Electronic Supplementary Information for Dalton Transactions

Zinc complexes of the carbahemiporphyrazines

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Supporting Information

General Experimental Methods:

All chemicals were purchased from Sigama-Aldrich or TCI America and used as received. All ^1H NMR spectra were recorded on Varian VXR or GEMINI spectrometers at 300 MHz. Mass spectrometry experiments were performed at the Mass Spectrometry and Proteomics Facility of Ohio State University on a Micromass ESI-Tof™ II (Micromass, Wythenshawe, UK) mass spectrometer equipped with an orthogonal electrospray source (Z-spray) operated in positive ion mode. Sodium iodide was used for mass calibration for a calibration range of m/z 100-2000. Samples were prepared in a solution containing acidified methanol and infused into the electrospray source at a rate of 5-10 μL min^{-1}. Optimal ESI conditions were: capillary voltage 3000 V, source temperature 110°C and a cone voltage of 55 V. The ESI gas was nitrogen. Data was acquired in continuum mode until acceptable averaged data was obtained. X-ray intensity data were measured at 100 K (Bruker KYRO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power. The crystal was mounted on a cryoloop using Paratone N-Exxon oil and placed under a steam of nitrogen at 100 K. The detector was placed at a distance of 5.009 cm from the crystal. Elemental analysis was conducted at the University of Illinois, School of Chemical Sciences Microanalysis Laboratory. The free base hemiporphyrazine macrocycles (**1-2**) were synthesized as described in the literature.[1,2]

Synthesis of **Zn1**: Free base **1** (50 mg, 1.1×10^{-4} mol) was weighted into a 50 mL flask and brought into an anaerobic glove box. Compound **1** was dissolved in 20 mL anhydrous pyridine and 130 μL of diethyl zinc solution (1 M in hexane, 1.3×10^{-4} mol) was then added to this solution. The solution was allowed to mix for 4 hours at ambient temperature. The volume of the solution was then reduced to 5 mL and crystals were grown upon diffusion of this solution with hexane: Yield: 48 mg (75%).

Zn1: High res. ESI MS (positive ion): 581.24 M/z (M^+ + H) CHN Analysis Calc. for $ZnC_{33}N_7H_{21}\cdot C_5H_5N$: C, 69.15; H, 3.97; N, 16.98. Found: C, 70.35; H, 4.01; N, 17.09. ^1H NMR ([D$_6$]DMSO, δ): 6.705 (d, 4H), 6.951 (s, 2H), 7.377 (t, 2H), 7.620 (m, 2H), 7.741 (m, 2H), 7.835 (q, 4H), 7.964 (q, 4H), 8.567 (m, 1H) ppm.

Synthesis of **Zn2py** and **Zn2THF**: The syntheses of these two compounds used a similar procedure. Free base **2** (50 mg, 1.0×10^{-4} mol) was weighted into a 50 mL flask and brought into an anaerobic glove box. Compound **1** was dissolved in 20 mL anhydrous solvent (pyridine or THF) and 110 μL of diethyl zinc solution (1 M in hexane, 1.1×10^{-4} mol) was then added to this solution. The solution was allowed to mix for 4 hours at ambient temperature. The volume of the solution was then reduced to 5 mL and crystals were grown upon diffusion of this solution with hexane. Yields: **Zn2py** 27 mg (41%); **Zn2THF** 25 mg (39%).

Zn2py: High res. ESI MS (positive ion): 567.89 M/z (M^+ - pyridine + H) Analysis Calc. for $ZnC_{37}N_8H_{25}$: C, 68.82; H, 3.91; N, 17.36. Found: C, 68.97; H, 4.27; N, 17.77. ^1H NMR ([D$_6$]DMSO, δ): 0.457 (t, 3H), 0.843 (q, 2H), 6.916 (d, 2H), 6.979 (s, 1H), 7.387 (t, 1H), 7.544 (m, 4H), 7.575 (m, 2H), 7.669 (m, 2H), 7.753 (m, 4H), 7.782 (m, 2H), 7.990 (m, 2H), 8.090 (q, 2H), 8.571 (m, 1H) ppm.

Zn2THF: High res. ESI MS (positive ion): 567.88 M/z (M^+ - THF +H) Analysis Calc. for $ZnC_{36}N_7H_{28}O$: C, 67.69; H, 4.42; N, 15.36. Found: C, 64.63; H, 4.21; N, 15.20. ^1H NMR ([D$_6$]DMSO, δ): 0.450 (t, 3H), 0.843 (q, 2H), 1.760 (p, 4H); 3.601 (t, 4H) 6.912 (d, 2H), 6.996 (d, 1H), 7.522 (t, 1H), 7.562 (m, 2H), 7.680 (m, 2H), 7.735 (m, 2H), 7.829 (m, 2H), 7.992 (q, 2H), 8.088 (q, 2H) ppm.

References:

[1] J. A. Elvidge, J. P. Linstead, *J. Chem. Soc.,* 1952, 5008.

[2] P. F. Clark, J. A. Elvidge, R. P. Linstead, *J. Chem. Soc.,* 1954, 2490; J. A. Elvidge, J. H. Golden, *J. Chem. Soc.,* 1957, 700.