Electronic Supplementary Information for Dalton Transactions

Design of base metal extractants. Part 1. Inter-ligand hydrogen bonding in the assembly of *pseudo*-macrocyclic bis(aminosulfonamidato)M(II) complexes.

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N-[*N*-(2-Ethylhexyl)-2-aminoethyl]-4-methylbenzenesulfonamide (**4**) was similarly prepared from **1** and 2-ethylhexanal as a colourless oil (88%), (Found: C, 62.3; H, 10.0; N, 8.6. Calc. for $C_{17}H_{30}N_2O_2S$: C, 62.39; H, 9.47; N, 8.56), δ_H ($CDCl_3$, 360 MHz): 0.84 (t, 3 H, J 7.2, C*H*$_3$), 0.92 (t, 3 H, J 7.0, C*H*$_3$), 1.27 (m, 8 H, C*H*$_2$), 2.35 (d, 2 H, J 5.6, C*H*$_2$), 2.45 (s, 3 H, C*H*$_3$), 2.69 (t, 2 H, J 5.6, C*H*$_2$), 3.00 (t, 2 H, J 5.6, C*H*$_2$), 7.32 (d, 2 H, J 7.9, Ar C*H*), 7.78 (d, 2 H, J 8.3, Ar C*H*), δ_C ($CDCl_3$ 63 MHz): 11 (*C*H$_3$), 14 (*C*H$_3$), 21 (*C*H$_3$), 23 (*C*H$_2$), 24 (*C*H$_2$), 29 (*C*H$_2$), 31 (*C*H$_2$), 39 (*C*H), 42 (*C*H$_2$), 52 (*C*H$_2$), 127 (2 C, Ar *C*H), 129 (2 C, Ar *C*H), 137 (Ar *C*), 143 (Ar *C*), IR (NaCl)/cm^{-1}: 661s, 815s, 1034m, 1094s, 1158s, 1304s, 1458s, 1599m, 2873s, 2958s, 3286m, ESI MS, *m/z* 327 (MH^+, 100.0%)

N-(3-Aminopropyl)-4-*tert*-butylbenzenesulfonamide (**6**) was obtained from 1,3-diaminopropane by the procedure used for **2** as a white crystalline solid after recrystallisation from water and drying *in vacuo* (24%), mp 226°C (Found: C, 50.4; H, 6.7; N, 12.8. Calc. for $C_{13}H_{22}N_2O_2S$: C, 50.45; H, 6.59; N, 13.07%), δ_H ($CDCl_3$, 200 MHz): 1.30 (s, 9 H, C*H*$_3$), 1.59 (tt, 2 H, J 6.2, C*H*$_2$), 2.80 (t, 2 H, J 6.1, C*H*$_2$), 3.07 (t, 2 H, J 6.3, C*H*$_2$), 7.50 (d, 2 H, J 8.8, Ar C*H*), 7.77 (d, 2 H, J 8.8, Ar C*H*), δ_C (DMSO-d_6, 63 MHz): 30 (*C*H$_2$), 31 (3 C, *C*H$_3$), 35 (Ar *C*(CH$_3$)$_3$), 38 (*C*H$_2$), 38 (*C*H$_2$), 126 (2 C, Ar *C*H), 126 (2 C, Ar *C*H), 138 (Ar *C*), 155 (Ar *C*), IR (KBr disc)/cm^{-1}: 2961s, 1596m, 1542w, 1465m, 1329s, 1156s, FAB MS, *m/z* 271 (MH$^+$, 100.0%).

N-(*N*-Benzyl-3-aminopropyl)-4-methylbenzenesulfonamide (**7**) was obtained by the procedure described for **3** from benzaldehyde and **5** as a white crystalline solid after recrystallisation from ethanol (38%), mp 82-84°C (Found: C, 63.9; H, 6.8; N, 8.8. Calc. for $C_{17}H_{22}N_2O_2S$: C, 64.10; H, 6.96; N, 8.80%), δ_H ($CDCl_3$, 200 MHz) 1.61 (tt, 2 H, J 6.0, C*H*$_2$), 2.40 (s, 3 H, C*H*$_3$), 2.65 (t, 2 H, J 5.9, C*H*$_2$), 3.03 (t, 2 H, J 6.0, C*H*$_2$), 3.69 (s, 2 H, C*H*$_2$), 7.27 (m, 7 H, Ar C*H*), 7.70 (d, 2 H, J 8.3, Ar C*H*), δ_C ($CDCl_3$, 50 MHz) 21 (*C*H$_3$), 28 (*C*H$_2$), 43 (*C*H$_2$), 48 (*C*H$_2$), 54 (*C*H$_2$), 127 (2 C, Ar *C*H), 127 (Ar *C*H), 128 (2 C, Ar *C*H), 128 (2 C, Ar *C*H), 129 (2 C, Ar *C*H), 137 (Ar *C*), 140 (Ar *C*), 143 (Ar *C*), IR (KBr disc)/cm^{-1}: 1156s, 1185w, 1326s, 1454m, 1477m, 1497m, 1598m, 2832s, 2873w, 2933w, 2964w, 3059m, 3467w, FAB MS, *m/z* 319 (MH$^+$, 100%).

N-[*N*-(2-Ethylhexyl)-3-aminopropyl]-4-methylbenzenesulfonamide (**8**) was obtained by the procedure described for **3** from 2-ethylhexanal and **5** as a colourless oil (66%),

(Found: C, 63.5; H, 9.6; N, 8.2. Calc. for $C_{18}H_{32}N_2O_2S$: C, 63.49; H, 9.47; N, 8.22%), δ_H ($CDCl_3$, 360 MHz): 0.90 (t, 3 H, J 7.3, C*H*$_3$), 0.93 (t, 3 H, J 6.7, C*H*$_3$), 1.62 (t, 2 H, J 5.5, C*H*$_2$), 2.67 (t, 2 H, J 5.6, C*H*$_2$), 2.45 (s, 5 H, C*H*$_2$, C*H*$_3$), 3.08 (t, 2 H, J 5.7, C*H*$_2$), 5.90 (m, 9 H, C*H*, 3 x C*H*$_2$), 7.32 (d, 2 H, J 8.1, Ar C*H*), 7.76 (d, 2 H, J 8.1, Ar C*H*), δ_C ($CDCl_3$, 90 MHz): 11 (*C*H$_3$), 14 (*C*H$_3$), 21 (*C*H$_3$), 23 (*C*H$_2$), 24 (*C*H$_2$), 29 (*C*H$_2$), 31 (*C*H$_2$), 39 (*C*H), 42 (*C*H$_2$), 52 (*C*H$_2$), 127 (2 C, Ar *C*H), 129 (2 C, Ar *C*H), 137 (Ar *C*), 143 (Ar *C*), IR (NaCl)/cm^{-1}: 515s, 659s, 1036m, 1095s, 1164s, 1328s, 1458s, 1496m, 1599m, 2362w, 2873s, 2928s, 3292m, ESI MS, m/z 341 (MH^+, 100.0%).

N-(*N*-Butyl-3-aminopropyl)-4-methylbenzenesulfonamide (**9**) was obtained by the procedure described for **3** from *n*-butanal and **5** as a sticky white solid which proved difficult to purify. Crystals suitable for X-ray structure determination separated directly from the oil obtained after evaporation of methanol for 5 days, δ_H ($CDCl_3$, 250 MHz): 0.91 (t, 3 H, J 7.1, C*H*$_3$), 1.46 (m, 6 H, C*H*$_2$), 2.41 (s, 3 H, C*H*$_3$), 2.53 (t, 2 H, J 7.0, C*H*$_2$), 2.68 (t, 2 H, J 5.8, 2 H, C*H*$_2$), 3.05 (t, 2 H, J 5.9, C*H*$_2$), 7.29 (d, 2 H, J 8.0, Ar C*H*), 7.73 (d, 2 H, J 8.3, Ar C*H*), EI MS, m/z 285 (MH^+, 100.0%).

N-(2-Aminophenyl)-4-methylbenzenesulfonamide (**10**) was prepared by the method of Cheng *et al.*[8]

N-(2-Aminophenyl)-4-*tert*-butylbenzenesulfonamide (**11**) was prepared by an adaptation of the method for **10.** A solution of 4-*tert*-butylbenzenesulfonyl chloride (5.35 g, 23 mmol) in pyridine (50 cm^3) was added dropwise to a solution of 1,2-diaminobenzene

(7.25 g, 67 mmol) in pyridine (100 cm^3) over 8 hours. The mixture was quenched with hydrochloric acid (15% aq, 300 cm^3), poured onto ice (500 g), and the resulting pale brown precipitate collected, dried and recrystallised from ethanol (100 cm^3) to give **11** as a white crystalline solid (3.30 g, 47%), mp 135-136°C (Found: C, 63.2; H, 6.6; N, 9.2. Calc. for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.20 %), δ_H ($CDCl_3$, 200 MHz): 1.31 (s, 9 H, C*H*$_3$), 4.02 (s, 2 H, N*H*$_2$), 6.49-6.52 (m, 2 H, Ar C*H*), 6.69 (s, 1 H, N*H*), 6.70-6.73 (m, 1 H, Ar C*H*), 6.98-7.05 (m, 1 H, Ar C*H*), 7.44 (d, 2 H, J 8.8, Ar C*H*), 7.66 (d, 2 H, J 8.8, Ar C*H*), δ_C ($CDCl_3$, 63 MHz): 31 (3C, *C*H$_3$), 35 (Ar *C*(CH$_3$)$_3$), 117 (Ar, *C*H), 118 (Ar, *C*H), 121 (Ar *C*), 126 (Ar, *C*H), 127 (Ar, *C*H), 128 (Ar, *C*H), 129 (Ar, *C*H), 136 (Ar *C*), 144 (Ar *C*), 157 (Ar *C*), IR (KBr disc)/cm^{-1}: 3465m, 3387s, 2965s, 2869m, 1625s, 1597s, 1464s, 1324s, FAB MS, *m/z* 305 (MH^+, 100.0%).

Bis[*N*-(2-aminoethyl)-4-methylbenzenesulfonamidato]cobalt(II) (**14**) was prepared using the same procedure as for **13** from cobalt(II) acetate tetrahydrate as a brown crystalline solid (46%), (Found: C, 44.5; H, 5.4; N, 11.4. Calc. for $C_{18}H_{26}N_4CoO_4S_2$: C, 44.53; H, 5.40; N, 11.54%), IR (KBr disc)/cm^{-1}: 1158m, 1372w, 1583m, 1626m, 2966w, 292w, 3683w, 3289s, 3448m. FAB MS, *m/z* 486 (MH^+, 54.1%).

Bis[*N*-(2-aminoethyl)-4-*tert*-butylbenzenesulfonamidato]copper(II) (**16**) was prepared from **2** in a similar manner to **15** as a purple crystalline solid (59%). Crystals suitable for X-ray structure determination were obtained by the diffusion of diethyl ether into a concentrated solution in methanol, (Found: C, 50.2; H, 6.8; N, 9.6. Calc. for

$C_{24}H_{38}N_4CuO_4S_2$: C, 50.02; H, 7.00; N, 9.72%), IR (KBr disc)/cm^{-1}: 835m, 981m, 1129m, 1252s, 1655m, 1686m, 2986m, 3632m, ESI MS, *m/z* 574 (MH^+, 65.0%).

Bis{*N*-[*N*-(2-ethylhexyl)-2-aminoethyl]-4-methylbenzenesulfonamidato}cobalt(II) (**18**) was prepared in a similar manner to **17** from cobalt(II) acetate tetrahydrate as a purple solid (32%), IR (KBr disc)/cm^{-1}: 668w, 1161w, 1332w, 1412w, 1560s, 2361w, 2961w, 3464m, FAB MS, *m/z* 709 (MH^+, 96.0%), HRMS m/z calc. for $C_{34}H_{59}N_4CoO_4S_2$ 710.3309, found 710.3314.

Bis{*N*-[*N*-(2-ethylhexyl)-2-aminoethyl]-4-methylbenzenesulfonamidato}copper(II) (**19**) was prepared in a similar manner to **17** from copper(II) acetate monohydrate as a purple solid (51%), (Found: C, 57.10; H, 8.14; N, 7.80. Calc. for $C_{34}H_{58}N_4CuO_4S_2$: C, 57.15; H, 8.18; N, 7.84%). IR data (KBr disc)/cm^{-1}: 667s, 1136s, 1274m, 1558s, 1685m, 2343m, 2362m, 2929m, 3447m. FAB MS, *m/z* 714 (MH^+, 10.1%).

Bis[*N*-(2-aminopropyl)-4-methylbenzenesulfonamidato]cobalt(II) (**20**) was prepared in a similar manner to **15** from **5** and cobalt(II) acetate tetrahydrate, collecting the purple crystals after 3 days, washing with methanol (3 x 5 cm^3) and drying *in vacuo* (36%), (Found: C, 46.5; H, 6.1; N, 10.6. Calc. for $C_{20}H_{30}N_4CoO_4S_2$: C, 46.78; H, 5.89; N, 10.91%), IR (KBr disc)/cm^{-1}: 709w, 1134s, 1684w, 3332m, 2929w, 2878w, 2846w, ESI MS, *m/z* 514 (MH^+, 6.3%).

Bis[*N*-(2-aminopropyl)-4-methylbenzenesulfonamidato]zinc(II) (**23**) was prepared by the procedure for **20** using zinc(II) acetate dihydrate as white crystals (38%), (Found: C, 46.1; H, 5.4; N, 10.8. Calc. for $C_{20}H_{30}N_4O_4S_2Zn$: C, 46.20; H, 5.82; N, 10.78%), IR (KBr disc)/cm^{-1}: 709w, 1173m, 1590m, 1653w 2848w, 2884w, 2934w, 3340m, ESI MS, *m/z* 519 (MH^+, 10.9%).

Bis[*N*-(2-aminophenyl)-4-methylbenzenesulfonamidato]nickel(II) (**25**) was prepared by the procedure for **15** from **10** and nickel(II) acetate tetrahydrate as a pale green solid (93%), (Found: C, 53.7; H, 4.4; N, 9.6. Calc. for $C_{26}H_{26}N_4NiO_4S_2$: C, 53.63; H, 4.50; N, 9.62%), IR (KBr disc)/cm^{-1}: 706w, 1163w, 1493s, 1599m, 3025w, 3448m, FAB MS, *m/z* 581 (MH^+, 7.2%).

Bis[*N*-(2-aminophenyl)-4-methylbenzenesulfonamidato]zinc(II) (**27**) was prepared as described for **25** using zinc(II) acetate dihydrate as white crystals (45%), (Found: C, 52.9; H, 4.56; N, 9.5. Calc. for $C_{26}H_{26}N_4O_4S_2Zn$: C, 53.11; H, 4.46; N, 9.53%), IR (KBr disc)/cm^{-1}: 707w, 1160w, 1197w, 1264s, 1306s, 1542w, 1601m, 3035w, 3065w, 3259s, 3335s, FAB MS, *m/z* 587 (MH^+, 5.7%).

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List of all hydrogen bonds observed in crystal structures with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
1					
N3A-H3A	0.997	1.856	168.92	2.841	N6B
N6A-H6AA	0.996	2.14	154.58	3.07	O1B [x-1, y+1, z]
N6A-H6AA	0.996	2.884	174.18	3.875	S2B [x-1, y+1, z]
N3B-H3B	0.978	1.848	176.05	2.824	N6A [x, y-1, z]
N6B-H6AB	0.974	2.159	165.09	3.11	O1A [x+1, y, z]
N6B-H6BB	0.951	2.284	153.28	3.163	O2B [x, y+1, z]
5					
N3A-H3A	0.951	1.959	173.98	2.906	N7A [-x+1, y+1/2, -z+1/2]
N7A-H7AA	0.945	2.441	134.42	3.175	O1A [x, y-1, z]
N7A-H7BA	0.867	2.414	165.41	3.261	O2A [-x+1, -y, -z]
7					
N3A-H3A	0.984	1.981	175.56	2.964	N7A [-x+1, -y+2, z-1/2]
9					
N7A-H7A	0.846	2.404	143.32	3.124	O1A [-x+1, -y+1, -z+1]
N3A-H3A	0.821	2.159	166.76	2.964	N7A [-x+1, y-1/2, -z+3/2]
10					
N3A-H3A	0.755	2.066	174.34	2.819	O2A [-x+1, y-1/2, -z+1]
N6A-H6BA	0.869	2.516	126.6	3.114	O1A
N6A-H6BA	0.869	2.966	126.12	3.549	S2A
N3B-H3B	0.672	2.274	174.96	2.944	O1B [-x+1, y+1/2, -z]
N6B-H6BB	0.908	2.404	145.65	3.194	O1B [-x+1, y-1/2, -z]
N6B-H6BB	0.908	2.563	125.36	3.176	O2B
N6B-H6BB	0.908	3.02	124.67	3.614	S2B
12					
N6A-H6A1	0.91	2.143	163.84	3.028	O1M [-x+2, -y-1, -z]
N6A-H6A2	0.91	2.32	125.4	2.942	O1A [x, -y-3/2, z+1/2]
N6B-H6B1	0.91	2.242	144.22	3.027	O1B [x, -y-3/2, z+1/2]
N6B-H6B1	0.91	3.015	118.19	3.537	S2B [x, -y-3/2, z+1/2]
N6B-H6B2	0.91	2.153	156.23	3.009	O2A [x, -y-3/2, z+1/2]
N6B-H6B2	0.91	2.884	155.39	3.731	S2A [x, -y-3/2, z+1/2]
N6C-H6C1	0.91	2.167	141.7	2.935	O1C [x, -y-1/2, z+1/2]
N6C-H6C2	0.91	1.995	163.34	2.878	O2M
N6D-H6D1	0.91	2.305	157.35	3.165	O2C [x, -y-1/2, z+1/2]
N6D-H6D1	0.91	2.989	160.35	3.858	S2C [x, -y-1/2, z+1/2]
N6D-H6D2	0.91	2.2	155.33	3.051	O2D [x, -y-1/2, z+1/2]
N6D-H6D2	0.91	2.93	129.83	3.582	S2D [x, -y-1/2, z+1/2]
O1M-H1M	0.83	2.385	134.8	3.028	N6A [-x+2, -y-1, -z]
O2M-H2M	0.83	1.967	158.06	2.755	O2A [-x+2, -y-1, -z]
13					
N6A-H6AA	0.91	2.197	122.87	2.798	O1A [-x+1, -y, -z]
N6A-H6AA	0.91	2.325	143.27	3.103	O1A [x, y-1, z]
N6A-H6BA	0.91	2.094	156.16	2.95	O2A [-x+1, y-1/2, -z-1/2]
16					
N6A-H6AA	0.92	2.033	165.28	2.932	O2B [x+1, y, z]
N6A-H6BA	0.92	2.078	138.65	2.834	O1B

N6A-H6BA	0.92	2.936	111.36	3.381	S2B
N6B-H6AB	0.92	2.213	119.69	2.786	O1A
N6B-H6AB	0.92	2.83	116.7	3.346	S2A
N6B-H6BB	0.92	2.075	163.78	2.969	O2A [x-1, y, z]