Supplementary Information

Controling the macrocycle size by the stoichiometry of the applied

template ion

Aleksandra Sarnicka, Przemysław Starynowicz and Jerzy Lisowski*

Department of Chemistry, University of Wrocław 14 F. Joliot-Curie, 50-383, Wrocław,

Poland. Fax: 48 71 3282348; Tel: 48 71 3757252; E-mail: jurekl@wchuwr.pl

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Methods

The NMR spectra were taken on Bruker Avance 500 spectrometer. The positive-mode electrospray mass spectra of methanol solutions of the complexes were obtained using Bruker microOTOF-Q instrument. The CD spectra were measured on Jasco J-715 Spectropolarimeter. The elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer.

Synthesis

S-2

4–*tert*–butyl–2,6–diformylphenol 2.062 g (10 mmol) dissolved in 20 mL of acetonitrile was combined with the stirred solution of 1.142 g (10 mmol) (1S, 2S)–diaminocyclohexane in 15 mL of acetonitrile. The resulted yellow suspensions was stirred at 50 °C for 12 h, filtered out, washed with acetonitrile and dried to give 2.38 g of yellow product (80%). Found: C, 74.97; H, 8.16; N 10.61. Calc. for C₅₆H₇₅N₇O₃: C, 75.21; H, 8.45; N, 10.96%. $\delta_{\rm H}$ (500 MHz; CDCl₃). 13.95 (br, s, 3H) 8.68 (s, 3H) 8.26 (s, 3H), 7.84 (d, 3H), 7.12 (br, s, 3H), 3.42 (m, 3H), 3.34 (q, 3H), 1. 84 (m, 12H), 1.76 (m, 6H), 1.47 (m, 6H), 1.19 (s, 27 H). $\delta_{\rm C}$ (125 MHz; CDCl₃) 163.87, 159.43, 156.25, 140.19, 130.53, 126.16, 122.90, 118.54, 75.51, 73.08, 33.93, 33.56, 33.20, 31.34, 24.45, 24.36. ESI-MS: *m*/z 853.6 ([S-2+H]⁺, 853.6 calcd. for [C₅₄H₇₃N₆O₃]⁺), 427.3 ([S-2+2H]²⁺, 427.2 (calcd. for [C₅₄H₇₄N₆O₃]²⁺)

R-2 was obtained in the same manner as *S*-2 starting from (1R, 2R)–diaminocyclohexane. *S*-3

0.5 mmol (0.057 g) of (1S, 2S) – diaminocyclohexane dissolved in 5 mL of methanol was added to the stirred solution of 0.5 mmol (0.103 g) of 4–*tert*–butyl–2,6–diformylphenol and 0.5 mmol (0.110 g) of Zn(CH₃COO)₂·2H₂O in 15 mL of methanol. The mixture was refluxed for 2 h. The orange solution was cooled down, left to stand overnight and the obtained yellow microcrystalline product was filtered, washed with small amount of MeOH and dried. A second crop of product was obtained after the filtrate was left overnight in the freezer. Yield 0.055 g (27%). Found: C, 58.90; H, 6.43; N 6.87. Calc. for C₄₀H₅₂N₄O₆Zn₂: C, 58.65; H, 6.06; N 6.70%. $\delta_{\rm H}$ (CD₃OD, 500 MHz) 8.53 (s), 7.70 (s), 4.54 (br, s), 3.60 (br, d), 2.60 (br, d), 2.06 (br, d), 1.87 (s) 1.57 (br, s), 1.35 (s). $\delta_{\rm H}$ (CDCl₃; 500 MHz) 8.30 (br, s), 7.35 (s), 4.09 (br, s) 3.50 (br, s), 2.51 (br, s), 2.01 (d), 1.72 (s), 1.56 (s), 1.48 (br, s), 1.28 (s).

S-**4**

Method A. 0.5 mmol (0.057 g) of (1S, 2S)–diaminocyclohexane dissolved in 5 mL of methanol was added to the stirred solution of 0.5 mmol (0.103 g) of 4–*tert*–butyl–2,6– diformylphenol and 0.25 mmol (0.0549 g) of $Zn(CH_3COO)_2 \cdot 2H_2O$ in 15 mL of methanol. The mixture was refluxed for 2 h, cooled down and left to stand in the fridge overnight to give 0.068 g (46%) of light yellow product.

Metod B. 0.25 mmol (0.0549 g) of Zn(CH₃COO)₂·2H₂O dissolved in 5 mL of methanol was added to the stirred suspension of the 3+3 macrocycle *S*-**2** (0.1420g, 0.167 mmol) in 15 mL of methanol. The mixture was refluxed for 2 h, cooled down and left to stand in the fridge overnight to give 0.105 g (67%) of light yellow product, which was recrystallized from chloroform and dried under vacuum. Found: C, 64.98; H, 8.86; N 8.21. Calc. for $C_{109}H_{145}Cl_3N_{12}O_6Zn3$: C, 64.75; H, 7.23; N, 8.31%. $\delta_{H}(500 \text{ MHz}; \text{CDCl}_3)$ 9.47 (s, 3H), 8.03 (s, 3H), 7.84 (d, 3H), 6.97 (d, 3H), 3.77 (m, 3H), 3.32, (m, 3H), 1.83 (d, 3H), 1.54-1.62 (m, 15H), 1.27 (m, 3H), 1.18 (s, 27H), 0.85 (m, 3H). $\delta_{C}(125 \text{ MHz}; \text{CDCl}_3)$ 171.09, 167.98, 163.00, 135.52, 135.30, 129.09, 127.05, 118.04, 75.88, 71.99, 33.62, 33.45, 31.45, 24.59, 24.39. ESI-MS: *m*/z 1895.9 ([S-4+H]⁺, 1895.9 calcd. for [$C_{108}H_{139}N_{12}O_6Zn_3$]⁺), 948.5 ([S-4+2H]²⁺, 948.4 calcd. for [$C_{108}H_{140}N_{12}O_6Zn_3$]²⁺), 632.6 ([S-4+3H]³⁺, 632.6 calcd. for [$C_{108}H_{141}N_{12}O_6Zn_3$]³⁺).

R-4 was obtained in the same way as *S*-4 in method B starting from *R*-2.

X-ray crystal structure determination.

Single crystals of (*S*-4a) and (*R*-4b) were grown by slow evaporation of methanol and chloroform solutions of the complexes, respectively. The crystallographic measurements were performed on a Kuma KM4 diffractometer equipped with a CCD counter. The collected data were corrected for polarization, Lorentz and absorption, the last calculated from the crystal habits captured from photo scans. Only the data collected for S-3 were of quality sufficient to warrant a well-determined solution. In the case of R-4b a great degree of disorder of solvent

molecules precluded reaching good final parameters, whereas S-4a was a poor diffractor: R_{σ} (= $\Sigma \sigma$ (F²)/ Σ F²) was 0.325 and R_{int} – 0.109. The structures were solved and refined with SHELXS97 and SHELXL97 programs [S1]. The positions of the C- and N-bonded hydrogen atoms were calculated geometrically, no attempts to localize the O-bonded H atoms were undertaken. All ordered non-H atoms were refined anisotropically, with the exceptions of C34 and C43 in S-4a, which were refined isotropically because of non-positive vibration tensor (C34) or very large components of the vibrations (C43). The positions of the C-bonded H atoms were constrained as 1.2 times of the trace of the thermal vibration tensors of the parent C atoms. Molecular structures were redrawn using MERCURY [S2].

References

[S1] Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

[S2] MERCURY, Ver. 1.4.1, Program for Crystal Structure Visualization and Exploration, CCDC Cambridge University.



Figure S1. Molecular diagram of *S*-**3** in two projections. The labels of Zn cations and coordinating atoms are shown.



Figure S2. Top and side spacefill views of R-4a (left) and R-4b (right). Black – carbon, white – hydrogen , red – oxygen, blue- nitrogen, purple – zinc



Fig. S3. Molecular diagram of R-4a in two projections. The labels of Zn cations and coordinating atoms are shown. The atoms generated by the (1-x,y,-z) operator are denoted by suffix i in their labels; the macrocycle generated by this symmetry is drawn in red.



Fig. S4. Molecular diagram of R-4b in two projections. The labels of Zn cations and coordinating atoms are shown. The atoms generated by the (-x,y,-z) operator are denoted by suffix i in their labels; the macrocycle generated by this symmetry is drawn in red.



Figure S5. The packing of R-4a viewed along the *b* axis direction (solvent molecules omitted).



Figure S6. The packing of **R**-**4a** viewed along the *c* axis direction (solvent molecules omitted).



Figure S7. The packing of **R-4b** viewed along the *b* axis direction (solvent molecules omitted).



Figure S8. The packing of **R-4b** viewed along the *c* axis direction (solvent molecules omitted).

Fig. S11. ¹H NMR spectrum of *S*-**3** in CDCl3.

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Fig. S14 Positive mode electrospray mass spectrum of S-4

Fig. S15. Experimental (top) and calculated (bottom) isotope pattern for the $[Zn_3(2_{-3H})_2+H]^+$ ion observed in the electrospray mass spectrum of *S*-4

Fig. S16. Experimental (top) and calculated (bottom) isotope pattern for the $[Zn_3(2_{-3H})_2+2H]^{2+}$ ion observed in the electrospray mass spectrum of *S*-4

Fig. S17. ¹H NMR spectrum (CD₃OD) of the crude product (solution evaporated to dryness) corresponding to a template synthesis of 3. s- residual solvent and water signals.

Fig. S18. The aromatic region of the ¹H NMR spectrum (CD₃OD) of the crude product (solution evaporated to dryness immediately after reflux was completed) corresponding to a template synthesis of **4**. s- residual solvent and water signals. Signals of 2+2 complex **3** and 3+3 complex **4** are indicated.

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Fig. S19. The NMR titration of macrocycle 3+3 with the solution of zinc(II) acetate. The aromatic region of the ¹H NMR spectrum (CD₃OD) of :

A - ligand *R*-2.

B – after addition of 1 equivalent of $Zn(CH_3COO)_2 \cdot 2H_2O$ per 2.

- C after additon of 1.5 equivalents of Zn(CH₃COO)₂·2H₂O, measured immediately.
- D solution C measured after 30 min.
- $E-after addition of 3 equivalents of Zn(CH_3COO)_2 \cdot 2H_2O$ measured immediately.
- F solution E measured after 1 day.
- G- spectrum of pure **3**.

Signals of ligand 2, 3+3 complex 4 and 2+2 complexs 3 are indicated.

Fig. S20. Experimental (top) and calculated (bottom) isotope pattern for the $[Ni_3(2_{-3H})_2(H_2O)+2H]^{2+}$ ion observed in the electrospray mass spectrum of crude reaction product of *R*-2 with Ni(II) salt.

Fig. S21. Experimental (top) and calculated (bottom) isotope pattern for the $[Ni_3(2_{-3H})_2(H_2O)_2+2H]^{2+}$ ion observed in the electrospray mass spectrum of crude reaction product of *R*-2 with Ni(II) salt.

Fig. S22. Experimental (top) and calculated (bottom) isotope pattern for the $[Ni_3(2_{-3H})_2(H_2O)_2+H]^+$ ion observed in the electrospray mass spectrum of crude reaction product of *R*-2 with Ni(II) salt.

Fig. S23. Experimental (top) and calculated (bottom) isotope pattern for the $[Cu_3(2_{-3H})_2+2H]^{2+}$ ion observed in the electrospray mass spectrum of crude reaction product of *R*-2 with Cu(II) salt.