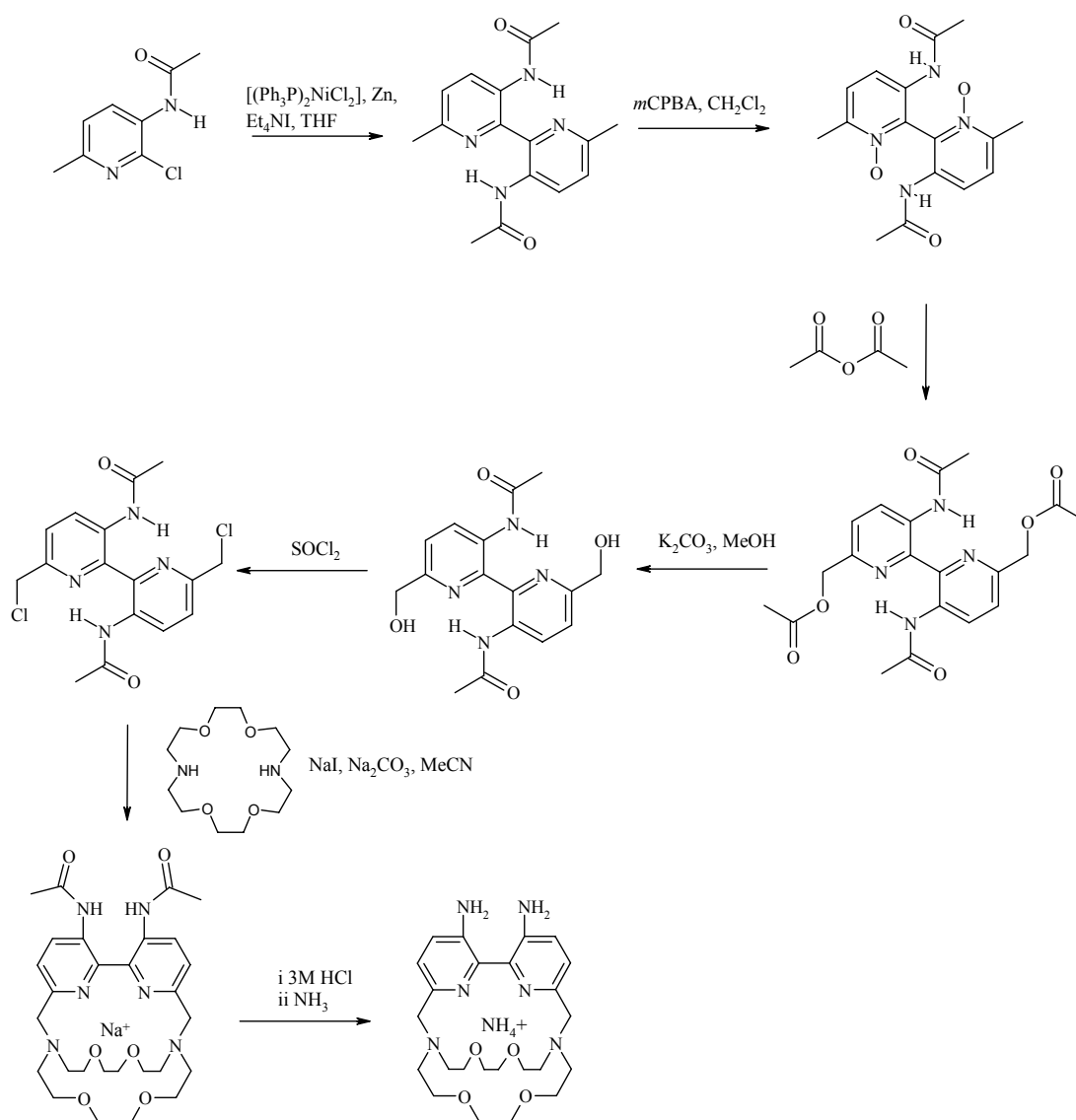


Chem. Commun., SI, Pope & Rice et al: Synthesis



Ammonium cryptate $[1\text{NH}_4]^+$. ^1H NMR (500 MHz, CD_3CN) δ_{H} 7.50, t, $J = 51.5$ Hz, 4H, NH_4^+ ; 7.16, d, $J = 8.2$ Hz, 2H, py; 7.12, d, $J = 8.2$ Hz, 2H, py; 4.46, s, 4H, $-\text{NH}_2$; 3.96, d, 2H, $J = 12.6$ Hz; 3.82, m, 2H, 3.70, m, 2H; 3.58 – 3.37, m overlapping, 12H, 3.16, m, 2H; 2.86, m, 4H, 2.16, m, 4H. ESI-MS 473 M + H^+ , HR ESI-MS found 473.2860 $\text{C}_{24}\text{H}_{37}\text{N}_6\text{O}_4$ requires 473.2870 (error 2.1 ppm).

Barium complex $[1\text{-Ba}](\text{ClO}_4)_2$. ^1H NMR (500 MHz, CD_3CN) δ_{H} 7.39, d, $J = 8.3$ Hz, 2H, py; 7.32, d, $J = 8.3$ Hz, 2H, py; 4.69, s, 4H, $-\text{NH}_2$; 3.92 – 3.53, m overlapping, 18H; 3.42, m, 2H; 3.10, m, 2H; 2.90, m, 2H; 2.82, m, 2H; 2.60, m, 2H. ESI-MS 305 $[1\text{Ba}]^{2+}$.

Barium cyclised complex $[2\text{-Ba}](\text{ClO}_4)_2$. ^1H NMR (500 MHz, CD_3CN) δ_{H} 7.30, d, $J = 8.2$ Hz, 2H, py; 7.14, d, $J = 8.2$ Hz, 2H, py; 5.50, d, $J = 3.6$ Hz, 2H, $-\text{NH}$; 4.33, m, 1H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-$; 4.16, d, $J = 13.6$ Hz, 2H; 3.78 – 3.57, m, overlapping, 14H; 3.28, m, 2H; 3.10, m, 2H; 2.94, m, 2H; 2.78, m, 2H; 2.65, m, 2H; 2.53, m, 2H; 1.77, m, 2H,

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-$; 1.52, m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-$; 0.95, t, $J = 7.3$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-$. ESI-MS 736 $\{[\mathbf{2Ba}]\text{ClO}_4\}^+$, HR ESI-MS found 736.1781 $\text{C}_{28}\text{H}_{42}\text{BaClN}_6\text{O}_8$ requires 763.1799 (error 2.4 ppm).

Crystals suitable for single crystal X-ray studies were obtained by dissolving the ammonium cryptate **1** (3 mg, 4.86×10^{-3} mmol) in water (1 ml) and adding an excess of $\text{Ba}(\text{ClO}_4)_2$ (8.1 mg, 2.4×10^{-2} mmol) and one drop of butanal. After standing overnight dark orange crystals were deposited.

Zinc complex $[\mathbf{1Zn}](\text{CF}_3\text{SO}_3)_2$. ^1H NMR (500 MHz, CD_3CN) δ_{H} 7.55, d, $J = 8.4$ Hz, 2H, py; 7.39, d, $J = 8.4$ Hz, 2H, py; 5.17, s, 4H, $-\text{NH}_2$; 4.00, s, 4H; 3.69, m, 4H; 3.60 – 3.50, m overlapping, 8H; 3.36 – 3.26, m overlapping, 8H; 2.86, m, 4H. ESI-MS 685 $\{[\mathbf{1Zn}]\text{CF}_3\text{SO}_3\}^+$, HR ESI-MS found 685.1603 $\text{C}_{25}\text{H}_{36}\text{F}_3\text{N}_6\text{O}_7\text{SZn}$ requires 685.1604 (error 0.16 ppm).

Zinc cyclised complex $[\mathbf{2Zn}](\text{ClO}_4)_2$. In a typical experiment to the ammonium cryptate $[\mathbf{1NH}_4]\text{I}$ (5 mg, 8.1×10^{-3} mmol) in MeCN (1 ml) was added an excess of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (15 mg, 4.0×10^{-2} mmol) and one drop of butanal. Diethyl ether was then slowly diffused in over 24 hrs. After this time orange crystals were deposited, which were collected by filtration (3 mg, 47 %). ^1H NMR (500 MHz, CD_3CN) δ_{H} 7.48, d, $J = 8.4$ Hz, 2H; 7.22, d, $J = 8.4$ Hz, 2H; 5.91, s, 2H; 4.15, m, 1H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-$; 4.01, m, 4H; 3.74 – 3.32, m overlapping, 18H; 3.15, m, 2H; 2.87, m, 4H; 1.86, m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-$; 1.56, m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-$; 0.97, t, $J = 7.3$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-$. ESI-MS 689 $\{[\mathbf{2Zn}]\text{ClO}_4\}^+$, HR ESI-MS found 689.2018 $\text{C}_{28}\text{H}_{42}\text{ClN}_6\text{O}_8\text{Zn}$ requires 689.2038 (error 2.89 ppm).

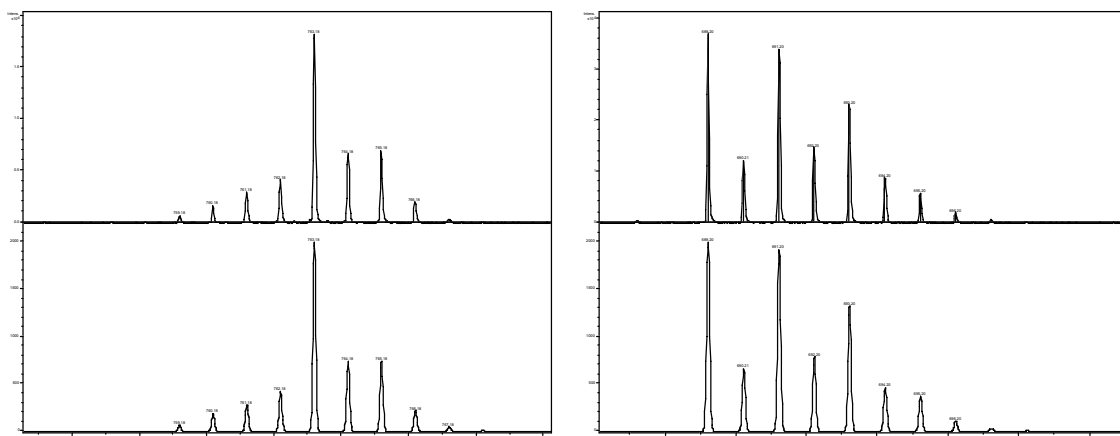


Fig 1: Comparison of theoretical (top) and obtained (bottom) isotope distributions from electrospray mass spectra of Ba^{2+} (left) and Zn^{2+} (right) complexes of **2**.

Additional photophysical data

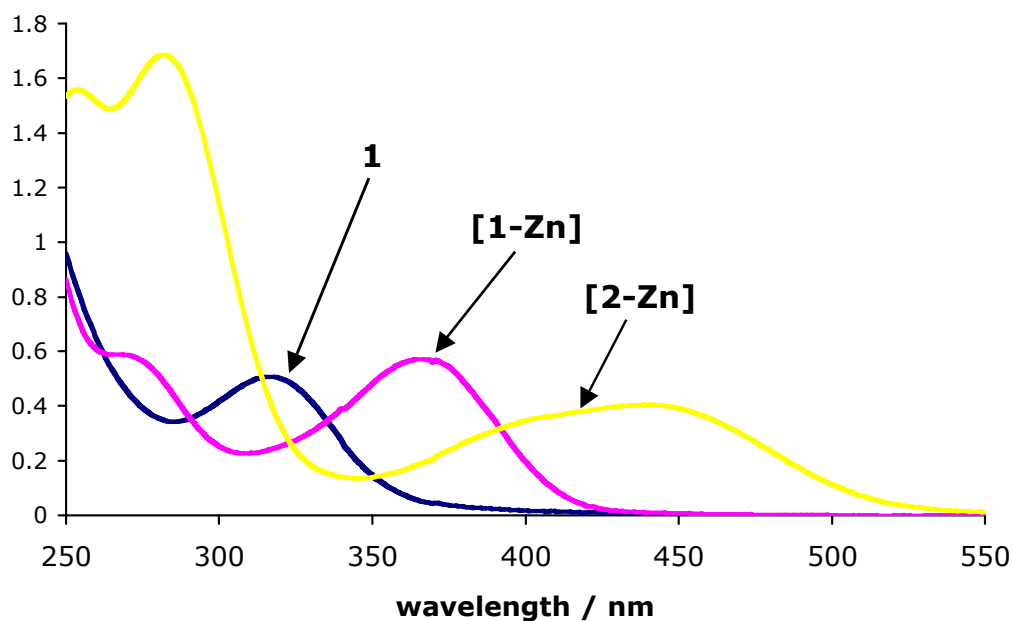


Fig 1: Electronic absorption spectra obtained on aqueous solutions at a concentration of 7×10^{-5} M.

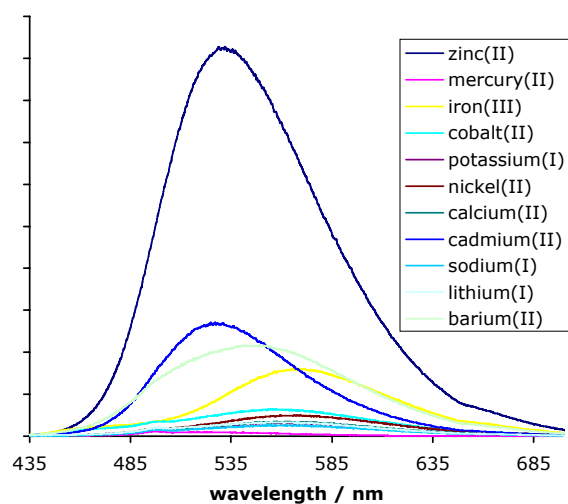


Fig 2: Comparison of emission spectra of **[2-M]ⁿ⁺** in water following exposure of **[1-M]ⁿ⁺** to an excess of butanal ($\lambda_{\text{ex}} = 425$ nm).

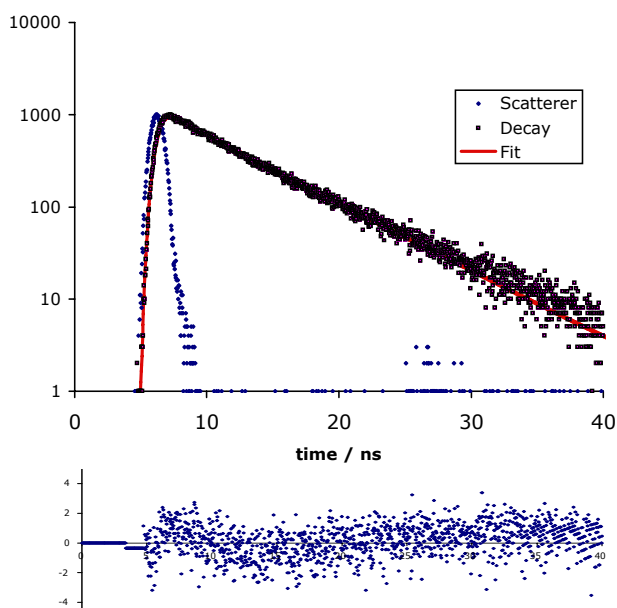


Fig 3: Fitted luminescence lifetime decay (top; $\lambda_{\text{ex}} = 459 \text{ nm}$, $\lambda_{\text{em}} = 530 \text{ nm}$) of $[\mathbf{2}\text{-Zn}]^{2+}$ in water and residual errors following deconvolution with detector response to scattered light, giving $\tau = 5.9 \text{ ns}$.

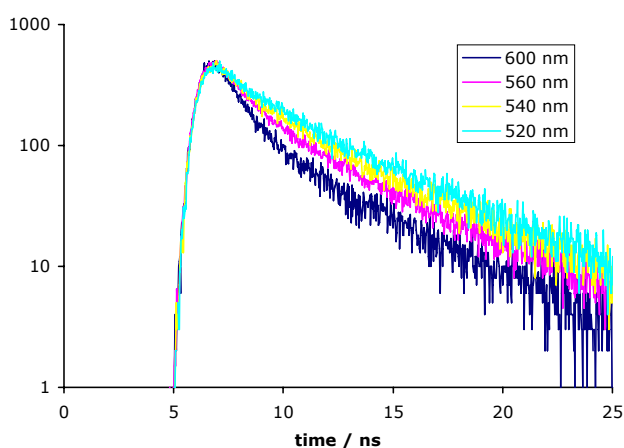


Fig 4: Luminescence lifetime decays ($\lambda_{\text{ex}} = 459 \text{ nm}$) at various detection wavelengths ($\lambda_{\text{em}} = 520, 540, 560$ and 600 nm) of $[\mathbf{2}\text{-M}]^{+/2+}$ in the presence of an ionic mixture of metal ions (4 mM ZnCl_2 in 140 mM NaCl , 4mM KCl , 1.2 mM MgCl_2 , 2.3 mM CaCl_2) at pH 7.4 (HEPES).

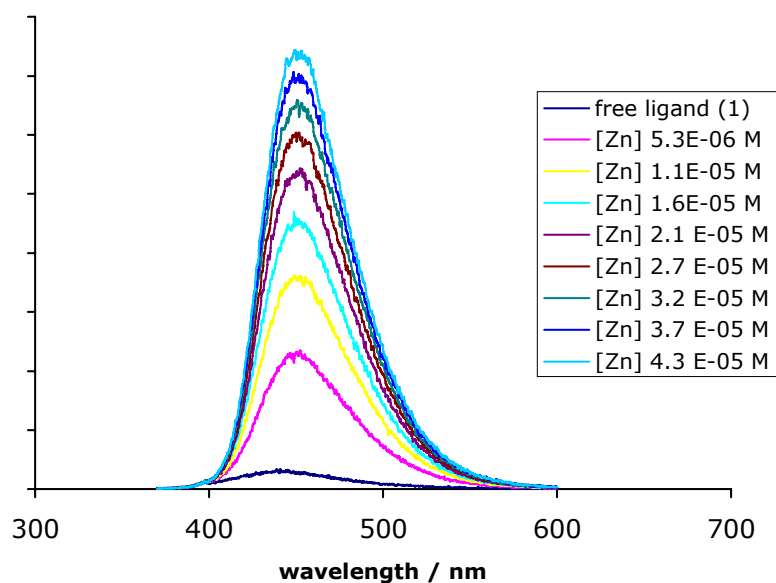


Fig 5: Luminescence titration of $\text{Zn}(\text{ClO}_4)_2$ with the diamino cryptate, **1** (1×10^{-4} M in water). ($\lambda_{\text{ex}} = 350$ nm, emission and excitation monochromator slits 1 nm).

All photophysical data were obtained on a JobinYvon-Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module and a Hamamatsu R5509-73 detector (cooled to -80 °C using a C9940 housing). The pulsed laser source was a pulsed NanoLed configured for 372 or 459 nm output and operating at 500 kHz. Lifetimes were obtained using the JY-Horiba FluoroHub single photon counting module and data fitted by deconvoluting the sample signal with the detector response to scattered light.

X-ray Crystallographic parameters for $[\mathbf{2}\text{-Ba}][\text{ClO}_4]_2$

Empirical formula	$\text{C}_{28}\text{H}_{42}\text{BaN}_6\text{O}_4, 2(\text{ClO}_4)$
Formula weight	862.92
Temperature	150(2)K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 11.9010(4)$ Å, $\alpha = 112.394(2)^\circ$ $b = 12.8430(5)$ Å, $\beta = 94.887(2)^\circ$

Volume	$c = 14.1790(5) \text{ \AA}$, $\gamma = 113.231(2)^\circ$
Z	1769.16(11) $\text{\AA}^3$
Density (calculated)	2
Absorption coefficient	1.620
F(000)	1.341
Crystal size	876
Theta range for data collection	$0.46 \times 0.10 \times 0.03 \text{ mm}^3$
Reflections collected	2.35 to 27.42°
Independent reflections	7946
Goodness-of-fit on F	5561
Final R indices [I > 2sigma(I)]	1.037
R indices (all data)	R1 = 0.0731, wR2 = 0.1746
	R1 = 0.1146, wR2 = 0.1977

Selected bond lengths and bond angles

Bond distances ($\text{\AA}$)			
N1-Ba1	2.911(5)		
N2-Ba1	2.836(5)		
N3-Ba1	2.910(6)		
N4-Ba1	2.908(6)		
O1-Ba1	2.888(5)		
O2-Ba1	2.855(4)		
O3-Ba1	2.823(5)		
O4-Ba1	2.809(5)		
O5-Ba1	2.888(5)		
O9-Ba1	3.006(6)		
Bond angles ($^\circ$)			
N1-Ba1-N2	61.45 (16)	O5-Ba1-N1	81.58(14)
N1-Ba1-N3	115.75(15)	O5-Ba1-N2	74.81(15)
N1-Ba1-N4	177.80(15)	O5-Ba1-N3	87.85(15)
N2-Ba1-N3	54.62(15)	O5-Ba1-N4	97.88(15)
N2-Ba1-N4	116.35(16)	O9-Ba1-N1	88.46(17)
N3-Ba1-N4	62.07(15)	O9-Ba1-N2	139.06(18)
O1-Ba1-N1	59.78(14)	O9-Ba1-N3	138.36(17)
O1-Ba1-N2	69.87(14)	O9-Ba1-N4	93.49(17)
O1-Ba1-N3	91.67(15)	O1-Ba1-O2	58.89(13)
O1-Ba1-N4	119.95(14)	O1-Ba1-O3	142.30(15)
O2-Ba1-N1	118.38(14)	O1-Ba1-O4	104.49(14)
O2-Ba1-N2	101.74(15)	O1-Ba1-O5	136.59(13)
O2-Ba1-N3	71.52(14)	O1-Ba1-O9	71.05(18)
O2-Ba1-N4	61.63(14)	O2-Ba1-O3	105.08(14)
O3-Ba1-N1	119.49(15)	O2-Ba1-O4	132.74(14)
O3-Ba1-N2	146.54(14)	O2-Ba1-O5	155.80(14)
O3-Ba1-N3	116.73(15)	O2-Ba1-O9	67.09(17)
O3-Ba1-N4	62.22(15)	O3-Ba1-O4	59.22(14)
O4-Ba1-N1	60.44(14)	O3-Ba1-O5	72.50(14)
O4-Ba1-N2	113.56(15)	O3-Ba1-O9	71.25(19)
O4-Ba1-N3	155.43(14)	O4-Ba1-O5	67.67(14)
O4-Ba1-N4	121.36(15)	O4-Ba1-O9	65.65(17)
		O5-Ba1-O9	130.86(17)

Data are collected at 150K were collected with a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystem Cooler. Structure solution by direct methods and refinement were by SHELX97 (*SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB] - Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.*) Hydrogen atoms were added at calculated positions and refined using a riding model.

Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 or 1.5 times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

The ClO₄ units occupy three independent sites as a result of some disorder. The first site [Cl(1),O(5)-O(8)] has full occupancy, the second [Cl(2), O(9)-O(12)] has 54.4% occupancy whereas the third is shared by two components [Cl(2a),O(9a)-O(12a)] and [Cl(2b), O(9b)-O(12b)] with a total occupancy of 45.6%. The large atomic displacement parameters observed for some of the oxygen atoms can be attributed to this disorder.