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Synthesis and structures of dinuclear cryptates with Zn(II), Cd(II) and Hg(II): tuning the cascade binding mode with metal ions†

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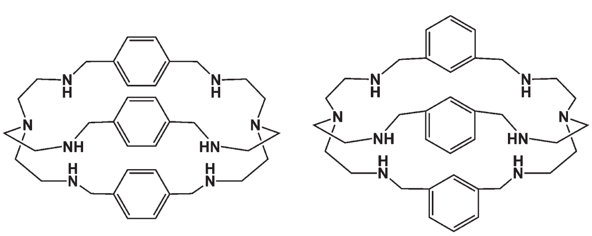
The crystal structures of eight cascade complexes, $[Zn_2L(\mu\text{-}Cl)](ClO_4)_3{\cdot}2H_2O{\cdot}3CH_3CN$ (**1**), $[Zn_2L(\mu\text{-}Br)](ClO_4)_3{\cdot}2H_2O{\cdot}3CH_3CN$ (**2**), $[Cd_2L(\mu\text{-}OH)]_2[CdI_4]_3{\cdot}6DMF$ (**3**), $[Cd_2L(\mu\text{-}Cl)][CdCl_4](Cl){\cdot}4.5H_2O$ (**5**), $[Cd_2L(\mu\text{-}Br)][CdBr_4](Br){\cdot}1.5H_2O$ (**6**), $[Hg_2L(\mu\text{-}Cl)][HgCl_4](Cl){\cdot}6H_2O$ (**9**), $[Hg_2L(\mu\text{-}Br)][HgBr_4](Br){\cdot}1.25H_2O$ (**10**), and $[Hg_2L(\mu\text{-}I)](NO_3)_3{\cdot}6H_2O$ (**11**), were presented, which reveal the influence of the coordinated metal ions on the selectivity in the cascade binding mode. The dizinc(II) cryptate shows the recognition of Cl^- and Br^- rather than that of F^- and I^-. Unexpectedly, the dicadmium(II) cryptate shows the recognition of OH^-, F^-, Cl^- and Br^- rather than that of I^-, while all of the above-mentioned anions can form stable cascade complexes with the dimercury(II) cryptate. For better understanding, the binding behaviors and stabilisation energies between $[M_2L]^{4+}$ and anions were calculated by DFT calculations.

Introduction

Anion recognition has drawn much attention over the past decades.[1] Anions are ubiquitous in nature and play a key role in many biological systems; they are also involved in some environmental problems.[2] Many research studies have been done with the aim of improving the selectivity towards certain anions.[1,3]

The first dinuclear cryptate was reported by Lehn,[4] who used the term "cascade" to illustrate the unique binding mode of dinuclear cryptates. The dinuclear cryptates have been shown as good receptors for various anions. Fabbrizzi reported[5] the binding behaviour of dicopper(II) cryptate $[Cu_2L^1]^{4+}$ towards a series of anions with different shapes and sizes, and found that the anions show higher stability constants if there is an appropriate distance between the coordinated dinuclear metal atoms. The concept of the fitness of binding length has been well adopted,[6] and has been proven to be an efficient strategy to gain better selectivity towards anions.

We previously reported the recognition of Cl^- and Br^- over that of F^- and I^- by using a dicobalt(II) cryptate $[Co_2L]^{4+}$.[7] The key factor to such selectivity is the rigidity of the ligand and the distance between two cobalt(II) cations. We consider that the recognition might be altered by using cations of different sizes. For this purpose, we used Cd^{2+} and Hg^{2+} to investigate if we can achieve enhanced selectivity for Cl^- over Br^-. Surprisingly, we found that $[Cd_2L]^{4+}$ and $[Hg_2L]^{4+}$ show universal binding properties, in which $[Cd_2L]^{4+}$ can bind not only larger Cl^- and Br^-, but also smaller F^- and OH^-; moreover, $[Hg_2L]^{4+}$ can form stable cascade complexes with all of the F^-, Cl^-, Br^-, I^- and OH^-. Herein we report the structures of $[Zn_2L(\mu\text{-}Cl)](ClO_4)_3{\cdot}2H_2O{\cdot}3CH_3CN$ (**1**), $[Zn_2L(\mu\text{-}Br)](ClO_4)_3{\cdot}2H_2O{\cdot}3CH_3CN$ (**2**), $[Cd_2L(\mu\text{-}OH)]_2[CdI_4]_3{\cdot}6DMF$ (**3**), $[Cd_2L(\mu\text{-}Cl)][CdCl_4](Cl){\cdot}4.5H_2O$ (**5**), $[Cd_2L(\mu\text{-}Br)][CdBr_4](Br){\cdot}1.5H_2O$ (**6**), $[Hg_2L(\mu\text{-}Cl)][HgCl_4](Cl){\cdot}6H_2O$ (**9**), $[Hg_2L(\mu\text{-}Br)][HgBr_4](Br){\cdot}1.25H_2O$ (**10**) and $[Hg_2L(\mu\text{-}I)](NO_3)_3{\cdot}6H_2O$ (**11**) To the best of our knowledge, **11** is the first structurally characterized iodide cascade complex in the cryptates. DFT calculations were also performed to evaluate the binding behaviors between $[M_2L]^{4+}$ and anions (Scheme 1).



L L[1]

Scheme 1 The structures of the ligands.

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Experimental

Materials and characterization

The ligand L was prepared by the literature method.[8] All the other solvents and chemicals are commercially available and used without further purification. Elemental analyses were performed using an Elementar Vario EL elemental analyzer. The IR spectra were recorded in the 4000–400 cm^{-1} region at room temperature by using KBr pellets and a Bruker EQUINOX 55 spectrometer.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care.

$[Zn_2L(\mu\text{-}Cl)](ClO_4)_3\cdot 2H_2O\cdot 3CH_3CN$ (1). A solution of $L\cdot 0.5H_2O$ (243 mg, 0.40 mmol) in methanol/acetonitrile (1:1, 10 mL) was added dropwise to a solution of $Zn(ClO_4)_2\cdot 6H_2O$ (296 mg, 0.80 mmol) and KCl (32 mg, 0.40 mmol) in 10 mL of CH_3CN. The mixture was stirred at room temperature for 4 h. The white precipitate obtained was filtered off, washed with ethanol, and then dissolved in acetonitrile. The resulting solution was evaporated slowly at room temperature. Colorless block-shaped crystals were obtained in 46% yield. Anal. calcd for $C_{36}H_{54}Cl_4N_8O_{12}Zn_2$ ($[Zn_2L(Cl)](ClO_4)_3$): C 40.66; H 5.12; N 10.54%. Found: C 40.45; H 5.58; N 10.86%. IR (KBr, cm^{-1}): 3428(m), 3283(m), 2948(m), 2826(m), 1622(w), 1474(m), 1443(m), 1286(m), 1088(s), 936(w), 812(m).

$[Zn_2L(\mu\text{-}Br)](ClO_4)_3\cdot 2H_2O\cdot 3CH_3CN$ (2). This compound was prepared as colorless block-shaped crystals in 51% yield by a procedure similar to that of **1** from the reaction of $Zn(ClO_4)_2\cdot 6H_2O$ (296 mg, 0.80 mmol), $L\cdot 0.5H_2O$ (243 mg, 0.40 mmol), and KBr (48 mg, 0.40 mmol). Anal. calcd for $C_{41}H_{65.5}BrCl_3N_{10.5}O_{14}Zn_2$ ($[Zn_2L(Br)](ClO_4)_3\cdot 2H_2O\cdot 2.5CH_3CN$): C 39.50; H 5.30; N 11.80%. Found: C 39.96; H 5.59; N 11.39%. IR (KBr, cm^{-1}): 3425(m), 3283(m), 2948(m), 2828(m), 1621(w), 1473(m), 1443(m), 1286(m), 1088(s), 936(w), 812(m).

$[Cd_2L(\mu\text{-}OH)]_2[CdI_4]_3\cdot 6DMF$ (3). CdI_2 (77 mg, 0.21 mmol) and $L\cdot 0.5H_2O$ (36 mg, 0.06 mmol) were added to 15 mL of DMF/H_2O (30:1). The mixture was stirred overnight, and the filtrate was fixed in a vial, followed by slow diffusion with ethyl ether. Colorless block-shaped crystals were obtained in a yield of 34%. Anal. calcd for $C_{90}H_{152}O_8N_{22}Cd_7I_{12}$ (**3**): C 27.16; H 3.85; N 7.74%. Found: C 27.29; H 3.90; N 7.80%. IR (KBr, cm^{-1}): 3566(w), 3243(m), 2961(w), 2921(m), 2862(m), 1667(s), 1511(w), 1463(m), 1442(m), 1282(m), 1078(m), 1056(m), 1022(m), 927(m), 882(m), 813(m).

$[Cd_2L(\mu\text{-}F)]_2[CdI_4]_3\cdot 6DMF$ (4). This compound was prepared as colorless plate-shaped crystals in 42% yield by a procedure similar to that of **3** from the reaction of CdI_2 (77 mg, 0.21 mmol), $L\cdot 0.5H_2O$ (36 mg, 0.06 mmol), and NaF (7.6 mg, 0.18 mmol). Anal. calcd for $C_{90}H_{150}Cd_7F_2I_{12}N_{22}O_6$ (**4**): C 27.13; H 3. 79; N 7.73%. Found: C 27.42; H 3.73; N 7.94%. IR (KBr, cm^{-1}): 3447(m), 3245(m), 2962(m), 2922(m), 2864(m), 1666(s), 1513(w), 1468(m), 1442(s), 1284(m), 1077(s), 1056(m), 1021(s), 927(m), 882(m), 813(m).

$[Cd_2L(\mu\text{-}Cl)][CdCl_4](Cl)\cdot 4.5H_2O$ (5). $CdCl_2\cdot 2.5H_2O$ (41 mg, 0.18 mmol) and $L\cdot 0.5H_2O$ (36 mg, 0.06 mmol) were added to 5 mL of H_2O. The mixture was stirred overnight, and the filtrate was evaporated slowly at room temperature to give colorless rhombus-shaped crystals in a yield of 74%. Anal. calcd for $C_{36}H_{63}Cd_3Cl_6N_8O_{4.5}$ (**5**): C 35.16; H 5.16; N 9.11%. Found: C 34.99; H 5.10; N 9.02%. IR (KBr, cm^{-1}): 3442(s), 3232(s), 2980(m), 2863(s), 1636(m), 1517(w), 1459(s), 1424(w), 1355(m), 1285(m), 1215(m), 1076(s), 1062(m), 1025(s), 996(m), 936(s), 881(m), 811(s).

$[Cd_2L(\mu\text{-}Br)][CdBr_4](Br)\cdot 1.5H_2O$ (6). $CdBr_2\cdot 4H_2O$ (62 mg, 0.18 mmol) and $L\cdot 0.5H_2O$ (36 mg, 0.06 mmol) were added to 12 mL of H_2O. The mixture was stirred overnight, and the filtrate was diffused with acetone. Colorless plate-shaped crystals were obtained in a yield of 52%. Anal. calcd for $C_{36}H_{57}Br_6Cd_3N_8O_{1.5}$ (**6**): C 29.97; H 3.98; N 7.76%. Found: C 30.07; H 3.94; N 7.76%. IR (KBr, cm^{-1}): 3535(m), 3452(m), 3239(m), 3199(s), 3130(m), 2921(m), 2862(s), 1627(m), 1518(w), 1468(m), 1446(s), 1285(m), 1210(m), 1072(s), 1020(s), 996(m), 927(m), 886(s), 806(s).

$[Hg_2L(\mu\text{-}OH)](ClO_4)_3$ (7). $Hg(ClO_4)_2\cdot 3H_2O$ (54 mg, 0.12 mmol) and $L\cdot 0.5H_2O$ (36 mg, 0.06 mmol) were added to methanol/acetonitrile (1:1, 20 mL), and the solution was stirred for 15 minutes, and the filtrate was evaporated slowly at room temperature to give light yellow hexagon-shaped crystals in a yield of 62%. Anal. calcd for $C_{36}H_{55}N_8Hg_2Cl_3O_{13}$ (**7**): C 32.87; H 4.21; N 8.52%. Found: C 32.99; H 4.34; N 8.46%. IR (KBr, cm^{-1}): 3556(m), 3292(m), 2922(m), 2868(s), 1518(w), 1468(m), 1448(m), 1099(s), 924(m), 876(m), 810(m).

$[Hg_2L(\mu\text{-}F)](ClO_4)_3$ (8). This compound was prepared as light yellow hexagon-shaped crystals in 64% yield by a procedure similar to that of **7** from the reaction of $Hg(ClO_4)_2\cdot 3H_2O$ (54 mg, 0.12 mmol), $L\cdot 0.5H_2O$ (36 mg, 0.06 mmol), and NaF (7.6 mg, 0.18 mmol). Anal. calcd for $C_{36}H_{54}N_8Hg_2Cl_3O_{12}F$ (**8**): C 32.82; H 4.13; N 8.51%. Found: C 32.71; H 4.18; N 8.34%. IR (KBr, cm^{-1}): 3556(m), 3292(m), 2923(m), 2868(s), 1518(w), 1468(m), 1448(m), 1100(s), 924(m), 876(w), 810(m).

$[Hg_2L(\mu\text{-}Cl)][HgCl_4](Cl)\cdot 2H_2O$ (9). $Hg(NO_3)_2\cdot H_2O$ (62 mg, 0.18 mmol) and $L\cdot 0.5H_2O$ (36 mg, 0.06 mmol) were added to 20 mL of H_2O, and the solution was stirred for 15 minutes. Then 5 mL of NaCl (21 mg, 0.36 mmol) aqueous solution was added, and the mixture was stirred overnight. The filtrate was evaporated slowly at room temperature to give colorless rhombus-shaped crystals in a yield of 58%. Anal. calcd for $C_{36}H_{66}N_8Hg_3Cl_6O_6$ (**9**$\cdot 4H_2O$): C 28.42; H 4.37; N 7.36%. Found: C 28.66; H 4.53; N 7.41%. IR (KBr, cm^{-1}): 3402(m), 3228(m), 2902(m), 2857(m), 1633(m), 1516(w), 1457(m), 1423(w), 1286(m), 1213(m), 1078(m), 1058(m), 1022(m), 935(m), 875(m), 809(s).

$[Hg_2L(\mu\text{-}Br)][HgBr_4](Br)\cdot 1.25H_2O$ (10). $Hg(NO_3)_2\cdot H_2O$ (62 mg, 0.18 mmol) and $L\cdot 0.5H_2O$ (36 mg, 0.06 mmol) were added to 20 mL of H_2O, and the solution was stirred for 15 minutes. Then 5 mL of NaBr (37 mg, 0.36 mmol) aqueous solution was added, and the mixture was stirred overnight. The filtrate was evaporated slowly at room temperature to give colorless rhombus-shaped crystals in a yield of 56%. Anal. calcd for $C_{36}H_{56.5}Hg_3Br_6N_8O_{1.25}$ (**10**): C 25.40; H 3.34; N

6.58%. Found: C 25.16; H 3.46; N 6.67%. IR (KBr, cm^{-1}): 3448 (m), 3197(m), 2910(w), 2852(m), 1624(m), 1518(w), 1443(m), 1384(s), 1285(w), 1207(w), 1077(m), 1056(m), 880(m), 803(m).

[$Hg_2L(\mu$-I)]($NO_3)_3$·6H_2O (11). $Hg(NO_3)_2 \cdot H_2O$ (41 mg, 0.12 mmol) and L·0.5H_2O (36 mg, 0.06 mmol) were added to 25 mL of H_2O, and the solution was stirred for 15 minutes. Then 5 mL of NaI (9.0 mg, 0.06 mmol) aqueous solution was added, and the mixture was stirred overnight. The filtrate was evaporated slowly at room temperature to give yellow needle-shaped crystals in a yield of 54%. Anal. calcd for $C_{36}H_{66}Hg_2IN_{11}O_{15}$ (11): C 30.43; H 4.68; N 10.84%. Found: C 30.56; H 4.72; N 10.77%. IR (KBr, cm^{-1}): 3425 (m), 3170(m), 2903(m), 2860(m), 1635(w), 1517(w), 1466(w), 1446(m), 1381(s), 1213(w), 1084(m), 1012(m), 881(m), 804(m).

X-ray crystallography. Single-crystal X-ray diffraction data for **3** were collected on a Rigaku R-AXIS Spider IP diffractometer with Mo Kα radiation (λ = 0.71073 Å). Data reduction, cell refinement and experimental absorption correction were performed with RAPID AUTO V2.40 software.[9] Single-crystal X-ray diffraction data for **1**, **2** and **5** were collected on a Bruker Smart 1000 CCD diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The empirical absorption corrections were applied using the SADABS program.[10] Single-crystal X-ray diffraction data for **4** and **6–11** were collected using an Agilent Technologies Gemini A Ultra CCD diffractometer with graphite monochromated Cu Kα radiation (λ = 1.54178 Å). The empirical absorption corrections were applied using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[11] The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the

Table 1 The crystallographic data

Compound	1	2	3	5
Formula	$C_{42}H_{67}Cl_4N_{11}O_{14}Zn_2$	$C_{42}H_{67}BrCl_3N_{11}O_{14}Zn_2$	$C_{90}H_{152}Cd_7I_{12}N_{22}O_8$	$C_{36}H_{63}Cd_3Cl_6N_8O_{4.5}$
Formula weight (fw)	1222.57	1267.07	3979.94	1229.84
Crystal system	Triclinic	Triclinic	Trigonal	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$R\bar{3}c$	$C2$
a/Å	13.149(5)	13.253(4)	17.6212(4)	10.1322(14)
b/Å	14.006(5)	14.040(5)	17.6212(4)	18.536(2)
c/Å	15.694(6)	15.795(5)	71.599(2)	26.333(4)
α/°	87.296(7)	87.470(6)	90	90
β/°	66.076(7)	65.997(6)	90	99.012(2)
γ/°	81.938(6)	82.199(6)	120	90
V/Å^3, Z	2615.6(16)	2659.8(15)	19 253.4(8)	4884.6(11)
Temperature/K	293(2)	291(2)	150(2)	163(2)
Z	2	2	6	4
No. of reflections measured	20 172	15 959	58 156	13 923
No. of independent reflections	11 058	11 231	4923	9580
R_{int}	0.0378	0.0201	0.0771	0.0320
R_1 ($I > 2\sigma(I)$)	0.0550	0.0554	0.0308	0.0459
wR_2 ($I > 2\sigma(I)$)	0.1370	0.1537	0.0738	0.1213
R_1 (all data)	0.1103	0.1004	0.0337	0.0520
wR_2 (all data)	0.1651	0.1823	0.0754	0.1272
Goodness of fit on F^2	1.012	1.033	1.005	1.063
Compound	6	9	10	11
Formula	$C_{36}H_{57}Br_6Cd_3N_8O_{1.5}$	$C_{36}H_{58}Cl_6Hg_3N_8O_2$	$C_{36}H_{56.50}Br_6Hg_3N_8O_{1.25}$	$C_{36}H_{66}Hg_2IN_{11}O_{15}$
Formula weight (fw)	1442.56	1449.37	1702.62	1421.08
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$C2/c$	$P2_1/n$	$Pna2_1$
a/Å	9.67100(10)	10.0947(3)	9.6410(2)	17.4241(3)
b/Å	33.8375(4)	18.4694(5)	33.6643(7)	10.4127(3)
c/Å	14.2619(2)	26.2626(7)	14.2372(3)	26.4970(10)
α/°	90	90	90	90
β/°	93.2200(10)	99.587(3)	92.897(2)	90
γ/°	90	90	90	90
V/Å^3, Z	4659.73(10)	4828.1(2)	4614.88(17)	4807.4(2)
Temperature/K	150.00(10)	150.00(10)	150.01(10)	150.00(10)
Z	4	4	4	4
No. of reflections measured	25 527	8346	17 760	11 256
No. of independent reflections	7372	3993	7554	5954
R_{int}	0.0480	0.0532	0.0453	0.0338
R_1 ($I > 2\sigma(I)$)	0.0413	0.0490	0.0407	0.0365
wR_2 ($I > 2\sigma(I)$)	0.0976	0.1264	0.0890	0.0880
R_1 (all data)	0.0467	0.0603	0.0542	0.0393
wR_2 (all data)	0.1003	0.1349	0.0954	0.0909
Goodness of fit on F^2	1.147	1.052	1.036	1.048

hydrogen atoms (except those of water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The positional disorders of DMF molecules in **3**, water molecules in **6** and nitrate and water molecules in **11** were treated with FVAR. All calculations were performed using the SHELXTL-97 system of computer programs.[12] Details of data collection, structure solution, and refinements can be found in Table 1. Relevant bond lengths and angles are included in Table 3.

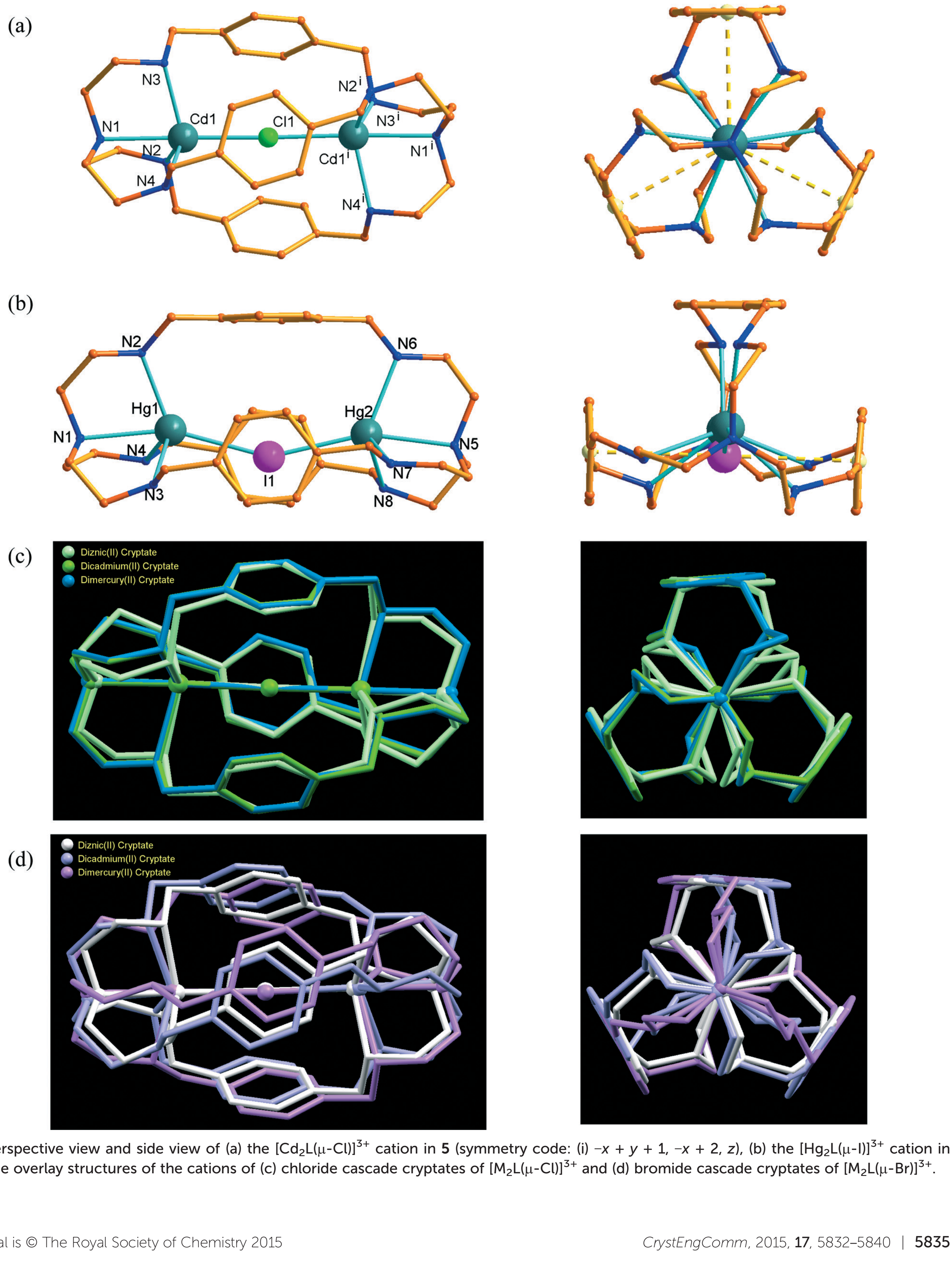

Fig. 1 Perspective view and side view of (a) the $[Cd_2L(\mu\text{-}Cl)]^{3+}$ cation in **5** (symmetry code: (i) $-x + y + 1$, $-x + 2$, z), (b) the $[Hg_2L(\mu\text{-}I)]^{3+}$ cation in **11**, and the overlay structures of the cations of (c) chloride cascade cryptates of $[M_2L(\mu\text{-}Cl)]^{3+}$ and (d) bromide cascade cryptates of $[M_2L(\mu\text{-}Br)]^{3+}$.

Table 2 The stabilisation energies gained by the interactions of the halides with the dinuclear cryptates in water[a] (kJ mol^{-1})

	OH^{b}	F^{-b}	Cl^-	Br^-	I^-
Zn^{2+}	−456.78	−341.48	−159.39	−138.64	−64.50
Cd^{2+}	−281.72	−225.39	−107.56	−71.11	−72.24
Hg^{2+}	−248.89	−180.89	−55.96	−40.00	−77.03

[a] $E = E([M_2L(\mu\text{-X})]^{3+}) - E([M_2L]^{4+}) - E(X^-)$. [b] For $[Zn_2L(OH)(H_2O)]^{3+}$/$[Zn_2L(F)(H_2O)]^{3+}$, $E(X^-) = E(OH^-)/E(F^-) + E(H_2O)$.

Computational details. All the calculations were performed with a Gaussian 09 program package, revision A 02.[13] On the basis of the corresponding crystal structures, the structures of the cations were fully optimized in vacuum without any symmetry constraints at the M06-L method[14] of DFT using a cc-pVDZ basis set[15] for C, H, N, O, F, and Cl and a cc-pVDZ-PP basis set[16] for Br, I, Zn, Cd, and Hg. The initial geometries of $[Zn_2L(OH)(H_2O)]^{3+}$ and $[Zn_2L(F)(H_2O)]^{3+}$ were based on the crystal structure of $[Co_2L(OH)(H_2O)]^{3+}$.[7] The initial geometries of $[Zn_2L(\mu\text{-OH})]^{3+}$ and $[Zn_2L(\mu\text{-F})]^{3+}$ were based on the crystal structure of $[Zn_2L(\mu\text{-Cl})]^{3+}$, the initial geometries of $[Zn_2L(\mu\text{-I})]^{3+}$ and $[Cd_2L(\mu\text{-I})]^{3+}$ were based on the crystal structure of **11**, and the initial geometries of $[Hg_2L(\mu\text{-OH})]^{3+}$ and $[Hg_2L(\mu\text{-F})]^{3+}$ were based on the crystal structure of **9**. The calculation for the structure of $[Zn_2L(\mu\text{-OH})]^{3+}$ was not successful, as the calculation did not get convergence data, probably due to the difficulty in forming such a cryptate. Cartesian coordinates for all the calculated structures are provided in the ESI,† Table S1. The single point energies of the optimized structures were calculated in aqueous solution with a polarizable continuum model (PCM) at the M06-L method of DFT using a cc-pVTZ basis set[15] for C, H, N, O, F, and Cl and a cc-pVTZ-PP basis set[16] for Br, I, Zn, Cd, and Hg. For reasons of computational expense due to the large size of our systems, frequency calculations were not carried out on the minima.

Results and discussion

Due to the poor crystal quality, the refinement of **4** failed to converge, but it has roughly the same framework as **3**. Compounds **7** and **8** have cell parameters similar to the previously reported cryptates,[17] but due to the high symmetry, the refinements were not successful.

It is interesting to note that $[Zn_2L]^{4+}$ can only form μ-X^- bridged cryptates with Cl^- and Br^- (**1** and **2**), while $[Cd_2L]^{4+}$ and $[Hg_2L]^{4+}$ can form μ-X^- bridged cryptates with OH^-, F^-, Cl^- and Br^- (**3**–**10**), and $[Hg_2L]^{4+}$ can encapsulate even the larger anion of I^- to form a cascade complex of $[Hg_2L(\mu\text{-I})]^{3+}$ (**11**). The crystal structures of $[M_2L(\mu\text{-X})]^{3+}$ cations are quite similar ($M^{2+} = Zn^{2+}$, Cd^{2+}, or Hg^{2+}; $X^- = Cl^-$ or Br^- in Zn(II) complexes and OH^-, F^-, Cl^-, or Br^- in Cd(II)/Hg(II) complexes), and the $[Cd_2L(\mu\text{-Cl})]^{3+}$ cation from **5** is shown as an example in Fig. 1a, while the $[Hg_2L(\mu\text{-I})]^{3+}$ cation from **11**, which adopts a different binding conformation, is shown in Fig. 1b, and will be discussed separately. In $[M_2L(\mu\text{-X})]^{3+}$, the M–X distances are in the normal range, and the tripodal skeleton of L forces the metal ions to adopt a five coordinated geometry, and each of the metal ion is coordinated with four nitrogen atoms from L and one bridged X^- anion. The parameters (τ) for the geometries[18] of five-coordinated metal ions are close to 1 in $[M_2L(\mu\text{-X})]^{3+}$ cations, with a minimum of 0.97 for **10** and a maximum of 1.12 for **3**, where τ = 1.00 for TBP (trigonal bipyramidal) and 0.00 for SP (square pyramidal), indicating that the geometries of M(II) ions in $[M_2L(\mu\text{-X})]^{3+}$ are TBPs. For **11**, the values of τ are 0.69 and 0.70 for two Hg^{2+} ions, indicating that Hg^{2+} has a distorted coordination geometry between TBP and SP.

For each $[M_2L(\mu\text{-X})]^{3+}$, the two bridgehead nitrogen atoms (N_{br}), the two M^{2+} ions and the X^- anion are almost collinear, with M–X–M angles of 180° in symmetric **3**. The collinearity of the metal ions and X^- ion is higher with a combination of smaller M^{2+} ions and an anion than that of the larger ones, and the maximum and minimum values are 179.04(5)° for **1** and 176.41(5)° for **10**, respectively (see Table 3). The M–X–M angle in **11** is 151.80(3)°. The M···M and $N_{br}\cdots N_{br}$ separations become larger as the radii of the M(II) ions and the encapsulated anions increase, whereas the shortest M···M and $N_{br}\cdots N_{br}$ were observed in **3** as 4.3829(6) and 9.368(7) Å, respectively, and the longest were observed in **11** as 5.4923(6) and 10.479(11) Å.

As shown in Fig. 1, the rigid triangle conformation of L makes the X^- tightly encapsulated into the cage, resulting in a well-wrapped stable cryptate. The average distances between the X^- and the centroid of the phenyl ring (X···Cg) are 3.230 Å for **1**, 3.250 Å for **2**, 3.281 Å for **5**, 3.394 Å for **6**, 3.279 Å for **9**, 3.397 Å for **10** and 3.617 Å for **11**. These distances are shorter than the sum of the van der Waals radii of Cl···C (3.45 Å), Br···C (3.55 Å) and I···C (3.68 Å), demonstrating the existence of anion···π interactions between the X^- anions and the phenyl rings of L.

We calculated the stabilisation energies gained by the interactions of the halides with the dinuclear cryptates in water by the equation $[M_2L]^{4+} + X^- \rightarrow [M_2L(\mu\text{-X})]^{3+}$, with $E = E([M_2L(\mu\text{-X})]^{3+}) - E([M_2L]^{4+}) - E(X^-)$ (see Table 2). For Zn–OH and Zn–F complexes, the energies for the formation of $[Zn_2L(OH)(H_2O)]^{3+}$, $[Zn_2L(\mu\text{-F})]^{3+}$ and $[Zn_2L(F)(H_2O)]^{3+}$ species were calculated. PCM was used to model the solvent effect. The main shortcoming of PCM is that it fails to account for the interactions between solute and solvent molecules in the first solvation shell;[19] thus the stabilisation energies of OH^- and F^- which form strong interactions with water were overestimated. The calculated stabilisation energy for the formation of $[Zn_2L(F)(H_2O)]^{3+}$ (−341.48 kJ mol^{-1}) is larger than that of $[Zn_2L(\mu\text{-F})]^{3+}$ (−225.49 kJ mol^{-1}), indicating that $[Zn_2L(F)(H_2O)]^{3+}$ is more stable than $[Zn_2L(\mu\text{-F})]^{3+}$.

We believe that $[Zn_2L(OH)(H_2O)]^{3+}$ will also be more stable than $[Zn_2L(\mu\text{-OH})]^{3+}$, though we could not get the optimized structure of $[Zn_2L(\mu\text{-OH})]^{3+}$. Indeed, we previously found that $[Co_2L]^{4+}$ forms $[Co_2L(OH)(H_2O)]^{3+}$ rather than $[Co_2L(\mu\text{-OH})]^{3+}$ in acetonitrile,[7] indicating $[Co_2L(OH)(H_2O)]^{3+}$ is the main species in solution. Except OH^- and F^- with overestimated stabilisation energies, the Zn(II)/Cd(II) cryptate forms a more stable complex with chloride, while the Hg(II) cryptate forms a more stable complex with iodide (Table 2).

It's interesting to compare the binding modes of $[M_2L]^{4+}$ with that of our previously reported $[Co_2L]^{4+}$.[7] Similar to $[Co_2L]^{4+}$ with the formation of $[Co_2L(OH)(H_2O)]^{3+}$ rather than

Table 3 Selected bond distances (Å) and angles (°) for **1–3**, **5**, **6**, and **9–11**[a]

1			
Zn(1)–Cl(1)	2.4829(13)	Zn(2)–Cl(1)	2.4700(13)
Zn(1)–N(1)	2.297(4)	Zn(2)–N(5)	2.294(4)
Zn(1)–N(2)	2.102(3)	Zn(2)–N(6)	2.094(3)
Zn(1)–N(3)	2.115(3)	Zn(2)–N(7)	2.110(3)
Zn(1)–N(4)	2.113(3)	Zn(2)–N(8)	2.123(3)
N(1)–Zn(1)–N(2)	80.24(14)	N(5)–Zn(2)–N(6)	80.82(14)
N(1)–Zn(1)–N(3)	80.38(13)	N(5)–Zn(2)–N(7)	80.44(14)
N(1)–Zn(1)–N(4)	80.89(13)	N(5)–Zn(2)–N(8)	80.52(13)
N(2)–Zn(1)–N(3)	117.54(14)	N(6)–Zn(2)–N(7)	117.27(14)
N(2)–Zn(1)–N(4)	116.72(14)	N(6)–Zn(2)–N(8)	116.88(14)
N(3)–Zn(1)–N(4)	117.73(13)	N(7)–Zn(2)–N(8)	118.00(14)
Cl(1)–Zn(1)–N(1)	179.17(10)	Cl(1)–Zn(2)–N(5)	178.80(10)
Cl(1)–Zn(1)–N(2)	99.81(11)	Cl(1)–Zn(2)–N(6)	98.81(11)
Cl(1)–Zn(1)–N(3)	98.88(10)	Cl(1)–Zn(2)–N(7)	100.73(10)
Cl(1)–Zn(1)–N(4)	99.81(10)	Cl(1)–Zn(2)–N(8)	98.66(10)
Zn(1)–Cl(1)–Zn(2)	179.04(5)		
2			
Zn(1)–Br(1)	2.5675(10)	Zn(2)–Br(1)	2.5707(10)
Zn(1)–N(1)	2.273(4)	Zn(2)–N(5)	2.270(4)
Zn(1)–N(2)	2.132(4)	Zn(2)–N(6)	2.113(4)
Zn(1)–N(3)	2.112(4)	Zn(2)–N(7)	2.116(4)
Zn(1)–N(4)	2.115(4)	Zn(2)–N(8)	2.129(4)
N(1)–Zn(1)–N(2)	81.27(15)	N(5)–Zn(2)–N(6)	81.16(16)
N(1)–Zn(1)–N(3)	81.62(15)	N(5)–Zn(2)–N(7)	82.04(16)
N(1)–Zn(1)–N(4)	81.81(16)	N(5)–Zn(2)–N(8)	81.44(15)
N(2)–Zn(1)–N(3)	118.06(16)	N(6)–Zn(2)–N(7)	117.68(16)
N(2)–Zn(1)–N(4)	117.83(17)	N(6)–Zn(2)–N(8)	118.52(16)
N(3)–Zn(1)–N(4)	117.76(16)	N(7)–Zn(2)–N(8)	117.43(16)
Br(1)–Zn(1)–N(1)	179.09(10)	Br(1)–Zn(2)–N(5)	178.93(11)
Br(1)–Zn(1)–N(2)	97.83(11)	Br(1)–Zn(2)–N(6)	99.90(12)
Br(1)–Zn(1)–N(3)	98.94(11)	Br(1)–Zn(2)–N(7)	97.56(12)
Br(1)–Zn(1)–N(4)	98.54(12)	Br(1)–Zn(2)–N(8)	97.89(11)
Zn(1)–Br(1)–Zn(2)	178.97(3)		
3			
Cd(1)–O(1)	2.204(4)	Cd(2)–O(1)	2.179(4)
Cd(1)–N(1)	2.463462(5)	Cd(2)–N(3)	2.355(3)
Cd(1)–N(2)	2.348(3)	Cd(2)–N(4)	2.522521(5)
N(1)–Cd(1)–N(2)	75.16(87)	N(3)–Cd(2)–N(4)	73.9974.02(8)
N(2)–Cd(1)–N(2)#1	113.68(6)	N(3)–Cd(2)–N(3)#1	112.720(7)
O(1)–Cd(1)–N(2)	104.84(8)	O(1)–Cd(2)–N(3)	106.015.98(8)
O(1)–Cd(1)–N(1)	180.000(1)	O(1)–Cd(2)–N(4)	180.0
Cd(1)–O(1)–Cd(2)	180.0		
5			
Cd(1)–Cl(1)	2.5209(5)	Cd(2)–Cl(2)	2.5067(5)
Cd(1)–N(1)	2.440(5)	Cd(2)–N(5)	2.416(6)
Cd(1)–N(2)	2.330(5)	Cd(2)–N(6)	2.311(6)
Cd(1)–N(3)	2.306(5)	Cd(2)–N(7)	2.325323(6)
Cd(1)–N(4)	2.307(6)	Cd(2)–N(8)	2.327326(6)
N(1)–Cd(1)–N(2)	76.8283(17)	N(5)–Cd(2)–N(6)	76.4(2)
N(1)–Cd(1)–N(3)	76.9492(19)	N(5)–Cd(2)–N(7)	76.9(2)
N(1)–Cd(1)–N(4)	76.9(2)	N(5)–Cd(2)–N(8)	77.5(2)
N(2)–Cd(1)–N(3)	114.1009(19)	N(6)–Cd(2)–N(7)	113.0(2)
N(2)–Cd(1)–N(4)	116.9190(18)	N(6)–Cd(2)–N(8)	117.2(2)
N(3)–Cd(1)–N(4)	114.01(2)	N(7)–Cd(2)–N(8)	115.0(2)
Cl(1)–Cd(1)–N(1)	177.89(16)	Cl(2)–Cd(2)–N(5)	179.3940(187)
Cl(1)–Cd(1)–N(2)	104.74(13)	Cl(2)–Cd(2)–N(6)	103.0406(16)
Cl(1)–Cd(1)–N(3)	103.54(14)	Cl(2)–Cd(2)–N(7)	103.09(16)
Cl(1)–Cd(1)–N(4)	101.04(15)	Cl(2)–Cd(2)–N(8)	103.00(16)
Cd(1)–Cl(1)–Cd(1)#1	178.40(13)	Cd(2)–Cl(2)–Cd(2)#2	179.0103(13)

Table 3 *(continued)*

6			
Cd(1)–Br(1)	2.7031(9)	Cd(2)–Br(1)	2.6985(9)
Cd(1)–N(1)	2.441(6)	Cd(2)–N(5)	2.421(6)
Cd(1)–N(2)	2.329(5)	Cd(2)–N(6)	2.357(5)
Cd(1)–N(3)	2.324(6)	Cd(2)–N(7)	2.337(5)
Cd(1)–N(4)	2.385(5)	Cd(2)–N(8)	2.359(5)
N(1)–Cd(1)–N(2)	76.69(19)	N(5)–Cd(2)–N(6)	76.09(19)
N(1)–Cd(1)–N(3)	76.26(19)	N(5)–Cd(2)–N(7)	75.99(19)
N(1)–Cd(1)–N(4)	75.7473(18)	N(5)–Cd(2)–N(8)	75.93(18)
N(2)–Cd(1)–N(3)	111.9(2)	N(6)–Cd(2)–N(7)	110.79(18)
N(2)–Cd(1)–N(4)	115.2524(19)	N(6)–Cd(2)–N(8)	116.8786(19)
N(3)–Cd(1)–N(4)	116.4(2)	N(7)–Cd(2)–N(8)	115.35(19)
Br(1)–Cd(1)–N(1)	175.08(13)	Br(1)–Cd(2)–N(5)	179.11(13)
Br(1)–Cd(1)–N(2)	100.70(14)	Br(1)–Cd(2)–N(6)	103.1415(14)
Br(1)–Cd(1)–N(3)	108.65(15)	Br(1)–Cd(2)–N(7)	103.93(14)
Br(1)–Cd(1)–N(4)	101.95(13)	Br(1)–Cd(2)–N(8)	104.86(13)
Cd(1)–Br(1)–Cd(2)	176.92(3)		
9			
Hg(1)–Cl(1)	2.5265(3)	Hg(1)–N(1)	2.464(8)
Hg(1)–N(2)	2.347(8)	Hg(1)–N(3)	2.334(8)
Hg(1)–N(4)	2.356(7)		
N(1)–Hg(1)–N(2)	75.9(3)	N(1)–Hg(1)–N(3)	76.5(3)
N(1)–Hg(1)–N(4)	76.2(3)	N(2)–Hg(1)–N(3)	113.6(3)
N(2)–Hg(1)–N(4)	117.5(3)	N(3)–Hg(1)–N(4)	112.4(3)
Cl(1)–Hg(1)–N(1)	177.9(2)	Cl(1)–Hg(1)–N(2)	105.66(19)
Cl(1)–Hg(1)–N(3)	103.9(2)	Cl(1)–Hg(1)–N(4)	101.75(19)
Hg(1)–Cl(1)–Hg(1)#1	177.96(15)		
10			
Hg(1)–Br(1)	2.67676767(9)	Hg(2)–Br(1)	2.6798(8)
Hg(1)–N(1)	2.489(6)	Hg(2)–N(5)	2.471(66)
Hg(1)–N(2)	2.378(8)	Hg(2)–N(6)	2.423423(7)
Hg(1)–N(3)	2.373373(9)	Hg(2)–N(7)	2.355355(8)
Hg(1)–N(4)	2.402(7)	Hg(2)–N(8)	2.360(8)
N(1)–Hg(1)–N(2)	75.44(2)	N(5)–Hg(2)–N(6)	74.7(2)
N(1)–Hg(1)–N(3)	75.0(2)	N(5)–Hg(2)–N(7)	76.2(3)
N(1)–Hg(1)–N(4)	75.1(2)	N(5)–Hg(2)–N(8)	76.1(2)
N(2)–Hg(1)–N(3)	115.2(3)	N(6)–Hg(2)–N(7)	115.9(3)
N(2)–Hg(1)–N(4)	116.6(3)	N(6)–Hg(2)–N(8)	114.4(3)
N(3)–Hg(1)–N(4)	109.2(3)	N(7)–Hg(2)–N(8)	111.8(3)
Br(1)–Hg(1)–N(1)	178.6969(17)	Br(1)–Hg(2)–N(5)	174.11(18)
Br(1)–Hg(1)–N(2)	105.7070(17)	Br(1)–Hg(2)–N(6)	102.6464(16)
Br(1)–Hg(1)–N(3)	105.0808(166)	Br(1)–Hg(2)–N(7)	109.68(1818)
Br(1)–Hg(1)–N(4)	103.66(16)	Br(1)–Hg(2)–N(8)	100.65(16)
Hg(1)–Br(1)–Hg(2)	176.41(5)		
11			
Hg(1)–I(1)	2.8593(8)	Hg(2)–I(1)	2.8036(8)
Hg(1)–N(1)	2.540(9)	Hg(2)–N(5)	2.480(9)
Hg(1)–N(2)	2.313(8)	Hg(2)–N(6)	2.350(9)
Hg(1)–N(3)	2.412(8)	Hg(2)–N(7)	2.461(9)
Hg(1)–N(4)	2.419(8)	Hg(2)–N(8)	2.457(9)
N(1)–Hg(1)–N(2)	74.5(3)	N(5)–Hg(2)–N(6)	75.7(3)
N(1)–Hg(1)–N(3)	73.7(3)	N(5)–Hg(2)–N(7)	73.1(3)
N(1)–Hg(1)–N(4)	73.1(3)	N(5)–Hg(2)–N(8)	73.2(3)
N(2)–Hg(1)–N(3)	117.8(3)	N(6)–Hg(2)–N(7)	104.8(3)
N(2)–Hg(1)–N(4)	107.4(3)	N(6)–Hg(2)–N(8)	117.5(3)
N(3)–Hg(1)–N(4)	112.3(3)	N(7)–Hg(2)–N(8)	115.6(3)
I(1)–Hg(1)–N(1)	159.4(2)	I(1)–Hg(2)–N(5)	159.6(2)
I(1)–Hg(1)–N(2)	125.8(2)	I(1)–Hg(2)–N(6)	124.4(2)
I(1)–Hg(1)–N(3)	91.5(2)	I(1)–Hg(2)–N(7)	101.6(2)
I(1)–Hg(1)–N(4)	100.5(2)	I(1)–Hg(2)–N(8)	92.3(2)
Hg(1)–I(1)–Hg(2)	151.80(3)		

[a] Symmetry codes for 3: #1: $-x + y + 1$, $-x + 2$, z; 5: #1: $-x + 1$, y, $-z + 1$; #2: $-x + 1$, y, $-z$; 9: #1: $-x + 1$, y, $-z + 3/2$.

$[Co_2L(\mu\text{-}OH)]^{3+}$, with $[Zn_2L]^{4+}$ metal ion radii close to Co(II), the Zn···Zn distance is relatively long; thus $[Zn_2L]^{4+}$ prefers to encapsulate both OH^- and H_2O within its cavity to form $[Zn_2L(OH)(H_2O)]^{3+}$/$[Zn_2L(F)(H_2O)]^{3+}$ rather than a F^-/OH^- bridged cryptate, and only Cl^- and Br^- bridged cryptates of $[Co_2L(\mu\text{-}Cl/Br)]^{3+}$ and $[Zn_2L(\mu\text{-}Cl/Br)]^{3+}$ were obtained. The larger Cd^{2+} and Hg^{2+} in $[M_2L]^{4+}$ make the Cd···Cd and Hg···Hg distances become shorter; thus it is not favourable to encapsulate both OH^- and H_2O within their cavities, and the bridged cryptates of $[Cd_2L(\mu\text{-}OH/F)]^{3+}$ and $[Hg_2L(\mu\text{-}OH/F)]^{3+}$ can be obtained. In addition, the soft acid Cd^{2+}/Hg^{2+} shows higher affinity with the soft base I^-. In water, the overall stability constant for the $[HgI_4]^{2-}$ anion is as high as $10^{29.83}$ in water;[20] therefore, a Hg–I–Hg cascade binding mode can be established even if the ligand is distorted by the binding of the large iodide anion. For the cadmium(II) complex, on the other hand, the overall stability constant of the $[CdI_4]^{2-}$ anion is only $10^{5.41}$ in water.[20] The energy gained from the formation of the Cd–I bonds cannot compensate the energy required for the distortion of the ligand; therefore, no iodide bridged complexes was isolated.

Conclusion

In conclusion, the cascade binding behavior of dimetallic cryptate $[Zn_2L]^{4+}$ is similar to that of $[Co_2L]^{4+}$, in which only Cl^- and Br^- bridged cryptates of $[Zn_2L(\mu\text{-}Cl/Br)]^{3+}$ can be formed, and the results of DFT calculations demonstrate that a smaller F^-/OH^- anion prefers to form $[Zn_2L(OH)(H_2O)]^{3+}$/$[Zn_2L(F)(H_2O)]^{3+}$ rather than a F^-/OH^- bridged cryptate due to the long Zn···Zn separation. In $[Cd_2L]^{4+}$ and $[Hg_2L]^{4+}$, however, besides the formation of Cl^- and Br^- bridged cryptates of $[Cd_2L(\mu\text{-}Cl/Br)]^{3+}$ and $[Hg_2L(\mu\text{-}Cl/Br)]^{3+}$, the larger Cd^{2+} and Hg^{2+} cations make the Cd···Cd and Hg···Hg distances become shorter; thus it can also form OH^-/F^- bridged cryptates of $[Cd_2L(\mu\text{-}OH/F)]^{3+}$ and $[Hg_2L(\mu\text{-}OH/F)]^{3+}$. In addition, due to the high affinity of Hg(II) with I^-, a μ-I^- bridged cryptate of $[Hg_2L(\mu\text{-}I)]^{3+}$ can be formed even if the ligand is distorted by the binding of the large iodide anion, while $[Cd_2L(\mu\text{-}I)]^{3+}$ cannot be formed due to the weaker interaction between Cd(II) and I^-. The above results demonstrate that the cascade binding modes of $[M_2L]^{4+}$ towards anions can be tuned by using metal ions with different radii and coordination habits.

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