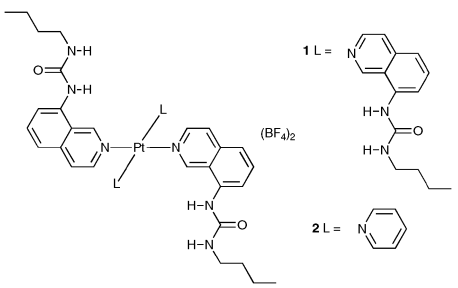
Metal–organic anion receptors: *trans*-functionalised platinum complexes†‡

Matthew G. Fisher,[a] Philip A. Gale,*[a] Mark E. Light[a] and Stephen J. Loeb*[b]

Received (in Austin, TX, USA) 12th September 2008, Accepted 18th September 2008
First published as an Advance Article on the web 14th October 2008
DOI: 10.1039/b816002c

The anion complexation properties of a *trans*-functionalised platinum(II) complex have been studied revealing a high affinity for sulfate in solution and 3 : 2 receptor : sulfate complex formation in the solid state with the anion bound in a pocket lined with 6 NH and 8 CH hydrogen-bond-donating groups.

The complexation of oxo-anions,[1] and particularly sulfate,[2] is an area of intense interest. For example, Custelcean and co-workers have recently reported an example of sulfate, SO_4^{2-}, bound to two tren-based tris-urea receptors *via* twelve NH···O hydrogen bonds.[3] Our groups[4] and others[5] have investigated the use of metal ions to template the formation of metal–organic anion receptors and shown that these compounds function as robust receptors for anionic species in solution. In 2004, we reported that a metal–organic anion receptor **1** consisting of a platinum centre bound to four urea-functionalised isoquinoline ligands was a particularly effective sulfate receptor, binding the anion *via* eight NH···O hydrogen bonds.[6] Here we report the synthesis and anion complexation properties of a *trans*-functionalised platinum isoquinoline pyridine complex **2** that is capable of binding sulfate in the solid state *via* NH···O and CH···O hydrogen-bonding interactions in a unique 3 : 2 receptor : sulfate complex.



Complex **2** was prepared in 48% yield by activation of *trans*-dichlorobis(pyridine)platinum(II)[7] with silver tetrafluoroborate in nitromethane at reflux followed by addition of a solution of 8-(n-butylurea)isoquinoline.[6]

Anion-binding studies were conducted by ^{1}H NMR titration techniques in highly competitive DMSO-d_6. The EQNMR program[8] was used to calculate stability constants from the NMR titration curves obtained (see ESI‡) with the results for halide anions shown in Table 1. Upon addition of tetrabutylammonium halides in DMSO-d_6, fast exchange was observed on the NMR timescale. The affinity of receptor **2** for halides is lower than receptor **1** due to the lower number of hydrogen-bond-donor groups in this system. However, as was observed with receptor **1**, receptor **2** binds halides in a 1 : 2 receptor : halide stoichiometry with a high K_1 and a lower K_2. We interpret this as the receptor adopting an *up–up* conformation at low anion concentrations wherein the anion is bound by two urea groups oriented in the same direction on one face of the complex, whereas at higher anion concentrations the receptor adopts an *up–down* conformation with the urea groups oriented on different faces of the complex with each urea binding a different halide.

Crystals of the bromide complex§ of **2** were grown by slow evaporation of a nitromethane solution of the tetrafluoroborate salt of **2** in the presence of excess tetrabutylammonium bromide. The structure (shown in Fig. 1) reveals that the receptor adopts an *up–down* conformation in the solid state, binding each bromide anion *via* four CH···Br^- hydrogen bonds (in the range C···Br 3.654(4)–3.775(5) Å) and a single urea NH···Br^- hydrogen bond (N···Br distance 3.474(4) Å).

Table 1 Stability constants (K_a/M^{-1}) for receptors **1** and **2** with tetrabutylammonium anion salts in DMSO-d_6 at 300 K[a]

	Receptor	
Anion	**1**[b]	**2**
Cl^-	K_1 = 11 700	K_1 = 2350
	K_2 = 2220	K_2 = 450
Br^-	K_1 = 1360	K_1 = 942
	K_2 = 450	K_2 = 131
I^-	K_1 = 1430	K_1 = 161
	K_2 = 52	K_2 = 16
SO_4^{2-}	$K_a > 10^4$	$K_1 > 10^{4c}$
		K_2 = 7800[d]
$H_2PO_4^-$	$K_a > 10^4$	$K_1 > 10^{4e}$

[a] All errors estimated to be <15%. [b] Data from ref. 6. [c] Estimated value-fitting the NMR titration curve between 0 and 1 equiv. gives a stability constant $>10^4$ M^{-1}. [d] Estimated value—as determined by a single point stability constant determination assuming a simple equilibrium between 1 : 1 and 1 : 2 receptor : anion complexes. [e] Estimated value—saturation is seen upon addition of one equivalent of the anion. Addition of further aliquots of dihydrogen phosphate causes precipitation.

[a] *School of Chemistry, University of Southampton, Southampton, UK SO17 1BJ. E-mail: philip.gale@soton.ac.uk; Fax: +44 (0)2380 596805; Tel: +44 (0)2380 593332*
[b] *Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, Canada N9B 3P4. E-mail: loeb@uwindsor.ca*

† Dedicated to Professor Javier de Mendoza, one of the pioneers of anion complexation, on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Further experimental details. CCDC 702189 & 702190. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b816002c

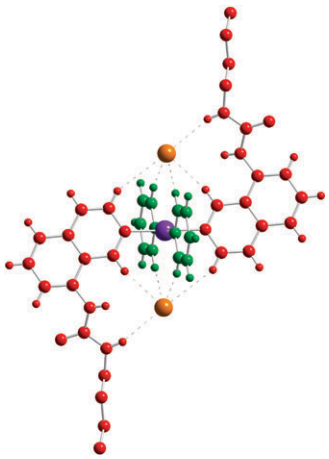


Fig. 1 X-Ray crystal structure of the bromide complex of receptor **1**. Selected hydrogen atoms have been omitted for clarity.

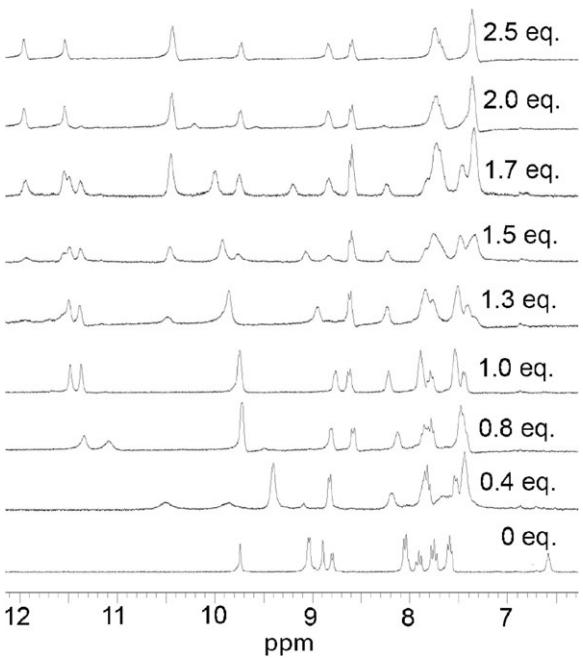


Fig. 2 Slow and fast exchange in the proton NMR titration of complex **2** with tetrabutylammonium sulfate in DMSO-d_6.

The urea nitrogen appended to the isoquinoline does not interact with the bromide but instead forms an intermolecular hydrogen bond to an adjacent complex in the crystal.

Upon addition of tetrabutylammonium sulfate[9] to solutions of receptor **2** in DMSO-d_6 a fast exchange process occurs in which the proton resonances corresponding to the free receptor shift up to one equivalent of added sulfate. Fitting this portion of the NMR titration to a 1 : 1 binding model gives a stability constant $K_1 > 10^4$ M^{-1}.[8] At this point further additions of sub-stoichiometric aliquots of sulfate result in a slow exchange process wherein resonances corresponding to the 1 : 1 receptor–sulfate complex disappear and resonances corresponding to a new complex appear (Fig. 2). This process is essentially complete upon addition of a second equivalent of sulfate. A single-point stability-constant determination at

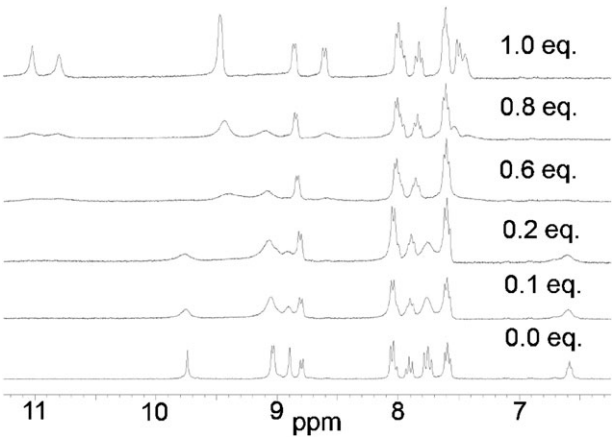
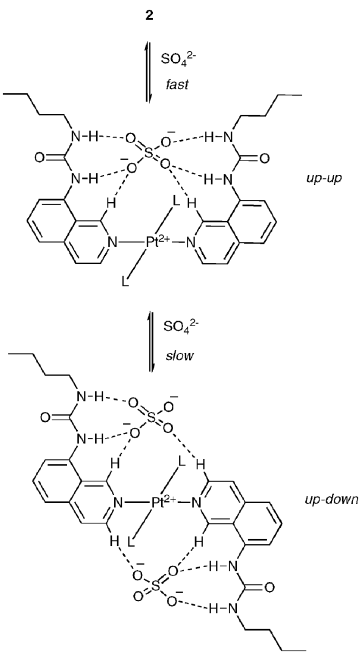


Fig. 3 Slow exchange in the proton NMR titration of complex **2** with tetrabutylammonium dihydrogenphosphate in DMSO-d_6.

1.67 equivalents of sulfate gave a stability constant of approximately 7800 M^{-1} assuming a simple equilibrium between 1 : 1 and 1 : 2 receptor–anion complexes. No further shifts in the ^{1}H NMR spectrum were observed upon addition of further aliquots of sulfate. We interpret this behaviour in a similar fashion to the halide binding process. Initially a 1 : 1 complex forms, but in this case the equilibrium between the 1 : 1 and 1 : 2 receptor–anion complexes is slow and both species can be observed as distinct complexes at 300 K in DMSO-d_6 (Scheme 1). This is presumably due to the stability of the 1 : 1 complex making the formation of the 1 : 2 complex less favourable. A slow exchange process is also observed and is complete over the addition of one equivalent of dihydrogen phosphate (Fig. 3) but the complex precipitates upon addition of excess of this anion.



Scheme 1 Sulfate complexation by complex **2** in DMSO-d_6 with proposed conformational interconversion of the platinum complex.

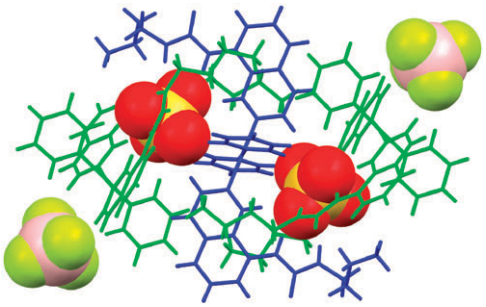


Fig. 4 X-Ray crystal structure of the sulfate complex of receptor **2**. Sulfate and tetrafluoroborate are shown in a space-filling representation. The central platinum complex adopts an *up–down* conformation (shown in blue) whilst the other two platinum complexes adopt *up–up* conformations (shown in green).

Crystals of the sulfate complex¶ of **2** were grown by slow evaporation of a nitromethane solution of the tetrafluoroborate salt of **2** in the presence of one equivalent of tetrabutylammonium sulfate.[9] The structure revealed the formation 3 : 2 receptor–sulfate complex with tetrafluoroborate anions coordinating to the platinum complexes *via* CH···F interactions at the periphery of the structure (Fig. 4). A central platinum complex adopts an *up–down* conformation with each urea group bound to a sulfate anion. Each of these sulfate ions is also bound to another platinum complex adopting an *up–up* conformation. Hence, each sulfate is bound to three urea groups. In addition, the aromatic CH groups in the α-position of the isoquinoline and pyridine rings of two platinum complexes form CH···O hydrogen bonding interactions with the sulfate ions. In all, there are fourteen NH and CH hydrogen-bond-donor groups around each sulfate (see ESI for more details of the sulfate coordination environment).‡ Interestingly, this complex contains both the bonding modes proposed for sulfate binding in solution, namely the *up–up* conformation binding sulfate at low sulfate concentrations and the *up–down* conformation at higher sulfate concentrations.

These new studies featuring *trans*-functionalised platinum complexes have provided deeper insight into the conformational interconversion processes occurring in solution for this class of anion receptor than was possible with the tetra-substituted derivative.[6] Importantly, the observation of both fast and slow exchange processes and a unique 3 : 2 complex between anion and receptor provides significant insight into how the conformational preferences of these receptors operate and should allow for further optimisation of receptor selectivity.

We would like to thank the EPSRC for a studentship (MGF) and the EPSRC together with Prof. Mike Hursthouse for access to the crystallographic facilities at the University of Southampton.

Notes and references

§ Data were collected on a Bruker Nonius Kappa CCD with a Mo rotating anode generator; standard procedures were followed. Crystal data for the bromide complex: $C_{38}H_{44}Br_2N_8O_2Pt$, M_r = 999.72, T = 120(2) K, monoclinic, space group $P2_1/n$, a = 14.0597(5), b = 9.3584(2), c = 14.9751(4) Å, β = 95.330(1)°, V = 1961.85(16) Å^3, ρ_{calc} = 1.692 g cm^{-3}, μ = 5.657 mm^{-1}, Z = 2, reflections collected: 20 717, independent reflections: 4480 (R_{int} = 0.0427), final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0318, w$R2$ = 0.0620, R indices (all data): $R1$ = 0.0435. w$R2$ = 0.0678.‡

¶ Crystal data for the sulfate complex (one of the butyl arms is modelled as disordered over 2 orientations): $C_{120}H_{150}B_2F_8N_{30}O_{26}Pt_3S_2$, M_r = 3251.71, T = 120(2) K, triclinic, space group $P\bar{1}$, a = 12.6995(4), b = 13.8948(4), c = 20.3426(5) Å, α = 76.749(2), β = 89.381(2), γ = 73.750(2)°, V = 3348.97(16) Å^3, ρ_{calc} = 1.612 g cm^{-3}, μ = 3.249 mm^{-1}, Z = 1, reflections collected: 49 439, independent reflections: 11 804 (R_{int} = 0.0820), final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0439, w$R2$ = 0.0929, R indices (all data): $R1$ = 0.0747. w$R2$ = 0.1050.‡

1 (*a*) P. A. Gale, S. E. García-Garrido and J. Garric, *Chem. Soc. Rev.*, 2008, **37**, 151–190; (*b*) P. A. Gale and R. Quesada, *Coord. Chem. Rev.*, 2006, **250**, 3219–3244; (*c*) J. L. Sessler, P. A. Gale and W.-S. Cho, *Anion Receptor Chemistry*, Royal Society of Chemistry, Cambridge, 2006; (*d*) *Supramolecular Chemistry of Anions*, ed. A. Bianchi, K. Bowman-James and E. García-España, Wiley-VCH, New York, 1997; (*e*) P. A. Gale, *Chem. Commun.*, 2008, 4525–4540; (*f*) C. Caltagirone and P. A. Gale, *Chem. Soc. Rev.*, 2009, DOI: 10.1039/b806422a.

2 (*a*) S. Kubik, R. Kirchner, D. Nolting and J. Seidel, *J. Am. Chem. Soc.*, 2002, **124**, 12752–12760; (*b*) J. L. Sessler and D. Seidel, *Angew. Chem.*, 2003, **115**, 5292–5333; J. L. Sessler and D. Seidel, *Angew. Chem., Int. Ed.*, 2003, **42**, 5134–5175; (*c*) S. O. Kang, M. A. Hossain, D. Powell and K. Bowman-James, *Chem. Commun.*, 2005, 328–330; (*d*) R. Custelcean, V. Sellin and B. A. Moyer, *Chem. Commun.*, 2007, 1541–1543; (*e*) D. A. Jose, D. K. Kumar, B. Ganguly and A. Das, *Inorg. Chem.*, 2007, **46**, 5817–5819; (*f*) C. Reyheller and S. Kubik, *Org. Lett.*, 2007, **9**, 5271–5274.

3 (*a*) R. Custelcean, P. Remy, P. V. Bonnesen, D.-e. Jiang and B. A. Moyer, *Angew. Chem., Int. Ed.*, 2008, **47**, 1866–1870; see also: (*b*) B. Wu, J. Liang, J. Yang, C. Jia, X.-J. Yang, H. Zhang, N. Tang and C. Janiak, *Chem. Commun.*, 2008, 1762–1764.

4 C. R. Bondy, P. A. Gale and S. J. Loeb, *Chem. Commun.*, 2001, 729–730; C. R. Bondy, P. A. Gale and S. J. Loeb, *J. Supramol. Chem.*, 2002, **2**, 93–96; I. E. D. Vega, P. A. Gale, M. E. Light and S. J. Loeb, *Chem. Commun.*, 2005, 4913–4915.

5 K. Sato, Y. Sadamitsu, S. Arai and T. Yamagishi, *Tetrahedron Lett.*, 2007, **48**, 1493–1496; J. A. Torvilla, P. Carlqvist, J. Benet-Buchholz, F. Maseras and R. Vilar, *Supramol. Chem.*, 2007, **19**, 599–611; V. Amendola, M. Boiocchi, B. Colasson and L. Fabbrissi, *Inorg. Chem.*, 2006, **45**, 6138–6147; R. Vilar, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1998, **37**, 1258–1261; C. R. Rice, *Coord. Chem. Rev.*, 2006, **250**, 3190–3199; J. Perez and L. Riera, *Chem. Soc. Rev.*, 2008, DOI: 10.1039/b707074h; K. J. Wallace, R. Daari, W. J. Belcher, L. O. Abouderbala, M. G. Boutelle and J. W. Steed, *J. Organomet. Chem.*, 2003, **666**, 63; S. J. Dickson, S. C. G. Biagini and J. W. Steed, *Chem. Commun.*, 2007, 4955.

6 C. R. Bondy, P. A. Gale and S. J. Loeb, *J. Am. Chem. Soc.*, 2004, **126**, 5030–5031.

7 P. C. Kong and F. D. Rochon, *Can. J. Chem.*, 1978, **56**, 441–445.

8 M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311–312.

9 M. J. Chmielewski, L. Zhao, A. Brown, D. Curiel, M. R. Sambrook, A. L. Thompson, S. M. Santos, V. Felix, J. J. Davis and P. D. Beer, *Chem. Commun.*, 2008, 3154–3156.