

Capsule Formation in Novel Cadmium Cluster Metallocavitands

Peter D. Frischmann & Mark J. MacLachlan*

*Department of Chemistry, 2036 Main Mall, Vancouver, BC Canada V6T 1Z1.
mmaclach@chem.ubc.ca*

Supporting Information

Table of Contents

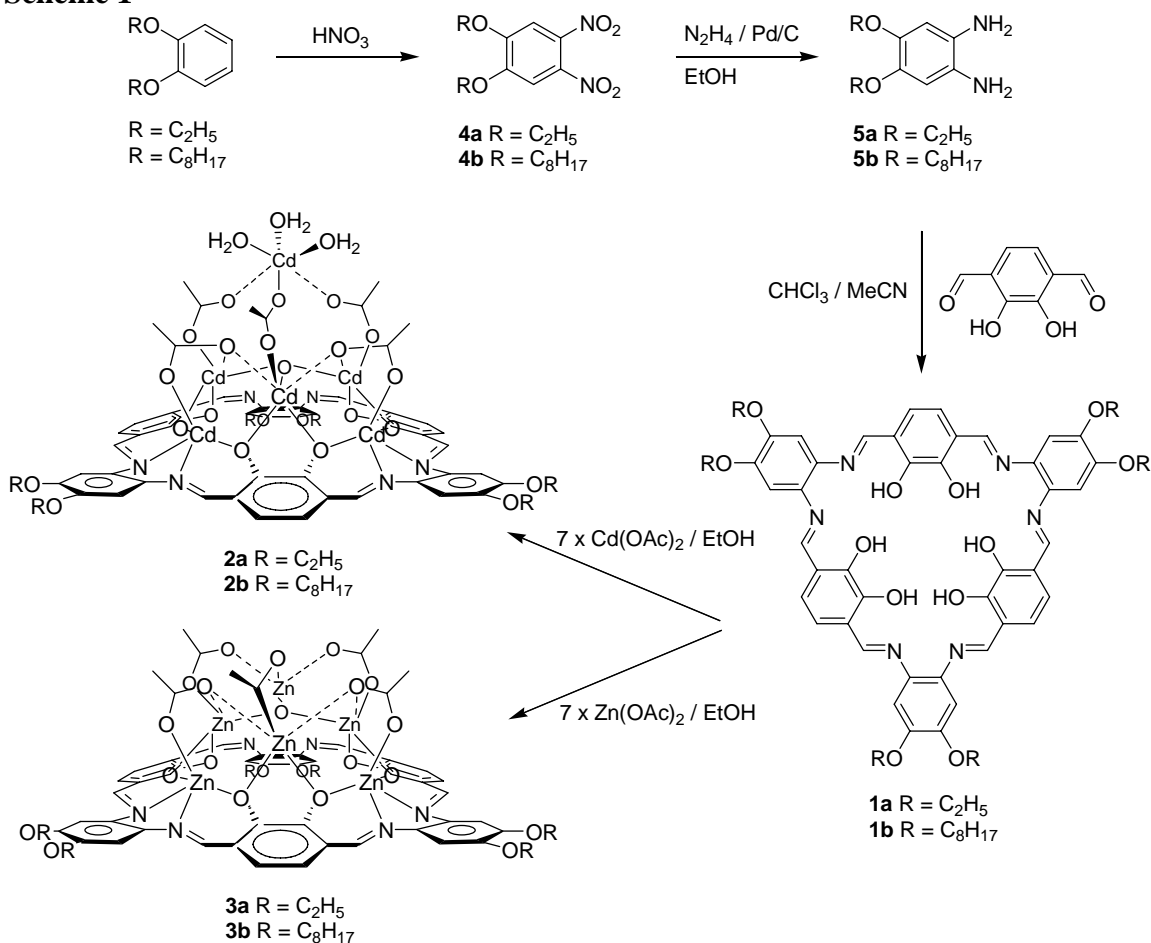
Experimental Section	S2
Variable Temperature-Variable Concentration ¹H NMR	S4
X-Ray Diffraction Study	S5
References	S6
Figure S1. ¹ H NMR spectrum of Cd complex 2a	S7
Figure S2. ¹³ C NMR spectrum of Cd complex 2a	S7
Figure S3. ¹ H NMR spectrum of Cd complex 2b	S8
Figure S4. ¹³ C NMR spectrum of Cd complex 2b	S8
Figure S5. ¹ H NMR spectrum of Zn complex 3b	S8
Figure S6. ¹³ C NMR spectrum of Zn complex 3b	S9
Figure S7. VTVC plot of 2b in benzene- <i>d</i> ₆	S9
Table S1. VTVC data of 2b in benzene- <i>d</i> ₆	S9
Figure S8. van't Hoff plot of 2b in benzene- <i>d</i> ₆	S10
Figure S9. VTVC plot of 2b in toluene- <i>d</i> ₈	S10
Table S2. VTVC data of 2b in toluene- <i>d</i> ₈	S10
Figure S10. van't Hoff plot of 2b in toluene- <i>d</i> ₈	S11
Figure S11. VTVC plot of 2b in <i>p</i> -xylene- <i>d</i> ₁₀	S11
Table S3. VTVC data of 2b in <i>p</i> -xylene- <i>d</i> ₁₀	S11
Figure S12. van't Hoff plot of 2b in <i>p</i> -xylene- <i>d</i> ₁₀	S12
Figure S13. VTVC plot of 3b in benzene- <i>d</i> ₆	S12
Table S4. VTVC data of 3b in benzene- <i>d</i> ₆	S12
Figure S14. van't Hoff plot of 3b in benzene- <i>d</i> ₆	S13

Experimental Section

Materials. Compounds **4a-b**, **5a-b**, macrocycles **1a-b**¹, and metallomacrocycle **3a**² were prepared by previously reported methods. All deuterated solvents were purchased from Cambridge Isotope Laboratories.

Equipment. All reactions were carried out under air unless otherwise noted. ¹H and ¹³C NMR spectra were recorded on either a Bruker AV-300 or AV-400 spectrometer. ¹³C NMR spectra were recorded using a proton decoupled pulse sequence. ¹H and ¹³C NMR spectra were calibrated to the residual protonated solvent at δ 7.27 and δ 77.23 ppm, respectively, in CDCl₃ (5.32 ppm for CD₂Cl₂), or at δ 8.03 and δ 163.15 for DMF-*d*₇. UV-vis spectra were obtained in CH₂Cl₂ (ca. 1×10^{-6} M) on a Varian Cary 5000 UV-vis-near-IR spectrophotometer using a 1 cm quartz cuvette. IR spectra were obtained as KBr discs with a Nicolet 4700 FT-IR. MALDI-TOF mass spectra were obtained in a trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]-malonitrile (DCTB) matrix (solvent free) at the UBC Microanalytical Services Laboratory on a Bruker Biflex IV instrument. Electrospray ionization (ESI) mass spectra were obtained on a Bruker Esquire LC instrument. The samples were analyzed in MeOH:CHCl₃ (1:1) at 100 μ M. Elemental analyses (C,H,N) were performed at the UBC Microanalytical Services Laboratory. Melting points were obtained on a Fisher-John's melting point apparatus.

Scheme 1



Synthesis of heptacadmium complex 2a (R = C₂H₅): Cadmium acetate dihydrate (408 mg, 1.53 mmol) was added to a suspension of macrocycle **1a** (200 mg, 0.20 mmol) in 8 mL of EtOH and heated to reflux for 1.5 h. The solution was cooled to room temperature precipitating a red solid that was then isolated on a glass frit. Recrystallization from hot DMF gave **2a** as a dark red microcrystalline solid. Yield: 247 mg (0.11 mmol, 57%). Low solubility of **2a** prevented observation of all of the peaks in the ¹³C NMR spectrum.

Data for 2a: ¹³C NMR (100.6 MHz, DMF-*d*₇) δ 165.9, 163.3, 150.6, 136.4, 120.5, 105.6, 66.3, 21.9, 15.6. ¹H NMR (400 MHz, DMF) δ 8.64 (s, 6H, imine), 7.50 (s, 6H, Ar), 6.52 (s, 3H, monomer Ar), 5.83 (s, 3H, dimer Ar), 4.33 (s, 12H, OCH₂CH₃), 1.96 (s, 18H, acetate), 1.49 (s, 18H, CH₂CH₃). UV-vis (CH₂Cl₂) λ_{max} (ε) = 349 (2.14 × 10⁵), 412 (5.36 × 10⁵) nm (L mol⁻¹ cm⁻¹). MALDI-TOF MS: many peaks around the molecular ion but none unambiguously assignable. IR (KBr): ν = 2979, 2931, 2883, 1608, 1565, 1503, 1454, 1415, 1395, 1331, 1264, 1182. Mp > 270 °C. Anal. Calc'd for **2a**: C₆₆H₇₂Cd₇N₆O₂₈·2DMF: N, 4.81; C, 37.11; H, 3.72. Found: N, 4.59; C, 37.12; H, 3.81.

Synthesis of heptacadmium complex 2b (R = C₈H₁₇): Cadmium acetate dihydrate (382 mg, 1.44 mmol) was added to a suspension of macrocycle **1a** (300 mg, 0.20 mmol) in 5

mL of EtOH and let stir at room temperature for 3 h. The solution was chilled to 0 °C for 16 h to precipitate a red powder that was isolated on a glass frit. The product was washed with hexanes yielding **2b** as a red microcrystalline powder. Yield: 410 mg (0.15 mmol, 75%)

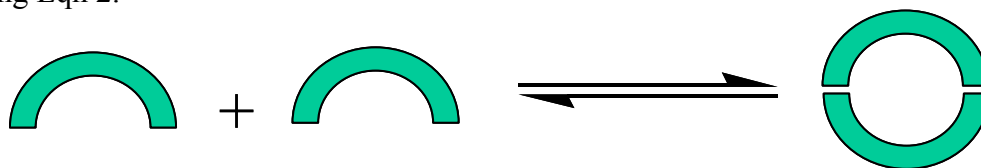
Data for 2b: ^{13}C NMR (100.6 MHz, CDCl_3) 183.0 (t, $J_{\text{Cd-C}}$ 21.9 Hz), 164.67, 164.61, 161.56, 161.51, 150.1, 134.8, 120.7, 119.5 (t, $J_{\text{Cd-C}}$ 18.5 Hz), 103.8, 70.2, 32.0, 29.6, 29.5, 26.2, 22.9, 14.3. ^1H NMR (300 MHz, CDCl_3) δ 8.29 (t, $J_{\text{Cd-H}}$ 34.2 Hz, 6H, imine), 6.89 (s, 6H, Ar), 6.59 (s, 6H, Ar), 4.08 (m, 12H, OCH_2CH_2), 2.19 (s, 9H, acetate), 2.03 (s, 9H, acetate), 1.87 (m, 12H, OCH_2CH_2), 1.52 (m, 12H, CH_2), 1.32 (Bs, 48H, CH_2), 0.91 (t, J_{HH} 6.6 Hz, 18H, CH_2CH_3). UV-vis(CH_2Cl_2) λ_{max} (ϵ) = 353 (3.28×10^5), 412 (5.75×10^5) nm ($\text{L mol}^{-1} \text{cm}^{-1}$). MALDI-TOF MS: many peaks around the molecular ion but none were unambiguously assignable. IR (KBr): ν = 2927, 2855, 1608, 1558, 1503, 1454, 1417, 1333, 1267, 1179. Mp > 270 °C. Anal. Calc'd for **2b**: $\text{C}_{102}\text{H}_{144}\text{Cd}_7\text{N}_6\text{O}_{28}\cdot\text{DMF}$: N, 3.55; C, 45.66; H, 5.51. Found: N, 3.47; C, 47.29; H, 5.54.

Synthesis of heptazinc Complex 3b (R = C₈H₁₇). Zinc acetate dihydrate (1.79 g, 8.1 mmol) was added to a solution of **1b** (1.7 g, 1.2 mmol) in 150 mL of EtOH. The dark red solution turned bright orange upon heating to reflux (80 °C). After 2 h, the reaction was cooled to RT and isolated on a glass frit. The crude solid was recrystallized from hot EtOH to give **2b**. Yield: 2.5 g (1.1 mmol, 94%).

Data for 3b. ^{13}C NMR (75.5 MHz, CDCl_3) δ 180.1, 178.9, 161.9, 158.7, 150.2, 134.2, 120.8, 119.3, 102.0, 69.7, 31.8, 29.4, 29.3, 29.2, 26.0, 23.4, 22.7, 21.7, 14.1 ppm; ^1H NMR (300 MHz, CDCl_3) δ 8.31 (s, 6H, imine), 6.96 (s, 6H, Ar), 6.69 (s, 6H, Ar), 4.06 (m, 12H, OCH_2), 1.93 (s, 9H, acetate), 1.85 (m, 12H, CH_2), 1.84 (s, 9H, acetate), 1.50 (m, 24H, CH_2), 1.30 (m, 36H, CH_2), 0.88 (t, $^3J_{\text{HH}}$ = 6.4 Hz, 18H, CH_2CH_3) ppm. UV-vis (CH_2Cl_2) λ_{max} (ϵ) = 414 (1.2×10^5), 347 (6.2×10^4), 242 (6.6×10^4) nm ($\text{L mol}^{-1} \text{cm}^{-1}$). ESI-MS: m/z = 2062 (**3b**- $\text{Zn}_2\text{O}(\text{OAc})_2 + \text{Na}$)⁺, 2244 (**3b** - $\text{ZnO} + \text{H}_2\text{O} + \text{H}$)⁺. IR (KBr): ν = 2959, 2927, 2856, 1617, 1506, 1459, 1447, 1391, 1324, 1264, 1216, 1185, 1105, 1022, 756, 669, 616 cm^{-1} . Mp. >270 °C. Anal. Calc'd for **3b** $\text{C}_{102}\text{H}_{138}\text{N}_6\text{O}_{25}\text{Zn}_7$: C, 53.13; H, 6.03; N, 3.64. Found: C, 53.42; H, 6.30; N, 3.94.

Variable Temperature ^1H NMR Experiment for 2a in DMF-*d*₇. A standard solution was prepared with 109.0 mg of **2a** dissolved in 1.75 mL of DMF-*d*₇ (28.5 mmol L⁻¹). A 50 μL aliquot of the standard was then diluted to 550 μL yielding a 2.6 mmol L⁻¹ solution. The 2.6 mmol L⁻¹ solution was chilled to 238, 247, 256, and 265 K and a ^1H NMR spectrum was taken at each temperature after equilibrating for 7 mins. The upfield and downfield aromatic proton peaks corresponding to monomer and dimer were then integrated and association constants were calculated using a standard monomer-dimer equilibrium equation. The association constants for dimerization (K_{dim}) calculated from H_a and H_c were averaged and the average association constants were used to make a van't Hoff plot. An estimated 5% error in integration was applied to the thermodynamic parameters.

Variable Temperature Variable Concentration ^1H NMR Experiments for **2b and **3b** in aromatic solvents.** Due to solubility constraints, the concentration range was limited (0.1 to 5.0 mM). A standard 5.00 mM solution was prepared by first dissolving 0.005 mmol of metallomacrocyclic (**2b** or **3b**) with heat in 1.00 mL of the deuterated solvent of choice. Except for the 5.00 mM samples, NMR tubes were primed with 500 μL of selected deuterated solvent and standard was then added via syringe to achieve the desired concentrations. The concentration and temperature dependence of the imine resonance was measured in CD_2Cl_2 , benzene- d_6 , toluene- d_8 , and p -xylene- d_{10} for **2b** and only in benzene- d_6 for **3b**. The data were treated with least-squares curve-fitting (monomer-dimer equilibrium model) to find the association constants for dimerization (Eqn 1). Thermodynamic parameters of dimerization were calculated from van't Hoff plots using Eqn 2.



$$(1) \quad (\delta - \delta_m) = (\delta_d - \delta_m) \left(1 + \frac{1 - \sqrt{8K_{\text{dim}} C_T + 1}}{4K_{\text{dim}} C_T} \right)$$

$$(2) \quad \ln K_{\text{dim}} = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R}$$

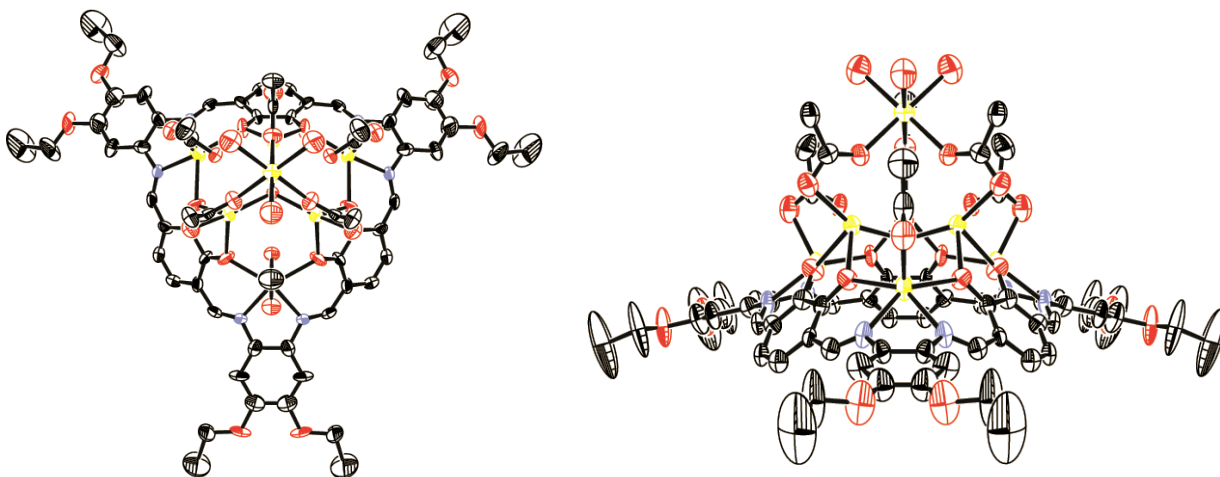
Crystallography of **2a:** X-ray crystal data for **2a**: $\text{C}_{87}\text{H}_{121}\text{Cd}_7\text{N}_{13}\text{O}_{35}$, $M_r = 2695.77 \text{ g mol}^{-1}$, red plate (0.25 x 0.25 x 0.10 mm^3), rhombohedral, space group R-3m, $a = b = 28.712(3)$, $c = 26.128(3) \text{ \AA}$, $V = 18654(4) \text{ \AA}^3$, $Z = 6$, $\rho_{\text{calcd}} = 1.440 \text{ g cm}^{-3}$, $F_{000} = 8100$, $\text{MoK}\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$, $T = 173(2) \text{ K}$, $2\theta_{\text{max}} = 45.0^\circ$, 46300 reflections collected, 2884 unique ($R_{\text{int}} = 0.1841$). Final GoF = 1.005, $R1 = 0.0665$, $wR2 = 0.1847$, R indices based on 1816 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods (G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, **1997**) and refined by full-matrix least-squares methods on F^2 . All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were added at geometrically expected positions and left isotropic. Hydrogen atoms from the capping aqua ligands were not modeled. The intermolecular $\text{O}_{\text{aqua}}\text{-O}_{\text{aqua}}$ distance is 4.504 Å ruling out hydrogen bonding.

Disordered solvent was found inside and outside the capsule. We were able to model with some certainty an oxygen atom inside the capsule, approximately 3 Å from the cadmium ion in the N_2O_2 pockets. This oxygen appeared to be part of DMF disordered over two different orientations. Within each capsule (2 metallocavitands), there are then 6 different sites with 2 DMF orientations each for a total of 12 possible orientations for the disordered solvent, rendering it nearly impossible to model the encapsulated solvent with certainty. The electron density from this disordered solvent located inside the capsule, as

well as solvent outside the capsule, was accounted for using the PLATON/SQUEEZE program (A. L. Spek, PLATON, Utrecht University, Utrecht, The Netherlands, **2002**). The output indicated that approx. 1716 electrons / unit cell were accounted for, corresponding to ca. 42 DMF molecules per unit cell. These 42 DMF molecules were included in the chemical formula.

CCDC- 643623 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ORTEP depictions of 2a (Ellipsoids at 50% probability level):



References

- 1 A. J. Gallant, J. K.-H. Hui, F. Zahariev, Y. A. Wang, M. J. MacLachlan, *J. Org. Chem.* 2005, **70**, 7936.
- 2 A. J. Gallant, J. H. Chong, M. J. MacLachlan, *Inorg. Chem.* 2006, **45**, 5248.

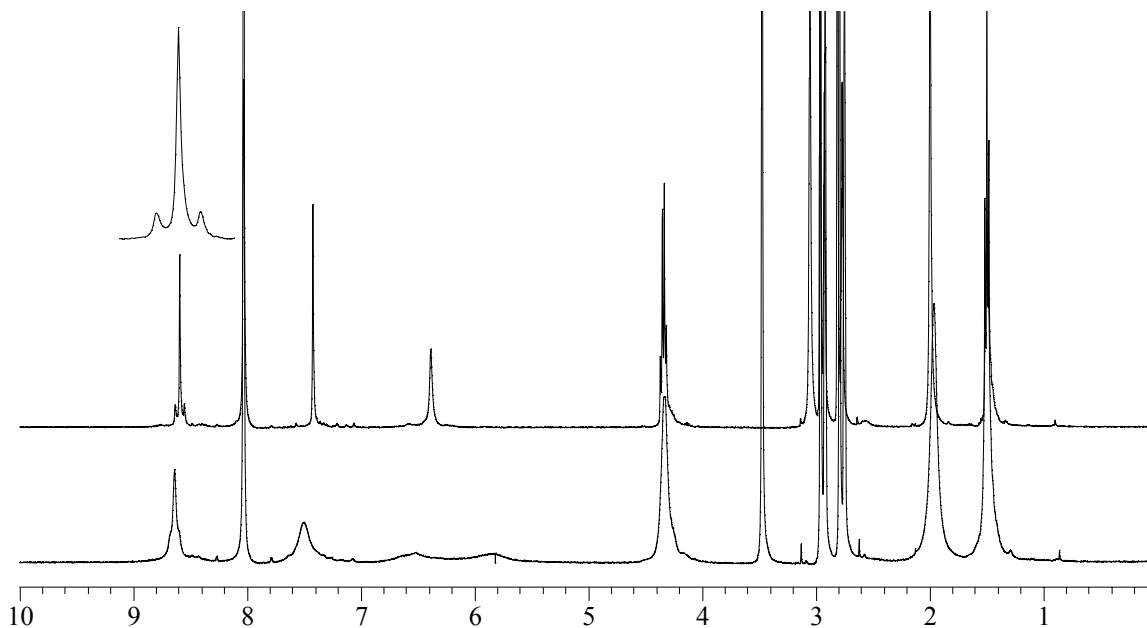


Figure S1: ¹H NMR spectra of Cd₇ complex **2a** at 357 K and 300 K, top and bottom respectively (400 MHz, DMF-*d*₇). Inset highlights ³J_{Cd-H} coupling of 34.2 Hz that is resolved at 357 K.

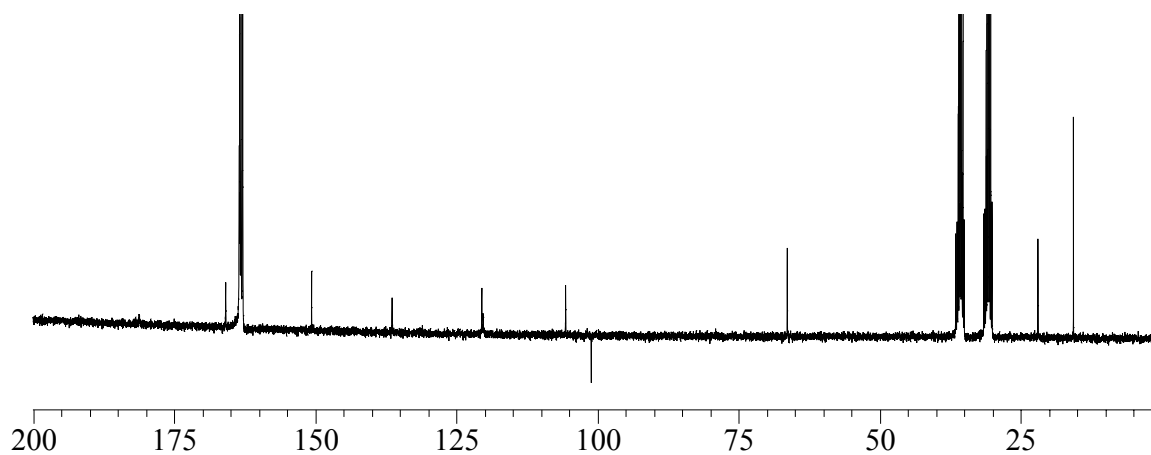


Figure S2: ¹³C NMR spectrum of Cd₇ complex **2a** (100.6 MHz, DMF-*d*₇).

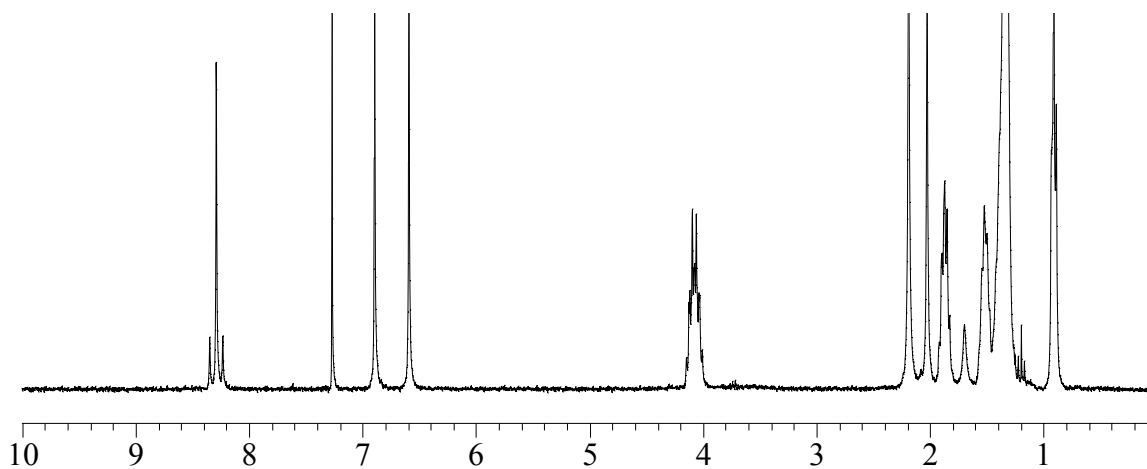


Figure S3: ¹H NMR spectrum of Cd₇ complex **2b** (300 MHz, CDCl₃).

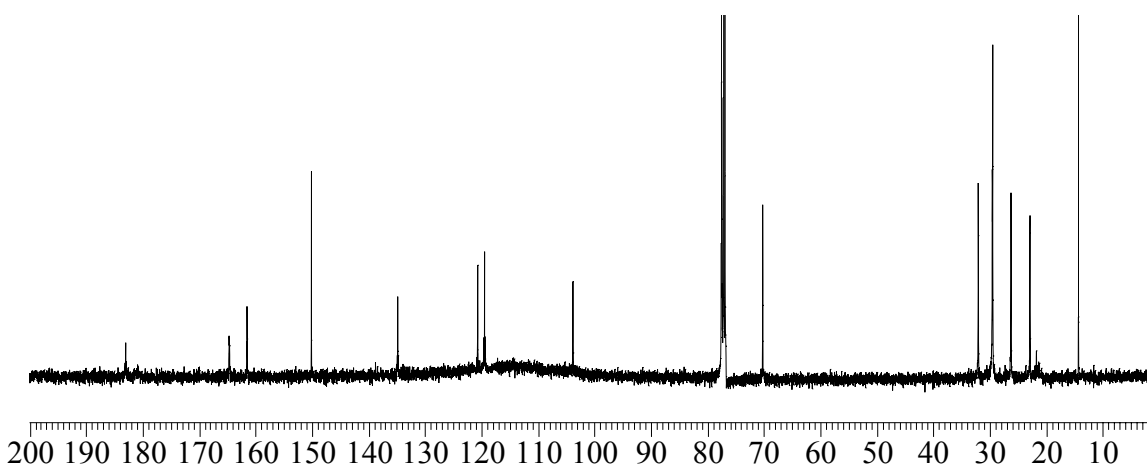


Figure S4: ¹³C NMR spectrum of Cd₇ complex **2b** (100.6 MHz, CDCl₃).

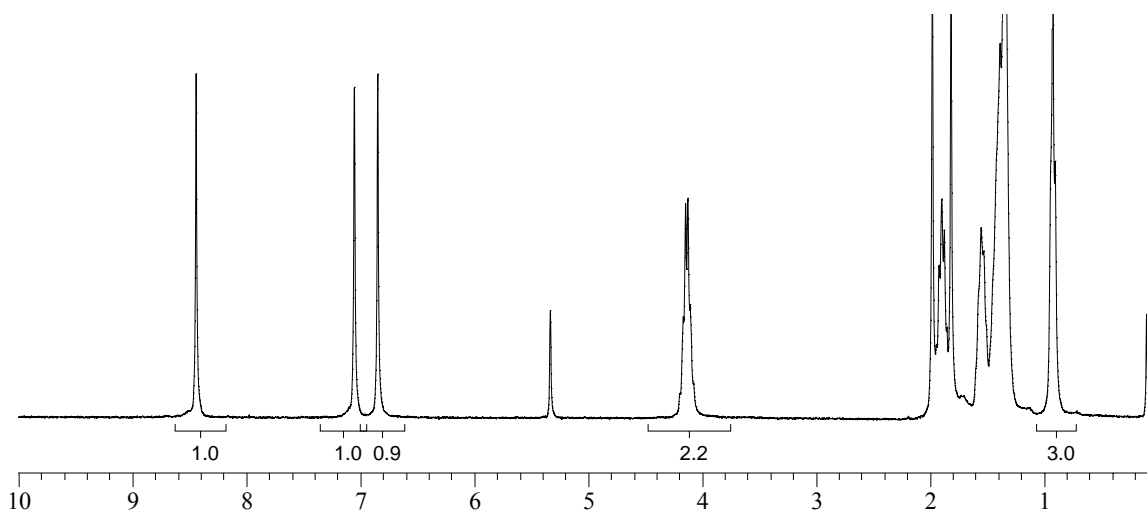


Figure S5: ¹H NMR spectrum of Zn₇ complex **3b** (400 MHz, CD₂Cl₂).

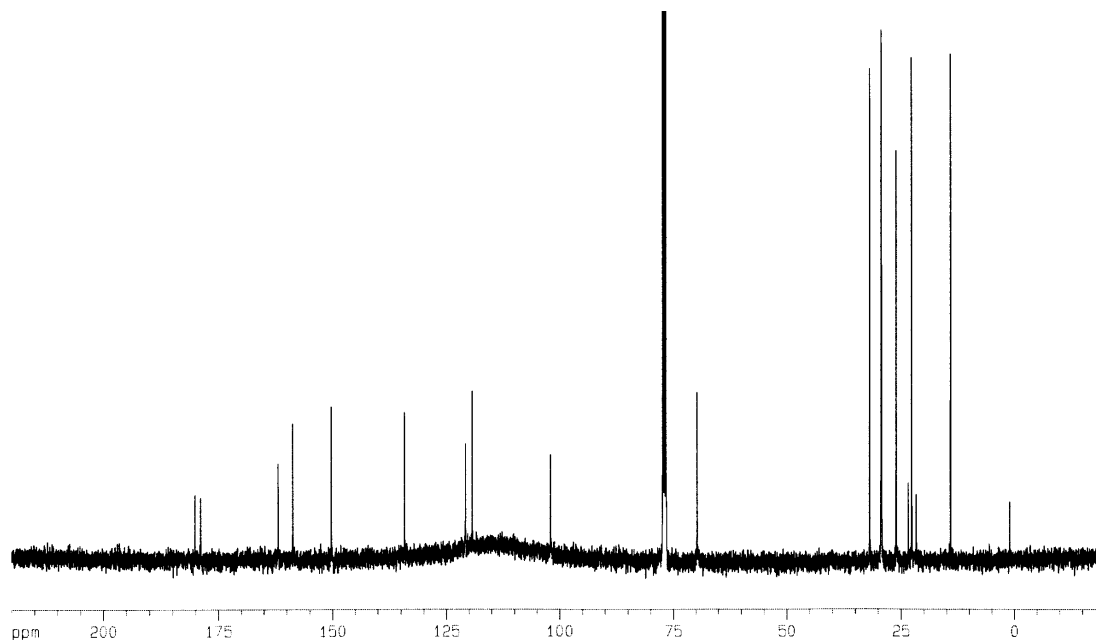


Figure S6: ^{13}C NMR spectrum of Zn_7 complex **3b** (100.6 MHz, CDCl_3).

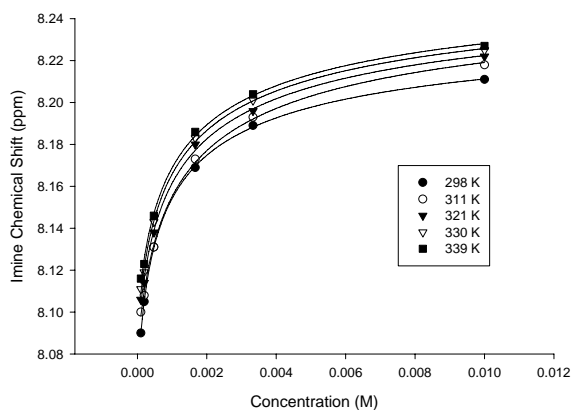


Figure S7: VTVC Imine chemical shift dependence of **2b** in benzene- d_6

Table S1: Imine chemical shift (ppm) and association constants of **2b** in benzene- d_6

Conc. (mM)	298 K	311 K	321 K	330 K	339 K
10.00	8.211	8.218	8.222	8.225	8.227
3.33	8.189	8.193	8.196	8.201	8.204
1.67	8.169	8.173	8.180	8.183	8.186
0.48	8.131	8.131	8.138	8.143	8.146
0.20	8.105	8.108	8.114	8.119	8.123
0.10	8.090	8.100	8.106	8.111	8.116
K_{dim}	900 ± 100	500 ± 100	600 ± 100	600 ± 100	600 ± 100

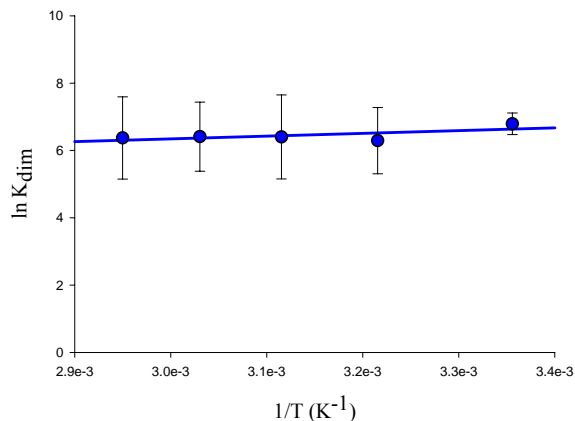


Figure S8: van't Hoff plot of **2b** in benzene- d_6

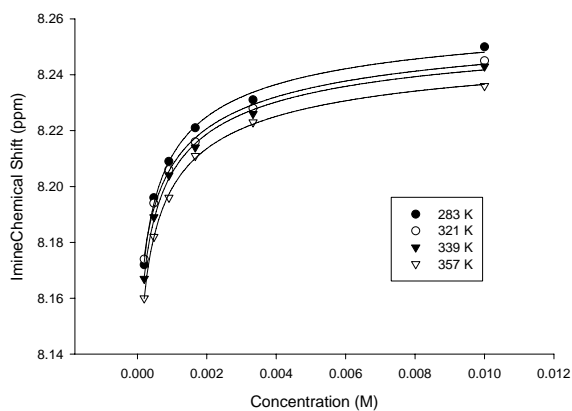


Figure S9: VTVC Imine chemical shift dependence of **2b** in toluene- d_8

Table S2: Imine chemical shift (ppm) and association constants of **2b** in toluene- d_8

Conc. (mM)	283 K	321 K	339 K	357 K
10.00	8.250	8.245	8.243	8.236
3.33	8.231	8.228	8.226	8.223
1.67	8.221	8.216	8.214	8.211
0.91	8.209	8.206	8.204	8.196
0.48	8.196	8.194	8.189	8.182
0.20	8.172	8.174	8.167	8.160
K_{dim}	1500 ± 700	1000 ± 300	1500 ± 400	1800 ± 300

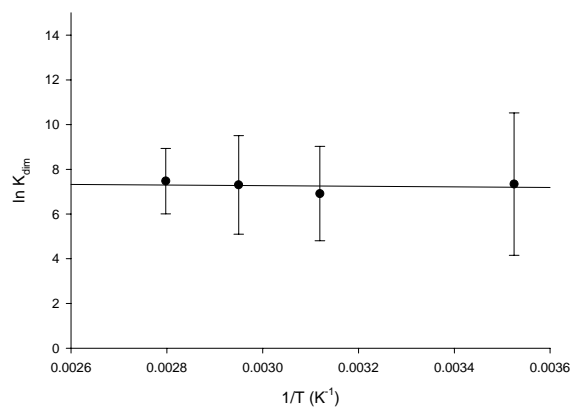


Figure S10: van't Hoff plot of **2b** in toluene- d_8

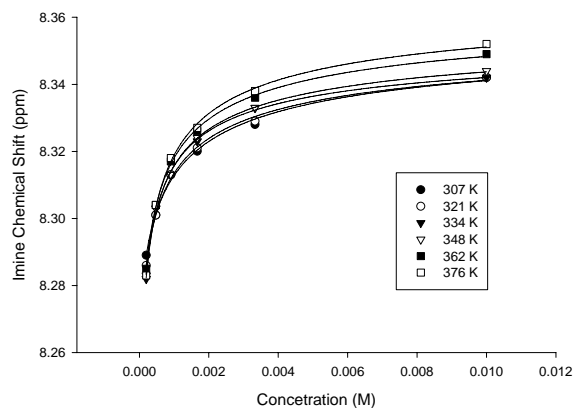


Figure S11: VTVC Imine chemical shift dependence of **2b** in p -xylene- d_{10}

Table S3: Imine chemical shift (ppm) and association constants of **2b** in p -xylene- d_{10}

Conc. (mM)	307 K	321 K	334 K	348 K	362 K	376 K
10.00	8.342	8.342	8.342	8.344	8.349	8.352
3.33	8.328	8.329	8.333	8.333	8.336	8.338
1.67	8.32	8.321	8.323	8.324	8.326	8.327
0.48	8.313	8.313	8.313	8.313	8.317	8.318
0.20	8.301	8.301	8.303	8.303	8.304	8.304
0.10	8.289	8.286	8.282	8.283	8.285	8.283
K_{dim}	800 ± 300	1300 ± 400	3700 ± 1400	2500 ± 700	1900 ± 400	2000 ± 600

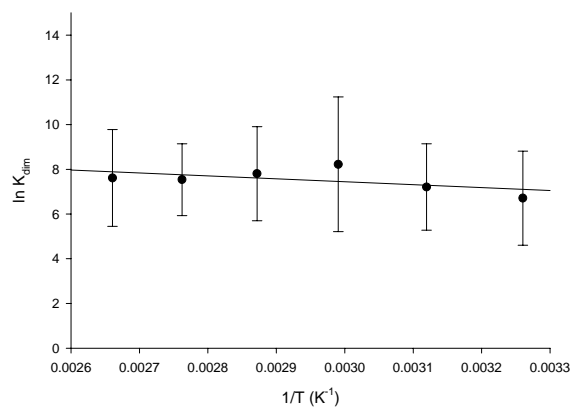


Figure S12: van't Hoff plot of **2b** in *p*-xylene-*d*₁₀

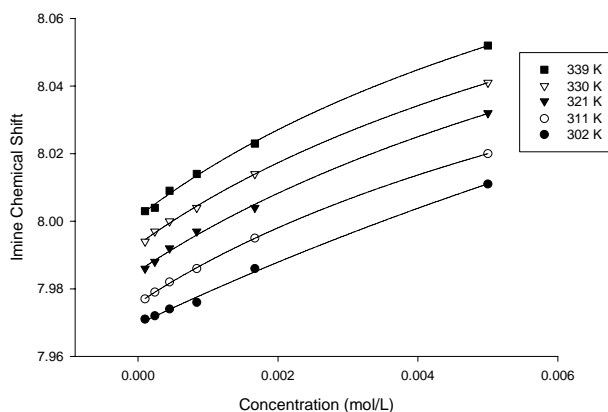


Figure S13: VTVC Imine chemical shift dependence of **3b** in benzene-*d*₆

Table S4: Imine chemical shift (ppm) and association constants of **3b** in benzene-*d*₆

Conc. (mM)	302 K	311 K	321 K	330 K	339 K
5.00	8.011	8.020	8.032	8.041	8.052
1.67	7.986	7.995	8.004	8.014	8.023
0.84	7.976	7.986	7.997	8.004	8.014
0.45	7.974	7.982	7.992	8.000	8.009
0.24	7.972	7.979	7.988	7.997	8.004
0.10	7.971	7.977	7.986	7.994	8.003
K_{dim}	10 ± 9	31 ± 3	27 ± 1	32 ± 6	33 ± 9

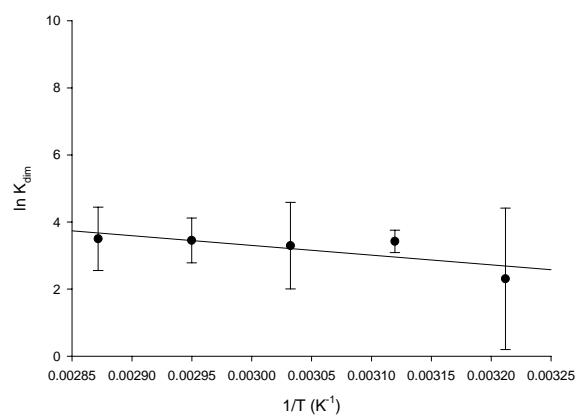


Figure S14: van't Hoff plot of **3b** in benzene- d_6