Metal organic anion receptors: *trans*-functionalised platinum complexes

Matthew G. Fisher,^a Philip A. Gale^{*,a}, Mark E. Light^a and Stephen J. Loeb^{*,b}

Electronic supplementary information



Figure S1¹H NMR spectrum of complex 2 in DMSO-d₆



Figure S2 ¹³C NMR spectrum (top) and DEPT 135 (bottom) of complex 2 in DMSO- d_6



Figure S3 ¹H NMR titration with tetrabutylammonium chloride in DMSO- d_6 . K₁ = 2350 Error = 0.5% K₂ = 450 Error = 0.4%



Figure S4 ¹H NMR titration with tetrabutylammonium bromide in DMSO- d_6 . K₁ = 942 Error = 1% K₂ = 131 Error = 4.9%



Figure S5 ¹H NMR titration with tetrabutylammonium iodide in DMSO- d_6 . K₁ = 161 Error = 1.5% K₂ = 16 Error = 10.4%



Figure S6 - NMR titration stack plot for complex 2 with (TBA)₂SO₄ in DMSO-d₆.



Trans-[bis(8-(n-butylurea)isoquinoline)bispyridineplatinum(II)]

tetrafluoroborate (2): Trans-dichlorobis(pyridine)platinum(II) (106.5mg, 0.25mmol) was dissolved in nitromethane (~20ml) with silver tetrafluoroborate (107.07mg, 0.55mmol). The solution was refluxed in darkness for 2.5hrs at 111°C. The refluxing solution was then exposed to light for 0.5hrs and hot filtered through microfibre paper into a solution of 8-(*n*-butylurea)isoquinoline (114.64mg, 0.5mmol) in nitromethane (~20ml). The solution was refluxed for a further 3hrs at 111°C. The resulting solution was filtered through a microfibre filter paper while hot reduced to minimum volume, and the complex precipitated with diethyl ether and collected by filtration. The crude product was triturated in acetonitrile and then in hot diethyl ether and filtered yielding a green powder which was washed with dichloromethane (121mg, 48%). ¹H-NMR $(300 \text{MHz}, \text{DMSO-}d_6) \delta 0.95 \text{ (t, 6H)}, \delta 1.38 \text{ (m, 4H)}, \delta 1.5 \text{ (m, 4H)}, \delta 3.16 \text{ (m, 4H)},$ δ6.57 (t, 2H), δ7.6 (t, 4H), δ7.76 (t, 4H), δ7.91 (t, 2H), δ8.04 (t, 4H), δ8.79 (d, 2H), δ8.88 (s, 2H), δ9.03 (d, 4H), δ9.73 (s, 2H). ¹³C-NMR (75MHz, DMSO-d₆) δ13.7 (CH₃), δ 19.6 (CH₂), δ 31.8 (CH₂), δ 39.3 (CH₂), δ 121.9 (CH), δ 123.5 (C), δ 124.4 (CH), *δ*127.5 (CH), *δ*134.7 (CH), *δ*136.2 (C), *δ*137.8 (C), *δ*141.0 (CH), *δ*141.7 (CH), δ 151.9 (CH), δ 153.8 (CH), δ 155.5 (C) One carbon resonance is missing. This is not one of the quaternary carbons and we presume that two of the aromatic CH carbons have coincident chemical shifts. MS (ESI+) m/z Calcd: 1013.5 Found: 420.4 (M- $(2BF_4)^{2+}$, 926.8 (M-BF₄)⁺. Anal. Calcd. for C₃₈H₄₄B₂F₈N₈O₂Pt+CH₂Cl₂: C=42.6%, H=4.2%, N=10.2% Found: C=42.8%, H=4.1%, N=10.5%.

D–H···A	<i>d</i> (<i>D</i> –H)	<i>d</i> (H··· <i>A</i>)	$d(D \cdots A)$	$\angle(DHA)$	
N4-H4Br21 ⁱⁱ	0.88	2.71	3.474(4)	145	
C1–H1Br21 ⁱⁱ	0.95	2.87	3.775(5)	159	
C5-H5Br21	0.95	2.86	3.766(5)	160	
C9–H9Br21 ⁱ	0.95	2.84	3.751(4)	161	
C14–H14Br21 ⁱⁱ	0.95	2.76	3.654(4)	157	

Table S1 Hydrogen bond distances (Å) and angles (°) in the bromide complex of 2.

Symmetry transformations used to generate equivalent atoms: (i) 1/2-x,-1/2+y,1/2-z, (ii) 1-x,-y,-z

D–H···A	<i>d</i> (<i>D</i> –H)	<i>d</i> (H··· <i>A</i>)	$d(D \cdots A)$	$\angle(DHA)$
N4–H904O4 ⁱ	0.88	2.31	3.102(7)	150
N5-H905O4 ⁱ	0.88	2.10	2.933(6)	158
N4–H904O5 ⁱ	0.88	2.42	3.108(6)	136
N8-H908O6 ⁱ	0.88	2.10	2.895(6)	149
N11-H11AO6	0.88	1.95	2.771(6)	154
N12B-H12BO6	0.88	2.15	2.915(7)	144
N7-H907O7 ⁱ	0.88	2.18	3.035(6)	164
N8-H908O7 ⁱ	0.88	2.56	3.340(6)	148
C1-H1O4 ⁱ	0.95	2.29	3.205(7)	162
C19–H19O4 ⁱ	0.95	2.58	3.523(8)	171
С39-Н39О5	0.95	2.69	3.542(8)	150
C43–H43O5 ⁱⁱ	0.95	2.53	3.386(6)	150
C44–H44O5 ⁱⁱ	0.95	2.22	3.105(7)	155
C10-H10O7 ⁱ	0.95	2.48	3.395(7)	162
C33–H33O7 ⁱ	0.95	2.10	3.040(6)	171
С39-Н39О7	0.95	2.45	3.311(7)	151
С52-Н52О6	0.95	2.34	3.213(7)	152

Table S2 Hydrogen bond distances (Å) and angles (°) in the sulfate complex of **2**.

Symmetry transformations used to generate equivalent atoms:

(i) -1+x,y,z, (ii) 1-x,2-y,-z

Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2008



Figure S8 A numbered diagram showing the bromide coordination environment in the bromide complex of **2**.



Figure S9 Intermolecular hydrogen bonding between N3 and O1.

Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2008



Figure S10 A numbered diagram showing the sulfate coordination environment in the sulfate complex of **2**.



Figure S11 An alternate view of the sulfate complex of **2**.

Stability constant determination with sulfate

Estimates of the binding constants K_a for receptor 2 with $(TBA)_2SO_4$ can be solved by explicitly looking at the two different binding events of anion to receptor:-

Up to one equivalent of anion the rate of anion binding is fast on the NMR timescale so K_1 can be determined by curve fitting the data in WINEQNMR to give:

NO. A PARAMETER DELTA ERROR CONDITION DESCRIPTION

- I I I.14804E+05 2.000E-01 I.205E+04 I.201E+00 KI
- 2 I 8.90859E+00 2.000E-01 5.365E-02 I.I36E+00 SHIFT M
- 3 I 1.14258E+01 I.000E+00 2.438E-02 I.297E+00 SHIFT ML



Figure S12 1H NMR titration curve with (TBA)₂SO₄ in DMSO-d₆

After 1 equivalent of anion is added the binding of another anion is slow on the NMR timescale resulting in two sets of peaks for 1:1 receptor:anion and 1:2 receptor:anion as shown in the titration stack plot. K₂ can be estimated by a single point stability constant determination giving $K_2 \approx 7800 \text{ M}^{-1}$