.22, 50.73, 48.33. Anal. Calcd for $C_{40}H_{52}CdCl_2N_4O_{12}$: C, 49.83; H, 5.44; N, 5.81. Found: C, 50.11; H, 5.65; N, 5.90. Λ_M = 138 Ω^{-1} cm^2 mol^{-1} (1×10^{-3} M, DMF) (1:2).

Binding Constant Measurements. Binding constants for host−guest associations were determined by monitoring changes in the chemical shift of a convenient guest ^{1}H NMR resonance while aliquots of the host complex, in the form of its diperchlorate salt in DMSO-d_6, were added to 1×10^{-3} mol dm^{-3} samples of the sodium salt of the guest in DMSO-d_6. A series of ^{1}H NMR spectra were recorded at 298 ± 0.5 K for each host−guest combination from host−guest ratios of 0:1−10:1. Approximately 14 different host−guest ratios were used to construct each titration curve, which was then fitted using a nonlinear curve-fitting procedure to yield the value of the binding constant.

Crystal Structure Determinations. Unit-cell and intensity data for [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$] and for [Cd((*S*)-thphpc12)-((L)-phenylalaninate)]ClO_4 were measured on a Siemens SMART[8] diffractometer using graphite-monochromated Mo Kα X-radiation. The data were corrected for absorption by C. Rickard of the University of Auckland, New Zealand, using *SADABS*[9]. Unit-cell and intensity data for [Cd((*S*)-thphpc12)(*p*-aminobenzoate)]ClO_4 were collected on a CAD-4/PC diffractometer using graphite-monochromated Mo Kα X-radiation. The data were corrected for absorption by Gaussian integration from the crystal shape. Parameters associated with unit-cell dimensions and intensity data collection and refinement for the structures are given in Table 1.

The structures were solved using *SIR92*;[10] otherwise, computer programs of the XTAL system[11] were used for all calculations. Non-hydrogen atomic coordinates and anisotropic displacement parameters for all atoms were refined by full-matrix least-squares calculations performed on F^2 by minimizing $\Sigma w(|F_o^2| - |F_c^2|)^2$ where $w = 1/s^2$. $s = [\sigma^2(F_o^2) + (0.04\,F_o^2)^2]^{0.5}$ for [Cd((*S*)-thphpc12)-((L)-phenylalaninate)]ClO_4, and $\sigma^2(F_o^2)$ for the other two structures. Neutral-atom scattering factors with anomalous dispersion corrections were used. For [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$], hydroxyl hydrogen atoms were located in a difference map; for [Cd((*S*)-thphpc12)(*p*-aminobenzoate)]ClO_4, hydroxyl and amino hydrogen atoms were located in a difference map. For [Cd((*S*)-thphpc12)((L)-phenylalaninate)]ClO_4, amino hydrogen atoms were located in a difference map, but hydroxyl hydrogen atoms could not be located and were not included in calculations. All other hydrogen atoms were placed at calculated positions, and although their coordinates and isotropic displacement parameters were not refined, the coordinates were recalculated several times during the

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Table 1. Crystal Data and Refinement Summary for [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$] (**1**), [Cd((*S*)-thphpc12)(*p*-aminobenzoate)]ClO_4 (**2**), and [Cd((*S*)-thphpc12)((L)-phenylalaninate)]ClO_4 (**3**)

compound	**1**	**2**	**3**
empirical formula	$C_{56}H_{68}N_6O_{14}Cd$	$C_{51}H_{66}N_5O_{14}CdCl$	$C_{53}H_{70}N_5O_{14}CdCl$
M	1161.60	1120.97	1149.01
system	tetragonal	triclinic	triclinic
space group	$P4_12_12$	$P1$	$P1$
a/Å	10.7328(1)	10.561(3)	10.809(1)
b/Å	10.7328(1)	11.823(4)	12.080(1)
c/Å	46.1644(6)	12.284(5)	12.564(1)
α/deg	90.00	111.50(4)	64.77(1)
β/deg	90.00	91.10(3)	87.04(1)
γ/deg	90.00	115.76(3)	64.20(1)
U/Å^3	5317.82(12)	1255.7(10)	1317.9(3)
λ/Å	0.71073	0.71073	0.71073
Z	4	1	1
color and shape	yellow prism	colorless prism	colorless prism
size/mm	0.22 × 0.17 × 0.17	0.40 × 0.30 × 0.18	0.27 × 0.25 × 0.16
diffractometer type	Siemens CCD	CAD-4/PC	Siemens CCD
D_c/Mg m^{-3}	1.451	1.482	1.463
F(000)	2424	584	600
T/K	203(2)	150(2)	200(2)
μ/mm^{-1}	0.484	0.560	0.540
T_{min}, T_{max}	0.825, 0.935	0.881, 0.914	0.848, 0.938
θ_{max}/deg	25.68	25.13	27.46
ranges			
h	−9; 9	−12; 12	−13; 13
k	−13; 13	−14; 12	−15; 15
l	−56; 56	−14; 14	−16; 16
R_{int}	0.020	0.02	0.014
no. reflections measured	5329	8766	12832
no. unique reflections	3008	4381	5689
no. used in refinement ($F^2 > 0$)	2982	4379	5023
no. parameters refined	348	647	698
$R(F)$	0.039	0.024	0.028
$R_w(F^2)$	0.058	0.074	0.073
GOF	1.73	1.46	1.27
final shift/error (max.)	0.0003	0.0001	0.0001
$\Delta\rho$/e Å^{-3}			
min.	−0.58	−0.98	−0.50
max.	0.51	0.39	0.60

refinements. In [Cd((*S*)-thphpc12)((L)-phenylalaninate)]ClO_4, two positions were found for O23 and the attached phenyl ring. This feature was modeled by two rigid groups involving the phenyl carbon and hydrogen atoms and the phenoxy oxygen atom. Results from this model refined reasonably with a population ratio of 0.608(8)/0.392(8). A Flack parameter[12] (−0.04(1)) was refined for [Cd((*S*)-thphpc12)(*p*-aminobenzoate)]ClO_4, but a similar procedure for the other structures did not refine satisfactorily; instead, the structures were refined using the entire Friedel independent data sets. The synthetic scheme precluded the presence of a center of symmetry in the space groups, and this result was confirmed by intensity statistics, the structure solution, and the program *BUNYIP*.[13]

Results and Discussion

Inclusion Compounds Derived from [Cd((*S*)-thphpc12)]-(ClO_4)$_2$. To address the objectives outlined in the Introduction, a series of experiments were conducted in which [Cd((*S*)-thphpc12)](ClO_4)$_2$ and the sodium salt of an aromatic anion were combined in either acetonitrile or methanol and the displaced sodium perchlorate (if any) was removed. Using this general procedure, we were able to isolate inclusion complexes involving the monooxoanion *p*-nitrophenolate, the dioxoxoanions benzoate, salicylate (*o*-hydroxybenzoate), *p*-aminobenzoate, 1- and 2-naphthalene carboxylate, and (L)-phenylalaninate, and the trioxoanion *p*-toluenesulfonate that has already been described.[1] Failure to isolate an inclusion complex under the experimental conditions investigated here does not necessarily preclude the possibility of a host−guest association in solution because the precipitation process may disturb such an equilibrium in favor of one of the reactants. This disturbance occurred in many instances, but it was important to isolate at least some inclusion products so that they could be studied by X-ray crystallography and so that the binding mechanism could be elucidated. From solution binding-constant measurements, which are discussed below, we are also aware that *p*-nitrobenzoate, phenoxyacetate, acetate, and (D)- and (L)-histidinate bind with measurable stability, even though we were unsuccessful in isolating analytically pure samples of the inclusion complexes.

Inclusion of *p*-Nitrophenolate in [Cd((*S*)-thphpc12)]-(ClO_4)$_2$. In earlier work, we reported on the inclusion of a single *p*-nitrophenolate within the structure of [Cd((*S*)-thphpc12)]$^{2+}$ without knowing, at that stage, the precise nature of the inclusion process.[1] During the work described here, we had occasion to react 1 equiv of sodium *p*-nitrophenolate with [Cd((*S*)-thphpc12)(*p*-toluenesulfonate)]-ClO_4 and found that we were able to precipitate small amounts of [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$] as well as isolate the intended compound [Cd((*S*)-thphpc12)(*p*-nitrophenolate)] *p*-toluenesulfonate. The isolation of the former, which was subsequently prepared systematically in high yield, was consistent with earlier indications from relative molar conductivity values and the relative magnitude of ^{13}C NMR displacements that the binding constant for *p*-nitrophenolate with [Cd((*S*)-thphpc12)]$^{2+}$ is substantially higher than that for *p*-toluenesulfonate. This led to the formulation of the latter complex, which is a 1:1 electrolyte in DMF, in the way shown, with *p*-nitrophenolate but not *p*-toluenesulfonate included. The yellow crystals of [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$] that were obtained enabled us to solve the solid-state structure of this complex by X-ray diffraction. This structure will be discussed below. It is interesting to note at this point, however, that various attempts to isolate inclusion compounds containing phenolate, *p*-*tert*-butyl phenolate, or picrate (2,4,6-trinitrophenolate) were unsuccessful, as were attempts using the neutrals *p*-nitrophenol, phenol, or *p*-aminophenol. Thus, among the different phenols, an element of selectivity is shown for the anionic form in which there is a sterically nonencumbering electron-withdrawing group.

Structure of [Cd(*(S)*-thphpc12)(*p*-Nitrophenolate)$_2$]. By solving the crystal structure of [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$], we determined that both *p*-nitrophenolate guests engage cofacially in the receptor cavity, with their phenolate

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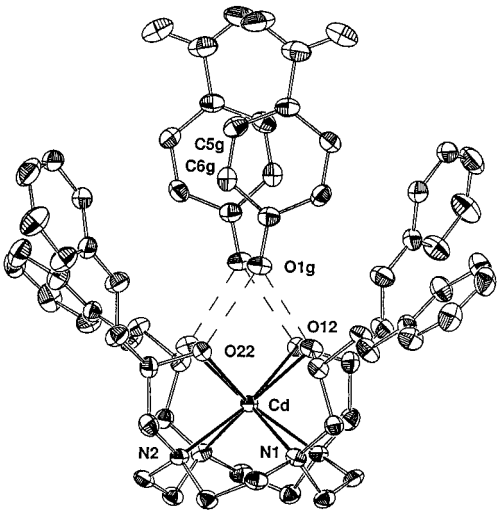

Figure 1. Molecular structure of [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$] viewed approximately normal to the *p*-nitrophenolate planes. Displacement ellipsoids are at the 50% probability level. Dashed lines indicate hydrogen bonds.

Table 2. Hydrogen-Bonding Geometry in the Crystal Structures of [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$] (**1**), [Cd((*S*)-thphpc12)(*p*-aminobenzoate)]ClO$_4$ (**2**), and [Cd((*S*)-thphpc12)((L)-phenylalaninate)]ClO$_4$ (**3**)

	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
1	O12−H12c···O1 g	1.03	1.68	2.546(4)	138.9
	O22−H22c···O1 g	0.93	1.84	2.630(4)	141.0
2	O12−H121′···O5	0.85	2.05	2.741(5)	138.1
	O22−H221′···O5	0.97	1.85	2.788(6)	162.4
	O32−H321′···O6	0.87	1.75	2.538(5))	149.5
	O42−H421′···O6	0.79	2.08	2.834(6)	159.4
3[a]	O12−(H)···O54			2.655(9)	
	O22−(H)···O55			2.689(10)	
	O32−(H)···O55			2.734(10)	
	O42−(H)···N51			2.681(7)	
	N51−H2N···O13	1.00	2.37	3.355(6)	166.3
	N51−H1N···O1	1.01	2.46	3.364(7)	148.3
	N51−H1N···O4	1.01	2.18	3.111(6)	151.8

[a] The H atoms of the amino group were located on a difference map, but those of the hydroxyl groups were not. In this case, the hydrogen bonds were inferred from geometrical considerations.

moieties directed toward the base. This orientation enables them to participate in hydrogen-bond formation with the four hydroxyl groups of the ligand. Full analysis revealed the expected[14] near-cubic structure (twist angle = 18.6°, where 0° corresponds to a cube) in the Cd(II)-ligand region of the complex, as shown in Figure 1. The Cd(II) ion lies on a crystallographic two-fold axis that passes between the two *p*-nitrophenolate ions, each of which is anchored in the cavity by two hydrogen bonds of unequal length ($O^-\cdots O$ = 2.546(4) and 2.630(4) Å) to a pair of adjacent hydroxyl groups. Full details are given in Tables 2 and 3. The O^- (phenolate)−Cd(II) distance is 3.927(3) Å, thereby eliminating the possibility of significant electrostatic interaction between the guest molecules and the metal ion. The planes of the two *p*-nitrophenolate anions are approximately parallel (angle between them = 3.5(1)°) but are rotated about a normal to the two-fold axis by 19.4° with respect to each other, so

(14) See, for example, Wainwright, K. P. *Coord. Chem. Rev.* **1997**, *166*, 35.

Table 3. Important Bond Lengths in the Crystal Stuctures of [Cd((*S*)-thphpc12)(*p*-Nitrophenolate)$_2$] (**1**), [Cd((*S*)-thphpc12)(*p*-Aminobenzoate)]ClO$_4$ (**2**), and [Cd((*S*)-thphpc12)((L)-Phenylalaninate)]ClO$_4$ (**3**)

bond	**1** (Å)	**2** (Å)	**3** (Å)
Cd−N1	2.464(3)	2.488(4)	2.500(6)
Cd−N2	2.509(3)	2.489(5)	2.496(4)
Cd−N3		2.498(5)	2.519(5)
Cd−N4		2.433(5)	2.478(4)
Cd−O12	2.454(2)	2.459(4)	2.516(4)
Cd−O22	2.476(2)	2.500(4)	2.467(4)
Cd−O32		2.411(3)	2.505(5)
Cd−O42		2.616(4)	2.441(3)

that the phenyl rings only partially overlap. The distances from the plane of the second phenyl ring to C5g and C6g are 3.281(4) and 3.195(4) Å, respectively. The phenolate oxygen atoms are separated by 3.226(4) Å. The 19.4° divergence angle prevents the eclipsing of any of the carbon atoms in opposing rings, thereby minimizing the $\pi-\pi$ repulsions and possibly providing for some measure of $\pi-\sigma$ attraction[15,16] without compromising the stabilizing effects of the hydrogen bonds in a major way. The nitrogen atoms of the nitro groups are separated by 4.146(5) Å, and each NO_2 plane is twisted by 1.2(1)° with respect to the plane of the phenyl ring to which it is attached.

Apart from a recently reported case involving a curcurbituril,[17] the solid-state structure of [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$] appears to be unique in that both guest anions interact cofacially while bound within a single molecular cavity. Similar situations of binding more than one guest in the same cavity are uncommon[18] and are generally confined to situations involving the self-assembly of molecular capsules. Recent work by MacGillivray,[19] Kobayashi,[20] and Rebek[21] has involved the assembly of hydrogen-bonded molecular capsules from preorganized bowl-shaped resorcinarenes and hydrogen-bond acceptors such as pyridines. While these structures have been shown to encapsulate two aromatic molecules per dimeric capsule, the structures differ from [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$] and the curcurbituril case in that they are essentially double cavities interlinked by a network of noncovalent bonds.

In DMSO or DMF solution, it appears that [Cd((*S*)-thphpc12)(*p*-nitrophenolate)$_2$] is almost fully dissociated into [Cd((*S*)-thphpc12)(*p*-nitrophenolate)]$^+$ and *p*-nitrophenolate. Evidence for this dissociation comes from the conductivity value in DMF, which at 61 Ω^{-1} cm^2 mol^{-1} is at the low end of the range of values normally seen for 1:1 electrolytes in this solvent[3] (65−90 Ω^{-1} cm^2 mol^{-1}), and from the ^{13}C NMR chemical shifts for the *p*-nitrophenolate resonances. These

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(21) Heinz, T.; Rudkevich, D. M.; Rebek, J. *Nature* **1998**, *394*, 764.

Table 4. $^{13}C\{^1H\}$ NMR Chemical Shifts for Free and Included *p*-Nitrophenolate

compound[a]	chemical shifts (ppm) of the guest-molecule resonances[b] C_1, C_4	$C_{2/6}$, $C_{3/5}$
sodium *p*-nitrophenolate (*p*-NO_2)	180.82, 127.99	127.75, 119.59
[Cd((*S*)-thphpc12)(*p*-NO_2)]ClO_4	173.95, 133.97	126.84, 118.21
[Cd((*S*)-thphpc12)(*p*-NO_2)]*p*−tosylate	172.84, 134.34	126.61, 117.91
[Cd((*S*)-thphpc12)(*p*-NO_2)$_2$]	175.64, 132.02	126.93, 118.30

[a] 0.05 M in DMSO-d_6 at 295 K. [b] Carbon atoms are numbered such that C_1 is the carbon atom to which the phenoxy group is bound.

resonances are listed in Table 4 and show smaller changes with respect to sodium *p*-nitrophenolate under the same conditions than do those seen in [Cd((*S*)-thphpc12)(*p*-nitrophenolate)]ClO_4 and [Cd((*S*)-thphpc12)(*p*-nitrophenolate)] *p*-toluenesulfonate. Only a single set of resonances occurs at temperatures from 298−223 K in DMF-d_7, which is consistent with the free and bound *p*-nitrophenolate undergoing fast exchange under these conditions. In addition, during the course of the ^1H NMR titration procedure used to measure the binding constant for *p*-nitrophenolate inclusion, to be discussed in detail later, no evidence was seen in DMSO-d_6 solution for the inclusion of two anions in the receptor. Consequently, the value for K_2, the binding constant for the second *p*-nitrophenolate association, must be small compared to the value of $K_1 = 10^{4.2}$ M^{-1}.

Inclusion of Carboxylates in [Cd((*S*)-thphpc12)]$(ClO_4)_2$. Having ascertained that *p*-nitrophenolate could be included within the structure of [Cd((*S*)-thphpc12)]$^{2+}$ by means of hydrogen bonds to two of the four available hydrogen-bond donors, it seemed possible that carboxylates, especially aromatic carboxylates that could derive some stability from the hydrophobic nature of the cavity, might bind by means of a pair of hydrogen bonds to each carboxylate oxygen atom. Inclusion complexes of this type were successfully isolated through the reactions of benzoate, *p*-aminobenzoate, salicylate, 1-naphthalene carboxylate, and 2-naphthalene carboxylate sodium salts with [Cd((*S*)-thphpc12)]$(ClO_4)_2$. In each case, the product was found to contain a single perchlorate ion and a single guest anion, despite some deliberate attempts to introduce a second guest anion. Each product also had a conductivity value in DMF corresponding to that of a 1:1 electrolyte, indicating that the guest was immobilized within the cavity. In addition, the ^{13}C NMR spectrum of each complex in DMSO-d_6 showed that the resonance position of the carbonyl carbon atom had moved downfield by 1−2 ppm compared to the corresponding resonance of the sodium salt of the relevant carboxylate in the same solvent, at the identical concentration and temperature. These results are characteristic of hydrogen bonding to the carboxylate group.[22,23] In the case of the *p*-aminobenzoate complex, recrystallization from an acetonitrile/water mixture produced colorless prisms that were suitable for X-ray crystallographic analysis. Solution of the structure verified that the *p*-aminobenzoate moiety is located within the receptor cavity, which is very similar in its overall configuration to that in the *p*-toluenesulfonate-containing structure reported earlier.[1] As shown in Figure 2, the carboxylate end of the guest is directed toward the base of the cavity, and each carboxylate oxygen atom forms a pair of hydrogen bonds to two cis hydroxyl groups: O12 and O22 or O32 and O42. The *p*-aminobenzoate is twisted away from the symmetrical position within the cavity such that the hydrogen bond O32−(H)···O6 is considerably shorter than the other three (Table 2). No particular alignment between any of the phenyl rings that would suggest a significant interaction between them is evident, but the phenyl ring attached to O13 lies almost parallel to the plane of the hydroxyl groups in the receptor because of an intermolecular attraction. This attraction arises through the formation of an NH-π interaction[24,25] between this ring and the NH_2 group (N5) of an adjacent [Cd((*S*)-thphpc)12)(*p*-aminobenzoate)]$^+$ entity and is similar to the corresponding tolyl CH-π interaction seen in the *p*-toluenesulfonate-containing structure.[1] The phenyl ring centroid-to-hydrogen (attached to N5) distance of 2.912 Å and the N5−H···centroid angle of 103.94° are comparable to those observed in other instances where this type of interaction occurs.[24]

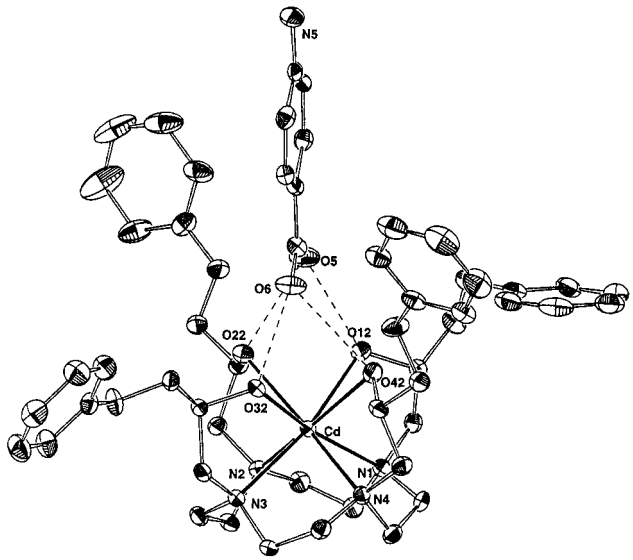

Figure 2. An ORTEP[27] view of the [Cd((*S*)-thphpc12)(*p*-aminobenzoate)]$^+$ cation with displacement ellipsoids shown at the 50% probability level. Dashed lines indicate hydrogen bonds. Hydrogen atoms and the perchlorate counterion are omitted.

Inclusion of Amino Acid Anions in [Cd((*S*)-thphpc12)]$(ClO_4)_2$. Establishing that aromatic carboxylates are capable of binding to [Cd((*S*)-thphpc)12)]$^{2+}$ indicated that it may also be possible to include naturally occurring α-amino acid anions within the cavity. We considered this possibility to be significant because the chirality of the receptor may cause it to discriminate between enantiomeric forms of the amino acid anion; however, we have yet to find any thermodynamic or kinetic evidence for such discrimination. Reacting sodium (L)-phenylalaninate and [Cd((*S*)-thphpc12)]$(ClO_4)_2$ in acetonitrile gave large colorless crystals of the 1:1 electrolyte [Cd((*S*)-thphpc12)((L)-phenylalaninate)]ClO_4 that were suit-

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(23) Dhami, K. S.; Stothers, J. B. *Tetrahedron Lett.* **1964**, *12*, 631.
(24) Steiner, T.; Mason, S. A. *Acta Crystallogr., Sect. B* **2000**, *56*, 254.
(25) Steiner, T. *Acta Crystallogr., Sect. A* **2000**, *56*, 874.

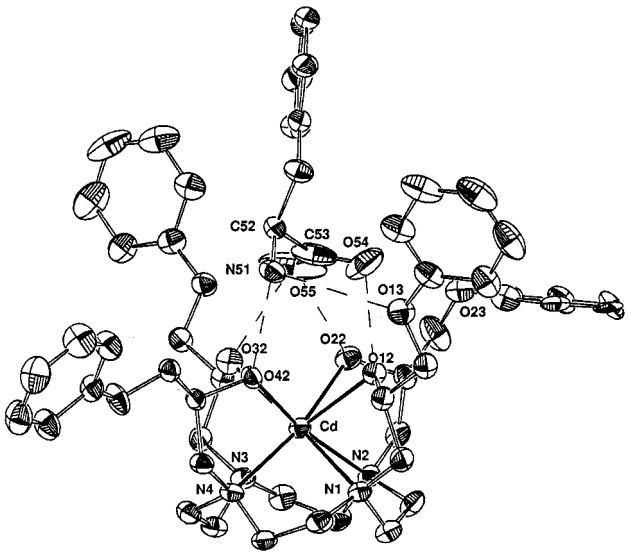

Figure 3. An ORTEP[27] view of the [Cd((*S*)-thphpc12)((L)-phenylalaninate)]$^+$ cation with displacement ellipsoids shown at the 50% probability level. Dashed lines indicate hydrogen bonds. Hydrogen atoms and the perchlorate counterion are omitted. Only one of the two positions of the phenyl ring attached to O23 is shown.

able for X-ray crystallography. By solving the crystal structure, we showed that the structure of the receptor is very similar to that in [Cd((*S*)-thphpc12)(*p*-aminobenzoate)]ClO_4. A network of five hydrogen bonds is responsible for retaining the guest in the cavity (Table 2 and Figure 3). The carboxylate moiety of the guest is the acceptor in three of the hydrogen bonds with hydroxy groups, and the amino nitrogen atom is the acceptor in one hydrogen bond. The fifth hydrogen bond is weaker and is located between the amino group (the donor) and one of the phenoxy oxygen atoms, O13. The other amino hydrogen atom forms a bifurcated hydrogen bond with the perchlorate group oxygen atoms (O1 and O4), although conductivity data discount the persistence of this hydrogen bond in solution. As observed previously, there is no intraassembly of the aromatic rings, but again, one phenyl ring (attached to O23) is aligned approximately parallel to the plane of the four hydroxyl groups in response to an intermolecular interaction with a phenyl hydrogen atom of a neighboring guest molecule. The geometrical details of this interaction are obscured by the disordering of the phenyl ring.

Reaction of sodium (D)-phenylalaninate with [Cd((*S*)-thphpc12)]$(ClO_4)_2$ under a variety of conditions failed to produce an isolable inclusion complex. Only the reactants could be recovered, suggesting that the product sought was either of lower stability or greater solubility than [Cd((*S*)-thphpc12)((L)-phenylalaninate)]ClO_4. This result suggested that it may be possible to resolve a racemic mixture of phenylalaninate by preferential crystallization of [Cd((*S*)-thphpc12)((L)-phenylalaninate)]ClO_4; however, when reactions were attempted using racemic sodium phenylalaninate, only [Cd((*S*)-thphpc12)]$(ClO_4)_2$ could be crystallized. This result suggests that the stability of the inclusion process is similar for both enantiomers, thus giving a mixture from which an inclusion compound fails to crystallize. As explained below, it was not possible to measure the binding

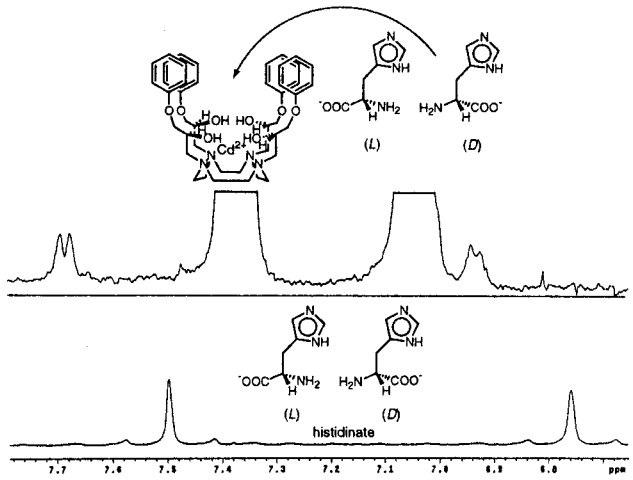

Figure 4. ^{1}H NMR spectra in DMSO-d_6 of racemic sodium histidinate (lower trace) and a 1:3 mixture of racemic sodium histidinate and [Cd((*S*)-thphpc12)]$(ClO_4)_2$ (upper trace) showing the ability of the receptor to act as a chiral shift reagent. The resonances fully shown are from the two aromatic protons of the imidazole moiety. In the upper trace, the farther downfield resonances of each pair originate from the (L)-enantiomer. The truncated resonances arise from the aromatic protons of the host.

constants for phenylalaninate with [Cd((*S*)-thphpc12)]$^{2+}$, but in situ measurements made on (D)- and (L)-histidinate indicated that within experimental error the binding constants are the same; notwithstanding, the fact that there are significant differences in the ^{1}H NMR spectra of the diastereomeric host−guest complexes, as shown in Figure 4, is indicative of a different binding environment for each enantiomer of the guest and demonstrates the behavior of [Cd((*S*)-thphpc12)]$^{2+}$ as a chiral shift reagent for aromatic anions.

Measurement of Binding Constants for Host−Guest Interactions. Measurements of binding constants for some of the host−guest inclusion equilibria were made by monitoring the change in a convenient ^{1}H NMR resonance position associated with the guest, which was dissolved in DMSO-d_6, as it was titrated with a solution of the receptor in the same solvent. This measurement was not possible for all host−guest combinations that were investigated because in some cases the appropriate guest resonances were totally obscured by those of the receptor (e.g., phenylalaninate) and in other cases there was very little change in the guest ^{1}H resonance positions, even though inclusion complexes could be isolated in the solid state (e.g., *p*-toluenesulfonate and *p*-aminobenzoate). Table 5 shows binding constants measured for various guests with [Cd((*S*)-thphpc12)]$^{2+}$, [Cd((*S*)-thpec12)]$^{2+}$, [Pb((*S*)-thpec12)]$^{2+}$, and [Cd(thec12)]$^{2+}$ ((*S*)-thpec12 and thec12 are analogous to (*S*)-thphpc12, except that they have Ph and H, respectively, in place of $PhOCH_2$ on each arm[4,6,7]). As the binding constants of [Cd((*S*)-thphpc12)]$^{2+}$ and [Cd((*S*)-thpec12)]$^{2+}$ approach 10^5 M^{-1}, they are located at the stronger end of the spectrum of known anion binders.[26] From the data obtained, two principal conclusions may be drawn. First, for the guests in question,

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Table 5. Binding Constants[a] Expressed as $\log(K/M^{-1})$ for the Inclusion of Guest Anions in $[Cd((S)\text{-thphpc12})]^{2+}$ and Related Receptors in DMSO-d_6 at 298 ± 0.5 K

	receptor complex		
guest anion	$[Cd((S)\text{-thphpc12})]^{2+}$	$[Cd((S)\text{-thpec12})]^{2+}$	$[Cd(thec12)]^{2+}$
p-nitrophenolate[b]	4.2 ± 0.1	4.0 ± 0.2	3.15 ± 0.06
p-nitrobenzoate	4.5 ± 0.4	4.9 ± 0.3	3.9 ± 0.3
phenoxyacetate[c]	>5	3.73 ± 0.05	>5
acetate	3.3 ± 0.2	3.6 ± 0.2	3.6 ± 0.1
(D)-histidinate[d]	4.2 ± 0.2		
(L)-histidinate[d]	4.2 ± 0.4		

[a] Determined by ^{1}H NMR titration. [b] Binding constant with $[Pb((S)\text{-thpec12})]^{2+}$: $\log K = 3.4 \pm 0.2$. [c] Binding constant with $[Pb((S)\text{-thpec12})]^{2+}$:$\log K = 3.09 \pm 0.08$. [d] $T = 313 \pm 0.5$ K.

the binding constants for $[Pb((S)\text{-thpec12})]^{2+}$ are generally smaller than the binding constants for $[Cd((S)\text{-thpec12})]^{2+}$, presumably because the larger ionic radius of Pb(II) forces it to sit closer to the O_4 plane than Cd(II) would sit, thereby increasing the separation between the hydroxyl hydrogen-bond donors to a distance that cannot comfortably be spanned by the acceptor atoms of the guest. This type of conformational change has been noted in an earlier study in which the shape of the binding cavity of (*S*)-thpec12 induced by metal ions of differing ionic radii was modeled.[6,7] Second, despite the fact that crystal structure determinations show no intramolecular interaction between any of the aromatic rings, the binding-constant data show that aromatic guests are retained more strongly in aromatic than in nonaromatic cavities. This result may indicate that the seemingly haphazard disposition of some of the aromatic rings in the solid state is a result of crystal-packing requirements and that in solution there is a closer, albeit weak, association of the aromatic rings. This suggestion is supported by the ^{13}C NMR data for the inclusion complexes in DMSO-d_6 solution (presented in detail in the Experimental Section), which indicate that they all have C_4 symmetry, at least on a time-averaged basis.

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Supporting Information Available: CIFs and fully labeled structural diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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