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Electronic Supplementary Information

Sulfate Recognition by a Hexaaza Cryptand Receptor

Pedro Mateus,*[a] Rita Delgado,*[a] Vânia André,[b] M. Teresa Duarte[b]

[a] *Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. da República, 2780–157 Oeiras, Portugal.*

[b] *Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049–001 Lisboa, Portugal.*

Contents: Figures and Tables not shown in the main text **Page**

Table S1 Overall (log $\beta_{H_hL_lA_a}$)[a] association constants for the indicated equilibrium reactions[b] in H_2O/MeOH (50:50 v/v); T = 298.2±0.1 K; I = 0.10±0.01 M in KTsO

Equilibrium reaction	Cl^-	NO_3^-	ClO_4^-	AcO^-	SO_4^{2-}	PO_4^{3-}
$7\ H^+ + pyrr + A \rightleftharpoons H_7pyrr(A)$	–	–	–	–	–	62.14(2)
$6\ H^+ + pyrr + A \rightleftharpoons H_6pyrr(A)$	45.21(2)	45.44(1)	44.86(3)	–	49.32(1)	56.07(3)
$5\ H^+ + pyrr + A \rightleftharpoons H_5pyrr(A)$	–	–	–	39.84(4)	43.12(1)	48.32(9)
$4\ H^+ + pyrr + A \rightleftharpoons H_4pyrr(A)$	–	–	–	33.74(4)	36.14(1)	41.08(6)
$3\ H^+ + pyrr + A \rightleftharpoons H_3pyrr(A)$	–	–	–	26.94(5)	28.28(1)	–
$2\ H^+ + pyrr + A \rightleftharpoons H_2pyrr(A)$	–	–	–	–	20.02(4)	–
$9\ H^+ + pyrr + 2\ A \rightleftharpoons H_9pyrr(A)_2$	–	–	–	–	–	84.92(2)
$8\ H^+ + pyrr + 2\ A \rightleftharpoons H_8pyrr(A)_2$	–	–	–	–	–	79.47(2)
$7\ H^+ + pyrr + 2\ A \rightleftharpoons H_7pyrr(A)_2$	–	–	–	–	–	72.57(2)
$6\ H^+ + pyrr + 2\ A \rightleftharpoons H_6pyrr(A)_2$	–	–	–	–	–	64.45(8)
$13\ H^+ + pyrr + A \rightleftharpoons H_{13}(pyrr)_2(A)$	–	–	–	–	–	109.06(3)

[a] Values in parentheses are standard deviations for the last significant figure. [b] Charges were omitted simplicity.

Table S2 Relevant distances (Å) and angles (°) for $[(H_6pyrr)(SO_4)(H_2O)_3](SO_4)_2 \cdot 9.3H_2O$

Bond lenght/Å					
N(3)–C(2)	1.510(2)	N(17)–C(16)	1.508(2)	N(31)–C(30)	1.513(2)
N(3)–C(4)	1.506(3)	N(17)–C(18)	1.511(2)	N(31)–C(32)	1.503(2)
N(9)–C(5)	1.376(2)	N(23)–C(19)	1.370(3)	N(37)–C(33)	1.376(3)
N(9)–C(8)	1.371(2)	N(23)–C(22)	1.372(2)	N(37)–C(36)	1.377(2)
N(11)–C(10)	1.509(3)	N(25)–C(24)	1.507(2)	N(39)–C(38)	1.506(2)
N(11)–C(12)	1.515(2)	N(25)–C(26)	1.521(2)	N(39)–C(40)	1.507(3)
Bond angles/°					
C(2)–N(3)–C(4)	112.99(14)	C(5)–N(9)–C(8)	109.59(13)	C(10)–N(11)–C(12)	114.56(13)
C(16)–N(17)–C(18)	113.46(12)	C(19)–N(23)–C(22)	109.45(15)	C(24)–N(25)–C(26)	115.01(12)
C(30)–N(31)–C(32)	112.35(13)	C(33)–N(37)–C(36)	108.91(15)	C(38)–N(39)–C(40)	114.00(14)
N(3)–C(2)–C(1)	111.49(13)	N(3)–C(4)–C(5)	112.99(15)	N(9)–C(5)–C(4)	121.88(14)
N(9)–C(5)–C(6)	107.88(15)	C(4)–C(5)–C(6)	130.02(16)	C(5)–C(6)–C(7)	107.13(15)
C(6)–C(7)–C(8)	107.93(15)	N(9)–C(8)–C(7)	107.45(15)	N(9)–C(8)–C(10)	122.17(14)
C(7)–C(8)–C(10)	130.26(16)	N(11)–C(10)–C(8)	110.07(14)	N(11)–C(12)–C(13)	113.19(13)
N(17)–C(16)–C(15)	112.48(14)	N(17)–C(18)–C(19)	114.13(13)	N(23)–C(19)–C(18)	122.38(16)
N(23)–C(19)–C(20)	108.07(15)	C(18)–C(19)–C(20)	129.32(18)	C(19)–C(20)–C(21)	107.32(18)
C(20)–C(21)–C(22)	107.25(16)	N(23)–C(22)–C(21)	107.91(16)	N(23)–C(22)–C(24)	122.44(16)
C(21)–C(22)–C(24)	129.57(16)	N(25)–C(24)–C(22)	112.26(13)	N(25)–C(26)–C(27)	110.66(13)
N(31)–C(30)–C(29)	109.89(14)	N(31)–C(32)–C(33)	113.41(13)	N(37)–C(33)–C(32)	123.13(16)
N(37)–C(33)–C(34)	107.97(16)	C(32)–C(33)–C(34)	128.75(18)	C(33)–C(34)–C(35)	107.80(19)
C(34)–C(35)–C(36)	107.22(16)	N(37)–C(36)–C(35)	108.10(17)	N(37)–C(36)–C(38)	122.58(16)
C(35)–C(36)–C(38)	129.30(16)	N(39)–C(38)–C(36)	110.21(15)	N(39)–C(40)–C(41)	112.20(14)

Table S3 Hydrogen Bond Details for $[(H_6pyrr)(SO_4)(H_2O)_3](SO_4)_2 \cdot 9.3H_2O$.

D–H···A[a]	Symm. Code[b]	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
N(3)–H(3A)···O(9W)	[ ]	0.90(3)	2.04(3)	2.905(2)	161(3)
N(3)–H(3B)···O(203)	[2665]	0.88(2)	1.84(2)	2.680(2)	157(3)
N(9)–H(9)···O(103)	[ ]	0.82(3)	2.05(3)	2.847(2)	162(3)
N(11)–H(11A)···O(13W)	[ ]	0.88(3)	1.92(3)	2.763(2)	160(3)
N(11)–H(11B)···O(303)	[1554]	0.90(2)	1.88(2)	2.756(2)	164(3)
O(13W)–H(11W)···O(1W)	[1445]	0.89(5)	2.29(6)	2.985(3)	134(4)
O(13W)–H(11W)···O(1W)	[2765]	0.89(5)	2.34(5)	3.019(2)	133(4)
O(13W)–H(12W)···O(102)	[ ]	0.83(4)	2.02(4)	2.836(2)	169(4)
O(1W)–H(13W)···O(104)	[1665]	0.76(5)	2.10(5)	2.847(3)	172(5)
N(17)–H(17A)···O(12W)	[ ]	0.84(3)	1.96(3)	2.773(3)	161(3)
N(17)–H(17B)···O(4W)	[1545]	0.92(3)	2.01(3)	2.887(3)	160(2)
O(12W)–H(21W)···O(7W)	[2556]	0.83(4)	1.91(5)	2.711(4)	163(5)
O(12W)–H(22W)···O(102)	[ ]	0.94(6)	1.89(6)	2.735(2)	149(6)
N(23)–H(23N)···O(102)	[ ]	0.87(3)	2.18(3)	3.011(2)	161(2)
O(2W)–H(23W)···O(202)	[ ]	0.90(4)	1.82(4)	2.721(3)	176(4)
O(2W)–H(24W)···O(302)	[2776]	0.90(5)	1.85(4)	2.721(3)	163(3)
N(25)–H(25A)···O(303)	[2656]	0.92	1.85	2.766(2)	171
N(25)–H(25B)···O(104)	[ ]	0.92	1.83	2.744(2)	177
N(31)–H(31A)···O(101)	[ ]	0.88(3)	2.02(3)	2.884(2)	166(2)
N(31)–H(31B)···O(204)	[1445]	0.87(3)	1.90(3)	2.759(2)	167(3)
O(3W)–H(31W)···O(10W)	[1445]	0.75(5)	2.01(5)	2.734(3)	163(5)
O(3W)–H(32W)···O(103)	[2555]	0.80(4)	2.04(4)	2.828(2)	167(3)
N(37)–H(37)···O(101)	[ ]	0.86(3)	2.24(3)	3.006(2)	149(3)
N(39)–H(39A)···O(301)	[2666]	0.96(3)	1.90(2)	2.752(3)	146(2)
N(39)–H(39B)···O(3W)	[2555]	0.90(2)	1.87(2)	2.770(2)	174(3)
O(9W)–H(91W)··· O(204)	[1445]	0.84(3)	1.89(3)	2.721(2)	178(4)
C(4) –H(4A)···O(104)	[ ]	0.99	2.44	3.396(2)	161
C(18)–H(18A)···O(13W)	[ ]	0.99	2.43	3.394(2)	163
C(18)–H(18B)···O(203)	[1545]	0.99	2.54	3.528(3)	174
C(38)–H(38A)···O(12W)	[ ]	0.99	2.52	3.504(3)	176
C(16)–H(48C)···O(202)	[1545]	0.99	2.53	3.405(3)	147
C(51)–H(51B)···O(204)	[1445]	0.99	2.59	3.472(3)	148
C(56)–H(56A)···O(303)	[2656]	0.99	2.49	3.456(3)	166

[a] D = O, N or C; A = O;[b] [2665] = 1-*x*,1-*y*,-*z*; [1554] = *x*,*y*,-1+*z*; [1545] = *x*,-1+*y*,*z*; [2556] = -*x*,-*y*,1-*z*; [2656] = 1-*x*,-*y*,1-*z*; [1445] = -1+*x*,-1+*y*,*z*; [2555] = -*x*,-*y*,-*z*; [2666] = 1-*x*,1-*y*,1-*z*; [2765] = 2-*x*,1-*y*,-*z*; [1665] = 1+*x*,1+*y*,*z*; [2776] = 2-*x*,2-*y*,1-*z*; [ ] = *x*,*y*,*z*.

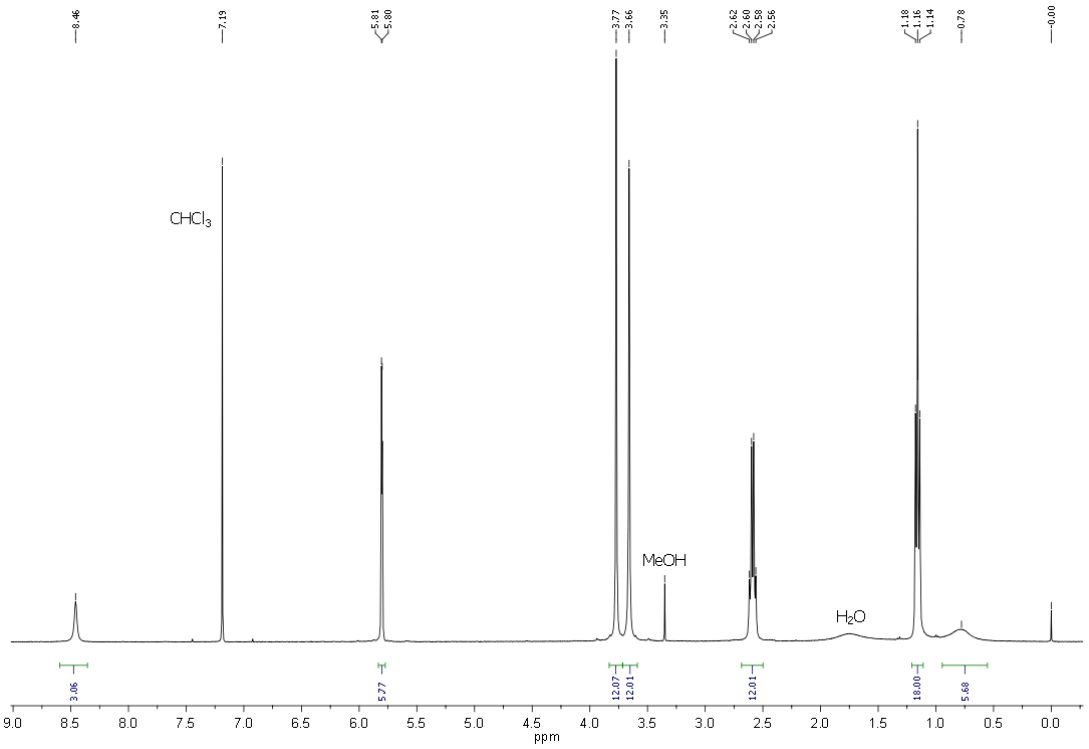

Fig. S1 ^{1}H spectrum of pyrr in $CDCl_3$.

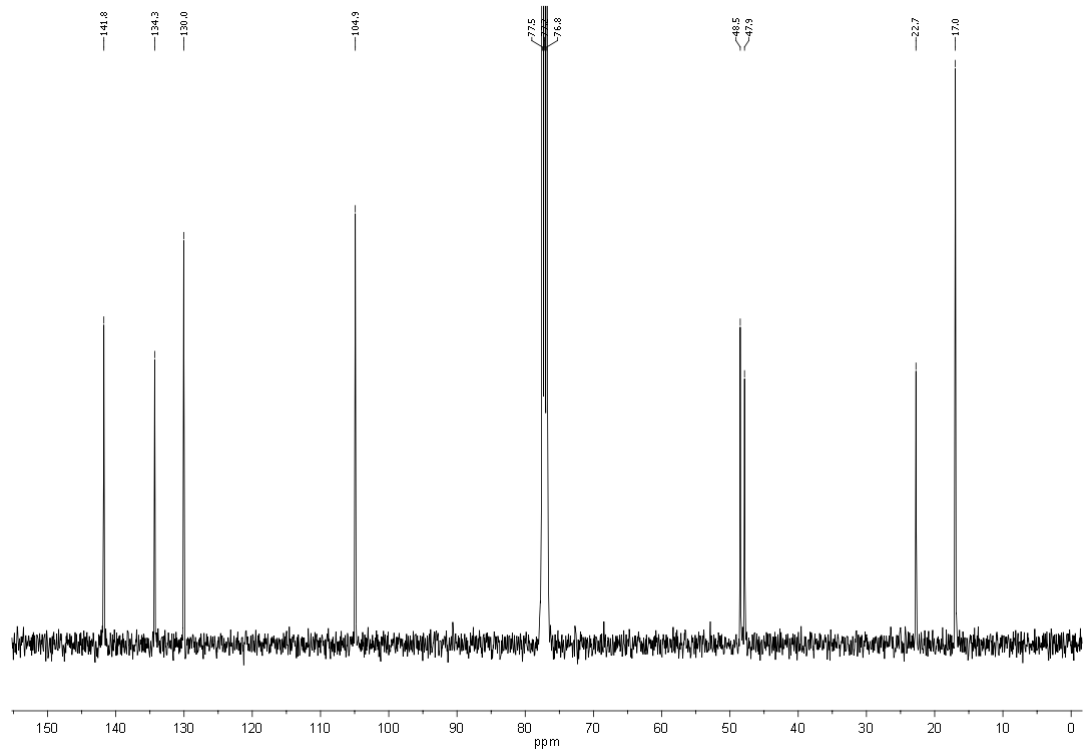

Fig. S2 ^{13}C NMR spectrum of pyrr in $CDCl_3$.

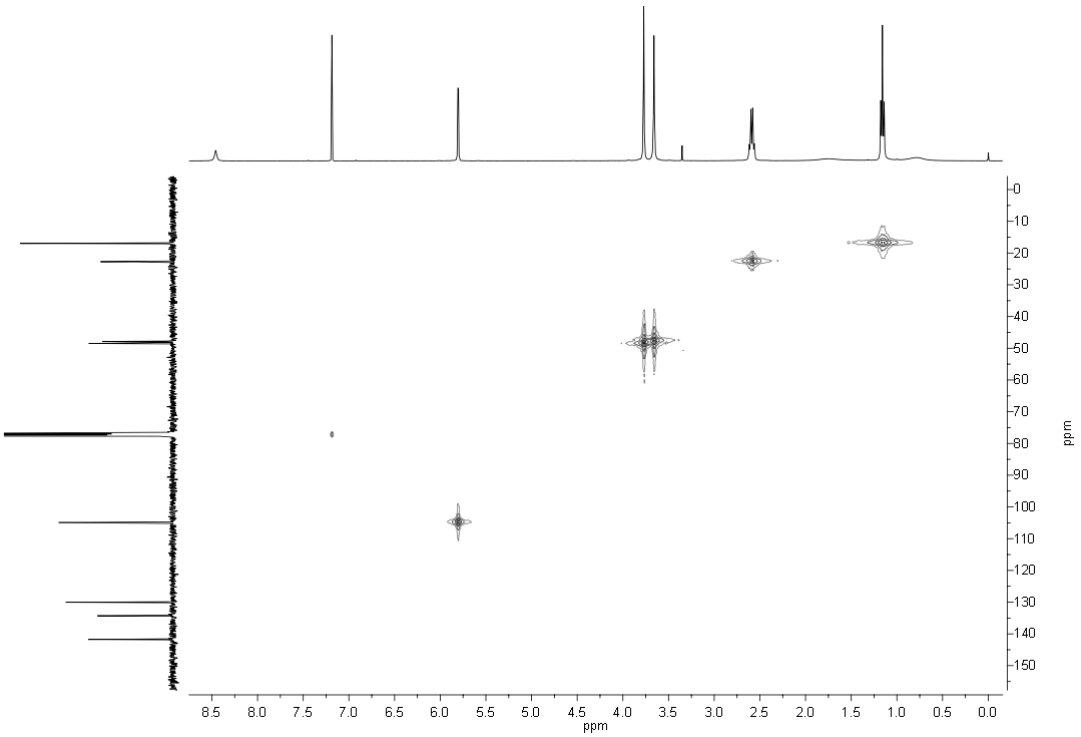

Fig. S3 HMQC spectrum of pyrr in $CDCl_3$.

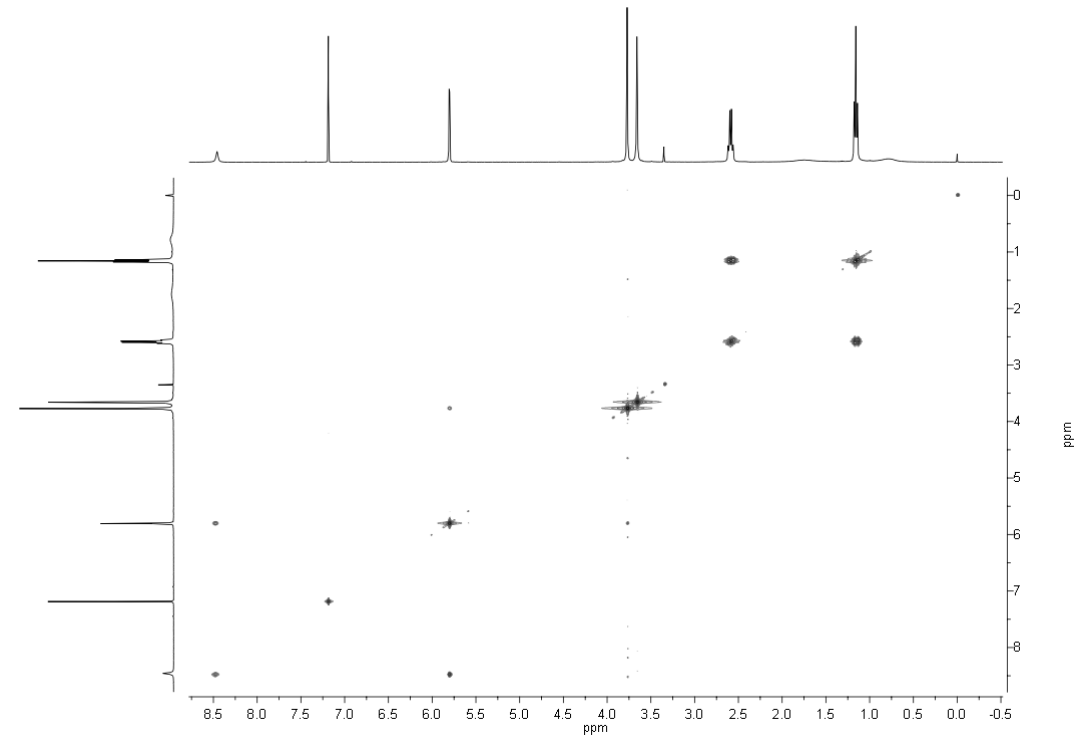

Fig. S4 COSY spectrum of pyrr in $CDCl_3$.

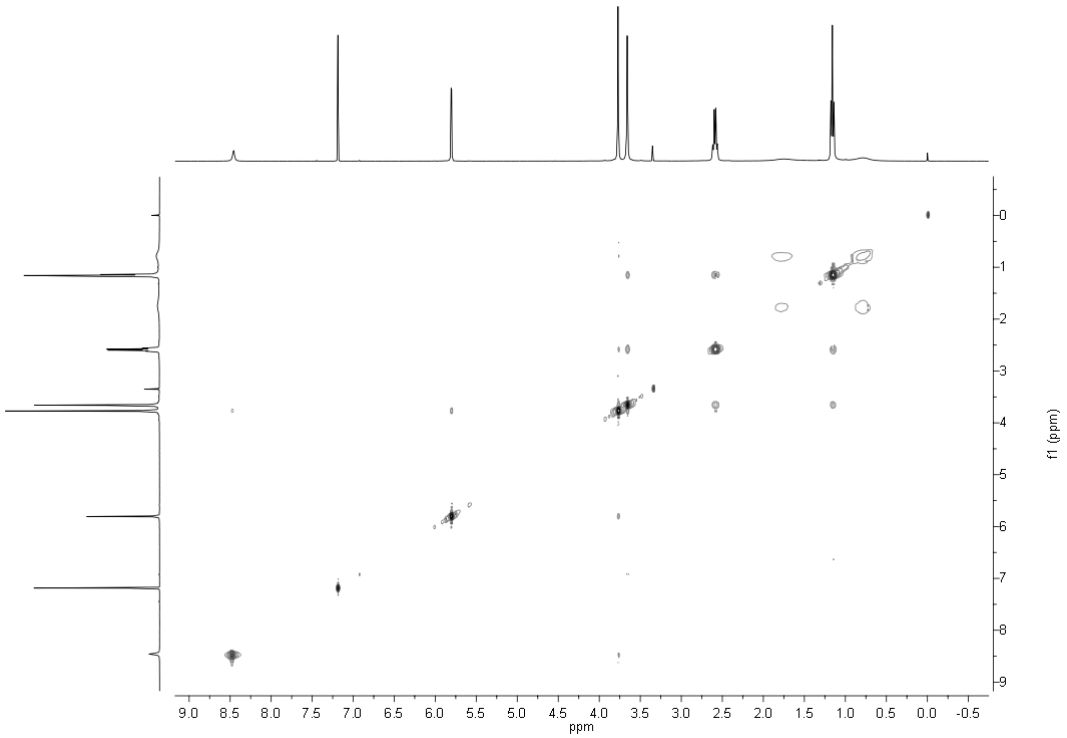

Fig. S5 NOESY spectrum of pyrr in $CDCl_3$.