NH *vs.* CH hydrogen bond formation in metal–organic anion receptors containing pyrrolylpyridine ligands†

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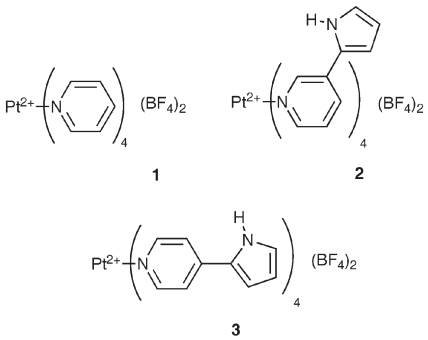
Anion complexation studies on a series of platinum(II) tetrakis(pyrrolylpyridine) salts demonstrate the importance of CH–anion hydrogen bonds in coordinating anionic guests in solution and the solid-state.

The coordination of anionic guest species by hydrogen bond donating receptors is an area of supramolecular chemistry that continues to attract attention.[1] A high proportion of the anion receptors reported thus far are 'built' upon organic scaffolds such as the calix[4]arenes.[2] However, the preparation of this type of receptor can often be synthetically challenging, a fact that prompted us to look for alternative means of arranging hydrogen bond donating groups in space. It occurred to us that some easy to prepare metal ligand complexes could be exploited as simple pieces of *inorganic* molecular scaffolding.[3] We initially chose to study square planar platinum(II) complexes due to their relative inertness towards ligand substitution and pyridine or iso-quinoline ligands due to their ease of synthesis and possibility of the hydrogen in the 2-position of the pyridine involving itself in potential CH···anion hydrogen bonding.[4] Brammer and co-workers have studied the application of related PtL_4^{2+} (L = nicotinamide) complexes in the construction of crystal-engineered networks[5] whilst Steed and co-workers have investigated the role anions can play in stabilising discrete complexes using similar organic ligands and kinetically labile templating metal centres.[6]

We decided to investigate the role CH···anion hydrogen bonds[7] play in stabilising the anion complexes in solution by synthesising a series of receptors containing either no NH hydrogen bond donors or a combination of NH and CH donors and to compare the affinity of these complexes for anions. Compound **2** offers the putative anionic guest *a choice* of hydrogen bond donor (NH or CH) as the pyrrole is free to rotate around the pyrrole–pyridine bond *without significantly changing the shape of the binding site*. On the other hand, complex **3** offers the anionic guest an electrostatic interaction and CH hydrogen bond donors at the centre of the complex or an NH hydrogen bond donor at the periphery.

Receptor **1**$(BF_4)_2$ was synthesised *via* literature procedures.[4,8] 3-(Pyrrol-2-yl)pyridine and 4-(pyrro-2-yl)pyridine were synthesised *via* a Paal Knorr[9] reaction with 4-oxo-4-(pyridin-3-yl)butanal[10] and 4-oxo-4-(pyridin-4-yl)butanal,[10] respectively, to afford substituted pyridines in up to 95 and 60% yields. The platinum complexes of these pyridines, **2**$(BF_4)_2$ and **3**$(BF_4)_2$, were prepared in an analogous fashion to **1**$(BF_4)_2$ (see ESI for details).†

Crystals of **2**$(BF_4)_2$ were obtained by slow evaporation of a nitromethane solution of the complex.‡ The structure (see Fig. 1) shows that the complex adopts the 1,2-alternate conformation in the solid state binding the BF_4^- anions *via* NH···F and CH···F hydrogen bonds (including N2···F1 2.882(3); N4···F2 2.884(3); C1···F3 3.322(3); C5···F1 3.447(3); C10···F3 3.442(4) Å).



The anion binding properties of complexes **1**$(BF_4)_2$, **2**$(BF_4)_2$ and **3**$(BF_4)_2$ were explored using ^{1}H NMR titration techniques in DMSO-d_6. Complex **1**$(BF_4)_2$, despite containing no NH hydrogen bond donor groups, was observed to interact with anions with downfield shifts of up to 0.50 ppm for the hydrogen in the 2-position of the pyridine ring in the presence of three equivalents of chloride ion (Table 1). In most cases, this data could be fitted to a 1 : 1 receptor : anion binding model with the results shown in Table 2. However, the possibility exists that a second anion may associate with the 1 : 1 complex with a low K_2 that has not been detected in this experiment. This is true of all the ^{1}H NMR titration experiments reported in this communication.

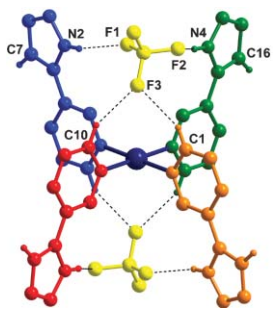


Fig. 1 A ball-and-stick representation of the X-ray crystal structure of **2** crystallized from nitromethane. The hydrogen bonding network is shown with BF_4 anions bound above and below the plane of the complex by CH···F and NH···F hydrogen bonds.

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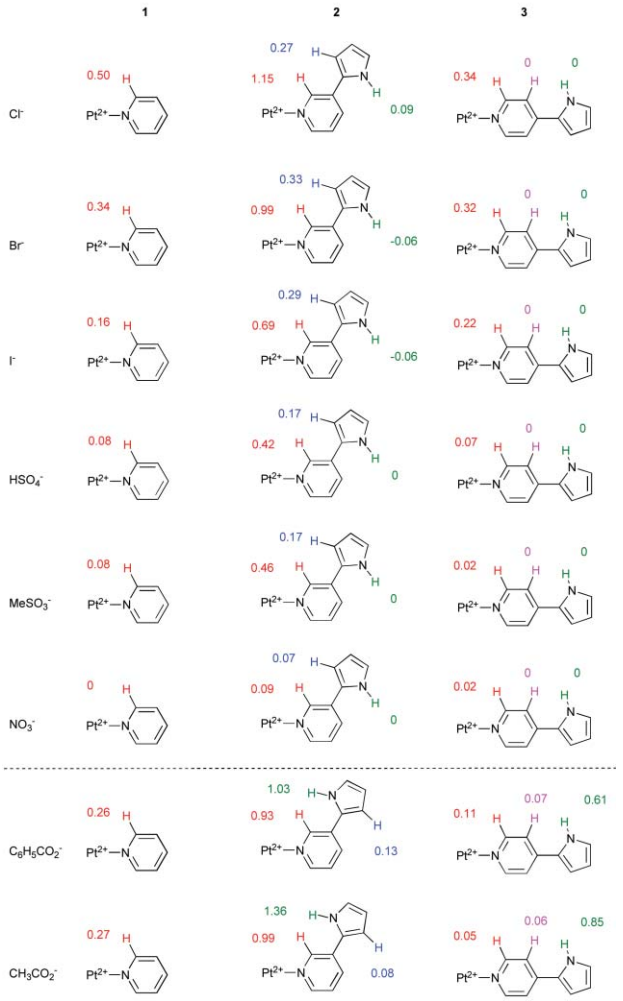
† Electronic supplementary information (ESI) available: Spectroscopic data for **1**, **2** and **3**. See http://dx.doi.org/10.1039/b510506d

Table 1 Proton NMR chemical shifts upon addition of three equivalents of tetrabutylammonium anion salt to solutions of $\mathbf{1}(BF_4)_2$, $\mathbf{2}(BF_4)_2$ and $\mathbf{3}(BF_4)_2$ in DMSO-d_6



Complex $\mathbf{2}(BF_4)_2$ shows the highest affinity for anions of the three receptors reported. Shifts of up to 1.15 ppm for the pyridine CH proton were observed with three equivalents of chloride. Most surprisingly however, the pyrrole NH proton does not shift significantly upon addition of Cl^-, Br^-, I^-, HSO_4^-, $MeSO_3^-$ or NO_3^-. In the cases of the most basic anions studied (acetate and benzoate) the NH resonance does shift downfield by 1.36 and 1.03 ppm, respectively, in the presence of three equivalents of the anions (although precipitation occurs in the case of benzoate and the ratio of the receptor to anion in solution is uncertain). Acetate binds in a 1 : 2 receptor : anion stoichiometry (planar anions were found to bind in a 1 : 2 fashion to the previous generation of nicotinamide based platinum complexes)[4] with $K_2 > K_1$. This suggests that an allosteric effect is operating which preorganises the second binding site upon complexation of the first equivalent of acetate. The same effect was also observed in the first generation nicotinamide systems.[4] In the case of the other anions, downfield shifts of a pyrrole CH proton were observed (Table 1). Amongst the non-carboxylate anions, the highest affinity was found with methanesulfonate (1115 M^{-1}) whilst HSO_4^- was bound considerably more strongly (837 M^{-1}) than was the case with complex $\mathbf{1}^{2+}$ (<10 M^{-1}).

Table 2 Stability constants of the tetrafluoroborate salts of $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ with anionic guests in DMSO-d_6 at 298 K calculated from the shift of the resonance of the pyridine hydrogen in the 2-position except where noted assuming 1 : 1 stoichiometry in all cases except where noted

Anion	$\mathbf{1}^{2+}$	$\mathbf{2}^{2+}$	$\mathbf{3}^{2+}$
Cl^-	195	960	216
Br^-	121	796	211
I^-	50	462	113
$CH_3CO_2^-$	84	$K_1 = 216^a$	117^a
	—	$K_2 = 2400^a$	—
$PhCO_2^-$	132	[b]	111^a
$MeSO_3^-$	45	1115	<10
NO_3^-	—	29	<10
HSO_4^-	<10	837	<10

[a] Calculated following the shift in the pyrrole NH proton. [b] Precipitation during the titration, however shifts of protons suggest a strong interaction of **2** with benzoate.

Complex $\mathbf{3}(BF_4)_2$ does not contain a potential convergent anion-binding site that could involve all four of the pyrrole NH groups. Indeed similar, although not identical, shifts of the pyridine CH resonance in the 2-position were observed with complexes $\mathbf{1}(BF_4)_2$ and $\mathbf{3}(BF_4)_2$. The exception to this are the interactions observed with the carboxylate anions. Here, as with complex $\mathbf{2}(BF_4)_2$, the pyrrole NH group was observed to shift downfield by between 0.61 and 0.85 ppm whilst only small shifts of the pyridine α-CH resonance were observed. These results are evidence that a different mode of binding occurs between complexes $\mathbf{2}(BF_4)_2$ and $\mathbf{3}(BF_4)_2$ and carboxylate anions than that which occurs between the complexes and the other less basic anions.

Crystals of $\mathbf{2}(MeSO_3)_2.H_2O$ were obtained by slow evaporation of a nitromethane solution of the salt (prepared by an analogous method using $AgMeSO_3$).§ Once again the complex adopts the 1,2-alternate conformation (see Fig. 2), binding the methanesulfonate anions *via* both pyrrole NH···O and pyridine CH···O hydrogen bonds in the solid state (including N2···O3A 2.926(8) Å; N4···O2A 2.850(8) Å; C1···O1A 3.542(7) Å; C10···O1A 3.100(6) Å).

The solution binding experiments and the crystal structure of the methanesulfonate complex of $\mathbf{2}^{2+}$ serve to reiterate the important point that crystal structure data cannot be relied upon to predict the structure of complexes in solution. There is no evidence that the pyrrole NH groups interact with the methanesulfonate anion in DMSO-d_6 solution, but rather that the pyrrole CH group is involved in a CH···O hydrogen bond with the anion

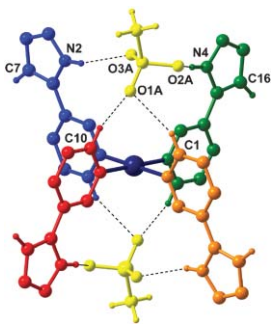


Fig. 2 A ball-and-stick representation of the X-ray crystal structure of the methanesulfonate salt of cation $\mathbf{2}^{2+}$. The hydrogen bonding network is shown with $MeSO_3^-$ anions bound above and below the plane of the complex by CH···O and NH···O hydrogen bonds.

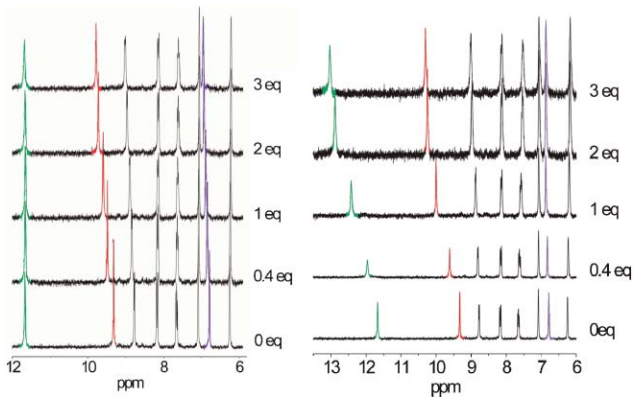


Fig. 3 Proton NMR titration of compound **2** in DMSO-d_6 with tetrabutylammonium methanesulfonate (left) and acetate (right) at 298 K showing a downfield shift of the pyridine CH proton in the 2-position (red) in both cases, the pyrrole proton in the 3-position is shown in blue whilst the pyrrole NH proton (green) does not shift upon addition of methanesulfonate but does shift downfield upon addition of acetate.

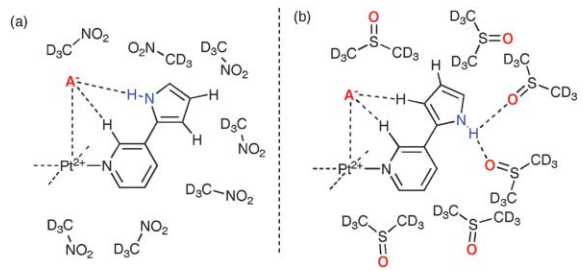


Fig. 4 Binding modes of one equivalent of methanesulfonate (A^-) to $\mathbf{2}^{2+}$ in (a) nitromethane-d_3 and (b) DMSO-d_6 solution.

(Fig. 3). A comparison of the shifts observed in compound $\mathbf{3}^{2+}$ with acetate and chloride shows the halide binding presumably to the centre of the complex so taking advantage of the electrostatic interaction, whilst the more basic carboxylate induces a larger shift in the pyrrole NH group.

In nitromethane, more typical behaviour is observed with compound $\mathbf{2}^{2+}$ upon addition of anions. For example, addition of aliquots of tetramethylammonium methanesulfonate to a nitromethane-d_3 solution of $\mathbf{2}(BF_4)_2$ causes the pyrrole NH resonance to shift downfield from 9.79 ppm to 11.56 ppm ($\Delta\delta$ = 1.77 ppm at 2.0 equiv $MeSO_3^-$). Unfortunately, upon further additions of this anion, the complex precipitates. These results led us to conclude that a solvent competition mechanism, such as that shown in Fig. 4, may be operating in DMSO solution. Nitromethane is a notoriously poor hydrogen-bond acceptor[11] and hence when an anion is added to the receptor in this solvent it will bind to the most acidic hydrogen bond donor (the NH). However in DMSO (a good hydrogen bond acceptor), the anionic guest will either bind to the pyrrole NH if it is a basic anion, or if it is less basic, the pyrrole NH groups may orientate themselves into the solvent allowing the formation of hydrogen bonds to the DMSO whilst the anion accepts CH hydrogen bonds from the platinum complex. This presumably leads to a greater overall stability of the complex than if the NH groups were oriented inwards and the solvent presented with the CH groups of the pyrrole. The profound effect of solvent on the binding mode of this receptor is an important phenomenon and should probably be looked at more closely as a design feature for future anion receptors containing NH hydrogen bond donor groups.[12]

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Notes and references

‡ All data were collected on a Bruker Nonius Kappa CCD with a Mo rotating anode following standard procedures. Crystal data for $\mathbf{2}(BF_4)_2(CH_3NO_2)_2$ $C_{38}H_{38}N_{10}B_2F_8O_4Pt$, M_r = 1067.49, T = 120(2) K, triclinic, space group $P\bar{1}$, a = 9.4410(3), b = 10.4860(3), c = 11.2470(4) Å, α = 77.568(2), β = 89.272(2), γ = 68.613(2)°, V = 1009.80(6) Å^3, ρ_{calc} = 1.755 g cm^{-3}, μ = 3.566 mm^{-1}, Z = 1, reflections collected: 15299, independent reflections: 4626 (R_{int} = 0.0362), final R indices [$I > 2\sigma I$]: R_1 = 0.0211, wR_2 = 0.0466, R indices (all data): R_1 = 0.0212. wR_2 = 0.0467. § Crystal data for $\mathbf{2}(MeSO_3)_2H_2O$ $C_{38}H_{40}N_8O_7PtS_2$, M_r = 979.99, T = 120(2) K, triclinic, space group $P\bar{1}$, a = 9.059(2), b = 10.489(3), c = 11.080(2) Å, α = 81.790(17), β = 73.740(16), γ = 69.240(14)°, V = 944.0(3) Å^3, ρ_{calc} = 1.724 g cm^{-3}, μ = 3.889 mm^{-1}, Z = 1, reflections collected: 16456, independent reflections: 4313 (R_{int} = 0.0423), final R indices [$I > 2\sigma I$]: R_1 = 0.0343, wR_2 = 0.0777, R indices (all data): R_1 = 0.0357. wR_2 = 0.0785. CCDC 281270–281271. See http://dx.doi.org/10.1039/b510506d for crystallographic data in CIF or other electronic format.

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