Platinum(II) nicotinamide complexes as receptors for oxo-anions†

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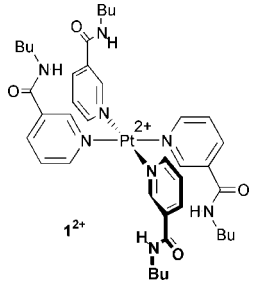
The coordination of four *n*-butylnicotinamide ligands to a platinum(II) centre provides a facile method of organizing amide H-bond donors for anion binding; the PF_6^- complex is an effective receptor for a variety of oxo-anions.

The coordination of anionic guest species by hydrogen bond donating receptors is an area of supramolecular chemistry that continues to attract attention.[1] A large number of the anion receptors reported so far are 'built' upon organic scaffolds such as calixarenes.[2] However, the preparation of these types of receptors can often be synthetically challenging, a fact that prompted us to look for alternative means of arranging hydrogen bond donating groups. 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 nicotinamide ligands due to their ease of synthesis. The homoleptic $[PtL_4]^{2+}$ complex cation is an ideal candidate to act as an anion receptor as it provides both hydrogen bond donating amides[4] and an electrostatic contribution from the metal centre. As a first test of this strategy, the complex $[Pt(L)_4]^{2+}$ (L = *n*-butylnicotinamide), **1**, has been synthesised as the PF_6^- salt and shown to act



as a polydentate anion receptor both in solution and in the solid state.†

The *n*-butylnicotinamide ligand was prepared from the nicotinamide ethylester and *n*-butylamine by standard methods.[5] The Pt^{II} complex was prepared by reacting 1 equiv. of $PtCl_2(EtCN)_2$ with 4 equiv. of ligand and 2 equiv. of $AgPF_6$ in MeCN solution.[6] After filtration to remove AgCl and evaporation of the solvent, crude $\mathbf{1}[PF_6]_2$ was recrystallized from $MeCN/Et_2O$ and isolated in 87% yield.‡ The material produced in this fashion was determined to be analytically pure and subsequently used in all anion receptor studies. Recrystallization of $\mathbf{1}[PF_6]_2$ from a CH_2Cl_2/Pr^i_2O solvent mixture produced crystals of $\mathbf{1}[PF_6]_2{\cdot}2CH_2Cl_2$ suitable for an X-ray structure determination.§

Fig. 1 shows a ball and stick representation of the X-ray structure of $\mathbf{1}[PF_6]_2{\cdot}2CH_2Cl_2$. By drawing an analogy to calix[4]arene nomenclature, there are four conformations (cone, partial cone, 1,3- and 1,2-alternate) possible for **1** due to facile

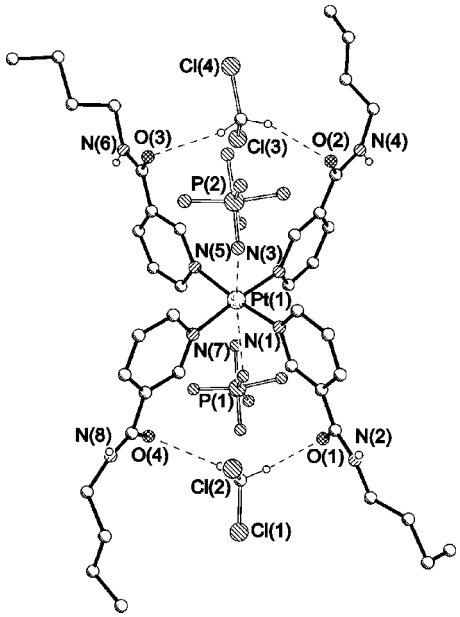
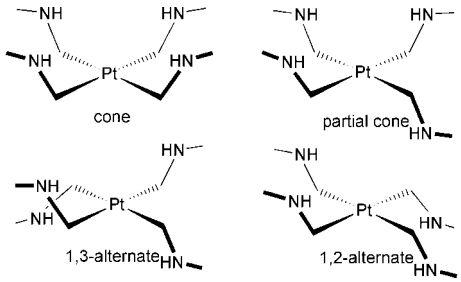


Fig. 1 X-Ray structure of $\mathbf{1}[PF_6]_2{\cdot}2CH_2Cl_2$ showing the basic numbering scheme. C–H···O distances (Å) and angles (°): H(50A)···O(4) 2.40, C(50)–H(50A)···O(4) 113; H(50B)···O(1) 2.43, C(50)–H(50B)···O(1) 118; H(60A)···O(2) 2.42, C(60)–H(60A)···O(2) 115; H(60B)···O(3) 2.47, C(60)–H(60B)···O(3) 125. Pt···F distances (Å) and angles (°): Pt(1)···F(1) 3.42, Pt(1)···F(1)–P(1) 147; Pt(1)···F(8) 3.28, Pt(1)···F(1)–P(1) 155.



rotation about the Pt–N bonds.[7] In the solid state, the four nicotinamide ligands adopt a centrosymmetric 1,2-alternate conformation which places two amide hydrogen bonding sites in a *cis* orientation on each side of the metal square plane. Interestingly, the amide NH groups do not interact with the PF_6^- anions which are situated above and below the Pt^{II} metal centre presumably to maximize electrostatic interactions and cation–anion crystal packing. In fact, it is the amide C=O groups which are involved in hydrogen bonding to the methylene hydrogens of the CH_2Cl_2 solvent molecules. It was therefore assumed that (i) the PF_6^- anions would not be competitive for the binding of the oxo-anions used in this study[8] and (ii) a 2:1 anion:host ratio is certainly possible and may predominate.

The ability of $\mathbf{1}[PF_6]_2$ to function as a receptor for oxo-anions in solution was determined by measuring association constants, K_a, in various solvents by ^1H NMR spectroscopic titration

† Electronic supplementary information (ESI) available: titration plots for $[PtL_4][PF_6]_2$ with various oxo-anions. See: http://www.rsc.org/suppdata/cc/b1/b101440o/

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Table 1 Association constants, K_a, for $\mathbf{1}^{2+}$ with various oxo-anions

Anion[a]	Solvent	K_a/M^{-1}
$CF_3SO_3^-$	CD_3CN	129
ReO_4^-	CD_3CN	150
NO_3^-	CD_3CN	K_1 = 562, K_2 = 132
HSO_4^-	CD_3CN/DMSO-d_6 3:1 *v/v*	149
$CH_3CO_2^-$	CD_3CN/DMSO-d_6 3:1 *v/v*	Precipitate[b]
$H_2PO_4^-$	CD_3CN/DMSO-d_6 1:9 *v/v*	Precipitate[b]
$CH_3CO_2^-$	CD_3CN/DMSO-d_6 1:9 *v/v*	K_1 = 230, K_2 = 491

[a] Anion added as the tetrabutylammonium salt. [b] Precipitation occurred during the titration. The precipitate re-dissolved upon further addition of anions, however the titration profile could not be fitted satisfactorily (see ESI†).

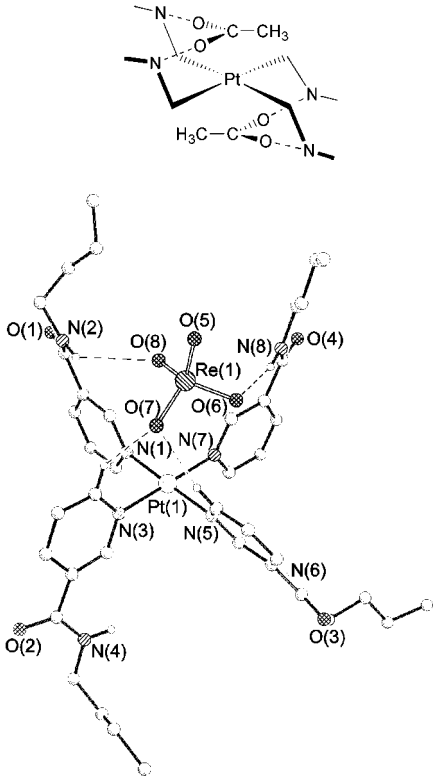

Fig. 2 X-Ray structure of the $[\mathbf{1}(ReO_4)]^+$ cation showing the basic numbering scheme. N–H···O distances (Å) and angles (°): H(2A)···O(8) 2.79, N(2)–H(2A)···O(8) 137; H(8A)···O(6) 2.13, N(8)–H(8A)···O(6) 168; H(11A)···O(7) 2.50, C(11)–H(11A)···O(7) 142; H(21A)···O(7) 2.37, C(21)–H(21A)···O(7) 171. Pt···O distances (Å) and angles (°): Pt(1)···O(6) 4.20, Pt(1)···O(6)–Re(1) 86; Pt(1)···O(7) 4.11, Pt(1)···O(7)–Re(1) 89; Pt(1)···O(8) 4.16, Pt(1)···O(8)–Re(1) 87. Pt(1)···Re(1) 4.42.

techniques. The results reported in Table 1 for $CF_3SO_3^-$, ReO_4^-, NO_3^-, HSO_4^-, $H_2PO_4^-$ and $CH_3CO_2^-$, show that receptor **1** is capable of acting as an effective host for oxo-anions. There appears a certain amount of selectivity towards planar bidentate anions such as NO_3^- and $CH_3CO_2^-$ and these are bound in a 1:2 receptor:anion ratio. This can be attributed to a shape specific match between two *cis* amido groups and a bidentate anion. In particular, the binding of acetate ion is relatively strong even in the very polar 9:1 DMSO/MeCN mixture. The fact that K_2 is greater than K_1 infers that binding of the first anion has a positive allosteric effect, which favours binding of the second.

The tetrahedral or pseudo-tetrahedral oxo-anions ReO_4^-, $CF_3SO_3^-$ and HSO_4^- are more weakly bound and solution evidence supports a simpler 1:1 receptor:anion ratio or at least a situation in which K_1 can be reliably obtained but K_2 is too small to be measurable. The 1:1 host:anion binding observed for the weakly coordinated ReO_4^-, $CF_3SO_3^-$ and HSO_4^- anions is supported by the X-ray structure§ of $\mathbf{1}[ReO_4]_2$ shown in Fig. 2. In particular, it can be seen that in order to try and maximise hydrogen bonding to a single ReO_4^- anion with 3-fold symmetry the relatively acidic nicotinamide CH's from the ligands on the opposite side of the square plane contribute to binding the anion. To do this, the complex must distort significantly from centrosymmetry, a fact that presumably disfavours the interaction with a second anion resulting in the observation of 1:1 binding in solution.

Although solubility problems and thus the need to vary solvent systems prohibited a direct comparison of all the available anions, there is sufficient evidence to suggest that this new type of anion receptor is worthy of further study. The results presented herein suggest that future re-design of this type of host might produce anion receptors with high selectivity and binding strength based on a simple inorganic scaffold.

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Notes and references

‡ *Selected data* for $\mathbf{1}[PF_6]_2$: ^{1}H NMR (CD_3CN): δ 9.36 (s, 4H, Ar), 8.94 (d, 4H, Ar, ^2J 5.7 Hz), 8.23 (d, 4H, Ar, ^2J 8.1 Hz), 7.62 (t, 4H, Ar, ^2J 5.7 Hz, 8.1 Hz), 7.36 (s, 4H, NH), 3.36 (q, 8H, NCH_2), 1.58 (q, 8H, CH_2), 1.39 (q, 8H, CH_2), 0.94 (t, 12H, CH_3), *Determination of* association constants: in a typical run, anion portions were added to the host solution (1×10^{-2} M) in aliquots of 0.1 to 5 equiv. and 0.5 to 7 equiv. K_a values were determined using EQNMR.[9]

§ *Crystal data*: for $\mathbf{1}[PF_6]_2 \cdot 2CH_2Cl_2$: $C_{42}H_{60}Cl_4F_{12}N_8O_4P_2Pt$, M = 1367.81, monoclinic, space group *Cc*, a = 16.2726(4), b = 8.9587(2), c = 39.2903(5) Å, β = 96.253(1)°, U = 5693.7(2) Å^3, T = 293(2) K, Z = 4, μ = 2.793 mm^{-1}, 5449 independent reflections (R_{int} = 0.0159). $R1$ = 0.0310, $wR2$ = 0.0802, ($I > 2\sigma I$), $R1$ = 0.0369, $wR2$ = 0.0844, (all data), goodness-of-fit = (F^2) = 1.033. For $\mathbf{1}[ReO_4]_2$: $C_{56}H_{42}N_8O_{12}PtRe_2$, M = 1586.47, triclinic, space group $P\bar{1}$, a = 10.182(1), b = 14.618(1), c = 17.408(2) Å, α = 72.888(3), β = 88.487(3), γ = 71.773(2)°, U = 2346.0(6) Å^3, T = 293(2) K, Z = 2, μ = 8.203 mm^{-1}, 6103 independent reflections (R_{int} = 0.0719). $R1$ = 0.0698, $wR2$ = 0.1518, ($I > 2\sigma I$), $R1$ = 0.1062, $wR2$ = 0.1714, (all data), goodness-of-fit = (F^2) = 1.028. Data were collected on a Bruker SMART CCD instrument and solutions performed using the SHELXTL 5.03 Program Library, Siemens Analytical Instrument Division, Madison, WI, USA, 1997. CCDC 158329 and 158330. See http://www.rsc.org/suppdata/cc/b1/b101440o/ for crystallographic data in .cif or other electronic format.

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7 Variable temperature ^{1}H NMR spectra showed no evidence of the different conformations in solution. This is presumably a result of facile interconversion *via* rotation about Pt–N bonds.

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