DALTON
FULL PAPER

Receptor versatility of tris(pyridin-1-ium-2-ylmethyl)amine in anion binding through hydrogen bonding †

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Received 23rd September 2002, Accepted 24th October 2002
First published as an Advance Article on the web 21st November 2002

The receptor ability of tris(pyridin-1-ium-2-ylmethyl)amine (triprotonated tris(2-pyridylmethyl)amine, H_3TPA^{3+}) toward inorganic anions such as PF_6^-, $CF_3SO_3^-$, Br^-, and Cl^- was investigated. Several spectroscopic studies revealed that H_3TPA^{3+} offered characteristic receptor selectivity in the anion complexation. Structural analysis of the receptor-anion complexes $[H_3TPA(PF_6)](PF_6)_2$, $[H_3TPA(CF_3SO_3)](CF_3SO_3)(PF_6)$, $[H_3TPA(Br)](PF_6)_2$, and $[H_3TPA(Cl)](PF_6)_2$ indicated that the H_3TPA^{3+} receptor nicely caught each anion guest (X^-) in its three dimensional cavity *via* hydrogen bonding (X ··· H ··· N) with pyridinium groups. Treatment of the $[H_3TPA(X)]^{2+}$ (X = PF_6^- or $CF_3SO_3^-$) complex with a large excess of KBr in the solid state led to the replacement of PF_6^- or $CF_3SO_3^-$ with Br^- to give $[H_3TPA(Br)]^{2+}$, whereas Cl^- in the $[H_3TPA(Cl)]^{2+}$ complex was not replaced. The PF_6^- anions located in and out of the H_3TPA^{3+} cavity were replaced stepwise with the added Cl^- or Br^-anion. The strength of the hydrogen bonding increased as the pK_b value of the anion decreased in the series $Cl^- > Br^- > CF_3SO_3^- > PF_6^-$.

Introduction

Although the coordination chemistry of anions has grown in various fields of biological, medical, catalytic, and environmental science,[1–5] its development is still behind that of cations. There are several difficulties in the synthesis of effective anion receptors. One of them is that the anions have larger sizes and lower charge densities than the isoelectronic cations.[6] Another is that anionic species have wide geometrical variations such as spherical, linear, trigonal, tetrahedral, and octahedral structures. Several macrocyclic polyammonium ligands have been developed as effective anion receptors. In their anion complexes, the guest anions are ligated by the polyammonium protons through hydrogen bonding, and the macrocyclic cage structures are retained by the electrostatic repulsion between the positively charged nitrogens of the receptors.[7–14] Tripodal and other acyclic receptors having thiourea, cobaltocenium, and amide groups have also been developed, which formed hydrogen bonding complexes with particular anions.[15–21] The protonated pyrrole and pyrazole groups were further introduced into the receptors to have extremely high affinities for anions; sapphyrins, polycalixpyrroles,[5,22–27] and $HB(3\text{-}^tBupzH)_3$ [$HB(3\text{-}^tBupzH)_3$ = hydrotris(3-*tert*-butyl-pyrazolin-2-ium)-borate][28] were typically reported. These examples emphasize the significance of hydrogen bonding formation in the anion recognition processes.

Here we report the versatile anion receptor properties of tris-(pyridin-1-ium-2-ylmethyl)amine (triprotonated tris(2-pyridylmethyl)amine, H_3TPA^{3+}). Since the pyridinium ligands have characteristic absorption, redox, and photochemical properties, they are expected to act as effective receptors for several inorganic anions. Tris(pyridin-1-ium-2-ylmethyl)amine, containing three pyridyl groups is a well-known effective tetradentate ligand for transition and lanthanide metal ions,[29,30] and forms both 1 : 1 and 1 : 2 (metal : ligand) complexes with various metal cations, the ionic radii of which range from 0.60 to 1.88 Å. These metal coordination characteristics provide a promising possibility that the protonated H_3TPA^{3+} can exhibit versatile coordination properties for a wide range of anions. We prepared here a series of its anion complexes and fully characterized them using X-ray, NMR, IR and electrochemical techniques. Toftlund and coworkers reported the crystal structure of a SO_4^{2-} complex with H_3TPA^{3+}, in which the SO_4^{2-} anion was accommodated in the three-dimensional receptor cavity *via* three hydrogen bonds between one oxygen of SO_4^{2-} and the three nitrogen atoms of the pyridiniumylmethyl groups.[29] However, we present the first systematic studies of the anion binding functions of the H_3TPA^{3+} receptor. The coordination structures and properties of its anion complexes are described in detail. Although PF_6^-, $CF_3SO_3^-$, Br^-, and Cl^- anions are nicely included in a three-dimensional fashion, the present type of receptor exhibits characteristic anion selectivity, which is significantly dependent upon the nature of the hydrogen bonding.

Experimental

Materials

TPA was prepared as described in the literature,[31] and its anion complexes were obtained as shown below. Acetonitrile was dried over calcium hydride and distilled under a nitrogen atmosphere. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was recrystallized twice from ethanol. All other commercially available reagents were used as purchased.

$[H_3TPA](PF_6)_3$

75 μl of 60% HPF_6 aqueous solution was added to 10 ml of a methanolic solution of TPA (50 mg, 0.17 mmol) and the resulting solution was stirred for 3 h to give a white microcrystalline powder. Yield 105 mg (85%). Anal. calc. for $C_{18}H_{21}N_4F_{18}P_3$ (FW: 728.28): C, 29.69; H, 2.91; N, 7.69. Found: C, 29.95; H, 3.09; N, 7.74%. UV-vis [CH_3CN, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 258 (16400). ^{1}H NMR (CD_3CN): δ 8.86 (3H, dd), 8.46 (3H, t), 7.94 (3H, d), 7.70 (3H, d), 7.90 (3H, d), 4.25 (6H, s).

† Electronic supplementary information (ESI) available: ORTEP drawing of $[H_3TPA(PF_6)]^{2+}$. See http://www.rsc.org/suppdata/dt/b2/b209331f/

Table 1 Crystallographic data for $[(H_3TPA)(CF_3SO_3)]CF_3SO_3 \cdot PF_6$, $\{[(H_3TPA)Br](PF_6)_2\}_2 \cdot CH_3CN \cdot CH_3OH$, and $\{[(H_3TPA)Cl](PF_6)_2\}_2$

	$[(H_3TPA)(CF_3SO_3)]CF_3SO_3 \cdot PF_6$	$\{[(H_3TPA)Br](PF_6)_2\}_2 \cdot CH_3CN \cdot CH_3OH$	$\{[(H_3TPA)Cl](PF_6)_2\}_2$
Formula	$C_{20}H_{21}N_4PF_{12}O_6S_2$	$C_{38}H_{42}N_9Br_2P_4F_{24}O$	$C_{36}H_{42}Cl_2P_4F_{24}N_8$
Fw	736.48	1380.47	1237.54
Crystal size/mm	0.60 × 0.40 × 0.20	0.40 × 0.30 × 0.20	0.40 × 0.20 × 0.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
T/°C	23	−60.0	−173
a/Å	12.3822(9)	47.164(6)	14.1667(2)
b/Å	12.2476(8)	9.366(7)	13.6026(2)
c/Å	20.431(1)	24.667(8)	26.5260(4)
β/°	98.580(3)	90.25(2)	100.9485(5)
V/Å^3	3063.7(4)	10895(8)	5018.6(1)
Z	4	8	8
D_c/g cm^{-3}	1.597	1.683	3.276
μ(Mo-Kα)/cm^{-1}	3.40	17.33	7.69
Unique reflections	7006	12491	11447
Observed reflections [$I > 2.0\sigma(I_o)$]	5409	5824	6877
R^a	0.086	0.072	0.051
wR^b	0.2656	0.229	0.156

^{a} $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. ^{b} $Rw = [(\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)]^{1/2}$.

$[H_3TPA(CF_3SO_3)](CF_3SO_3)(PF_6)\cdot 4H_2O$

88 μl of CF_3SO_3H was added to 10 ml of a methanolic solution containing TPA (100 mg, 0.34 mmol). To the resulting solution, NH_4PF_6 (163 mg, 1.0 mmol) in a minimum amount of methanol was added and the solution was kept in a refrigerator for two days until it provided white crystals. Yield 175 mg (64%). Anal. calc. for $C_{20}H_{29}O_{10}N_4PS_2F_{12}$ (FW: 808.55): C, 29.71; H, 3.62; N, 6.93; S, 7.93. Found: C, 29.83; H, 3.26; N, 7.25; S, 7.99%. UV-vis [CH_3CN, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 258 (11600). ^{1}H NMR (CD_3CN): δ 8.77 (3H, d), 8.52 (3H, t), 8.05 (3H, s), 7.98 (3H, t), 4.24 (6H, d).

$[H_3TPA(Br)](PF_6)_2\cdot H_2O$

172 μl of 48% HBr aqueous solution was added to 10 ml of a methanolic solution containing TPA (100 mg, 0.34 mmol), and NH_4PF_6 (110 mg, 0.68 mmol) in 5 ml methanol was added to the solution after 30 min. The precipitated white powder was dissolved in 1 ml of CH_3CN and allowed to stand for one night to give colorless crystals, which were collected by filtration and air-dried. Yield 140 mg (60%). Anal. calc. for $C_{18}H_{23}N_4F_{12}BrOP_2$ (FW: 681.24): C, 31.74; H, 3.40; N, 8.22; Br, 11.73. Found: C, 31.46; H, 3.30; N, 8.58; Br, 11.86%. UV-vis [CH_3CN, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 258 (16200). ^{1}H NMR (CD_3CN): δ 8.84 (3H, d), 8.56 (3H, t), 8.03 (6H, q), 4.26 (6H, s).

$[H_3TPA(Cl)](PF_6)_2$

To a methanolic solution (10 ml) of TPA (100 mg, 0.34 mmol), 85 μl of 12 N HCl was added. White powder was precipitated after 30 min of stirring and then 1 ml of CH_3CN containing NH_4PF_6 (110 mg, 0.68 mmol) was added. The suspension was heated and the resulting solution was allowed to stand for several days. The precipitated colorless crystals were collected and dried in air. Yield 150 mg (71%). Anal. calc. for $C_{18}H_{23}N_4F_{12}ClOP_2$ (FW: 618.77): C, 34.94; H, 3.42; N, 9.05; Cl, 5.73. Found: C, 34.57; H, 3.39; N, 9.30; Cl, 5.71%. UV-vis [CH_3CN, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 258 (15000). ^{1}H NMR (CD_3CN): δ 8.82 (3H, d), 8.56 (3H, t), 8.04 (3H, d), 8.02 (3H, d), 4.23 (6H, s).

X-Ray structural determinations

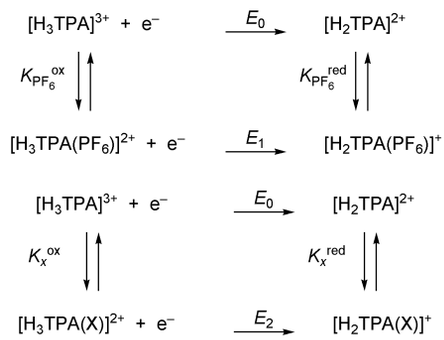
Single crystals of $[H_3TPA(CF_3SO_3)](CF_3SO_3)(PF_6)$, $\{[H_3TPA(Br)](PF_6)_2\}_2\cdot CH_3CN\cdot CH_3OH$, and $\{[H_3TPA(Cl)](PF_6)_2\}_2$ were obtained from CH_3OH, CH_3OH and CH_3OH–CH_3CN solutions, respectively. X-Ray data of $[H_3TPA(CF_3SO_3)](CF_3SO_3)(PF_6)$ and $\{[H_3TPA(Cl)](PF_6)_2\}_2$ were collected with graphite-monochromated Mo-Kα radiation on a Rigaku RAXIS-RAPID imaging plate area detector at 20 °C and −173 °C, respectively. X-Ray data of $\{[H_3TPA(Br)](PF_6)_2\}_2\cdot CH_3CN\cdot CH_3OH$ were collected with graphite-monochromated Mo-Kα radiation on a Rigaku AFC7R diffractometer at −60 °C. The structures were solved by direct methods (DIRDIF)[32] and expanded using Fourier techniques. The non-hydrogen atoms of all complexes were refined anisotropically except the carbon and oxygen atoms of the solvent CH_3OH in $\{[H_3TPA(Br)](PF_6)_2\}_2\cdot CH_3CN\cdot CH_3OH$ by the full-matrix least-squares method. Because the two atom types were not distinguishable, hydrogen atoms were located on calculated positions except for the hydrogen atoms on CH_3OH and CH_3CN in $\{[H_3TPA(Br)](PF_6)_2\}_2\cdot CH_3CN\cdot CH_3OH$ and hydrogen atoms bonded to nitrogen atoms in $\{[H_3TPA(Cl)](PF_6)_2\}_2$. Attachment of the hydrogens of the solvents was not made and hydrogens bonded to nitrogen atoms in $\{[H_3TPA(Cl)](PF_6)_2\}_2$ were found from the difference map and refined. All calculations were performed using SHELX-97[33] and TEXSAN.[34] The crystallographic data of the three anion complexes are summarized in Table 1.

CCDC reference numbers 184348–184350.

See http://www.rsc.org/suppdata/dt/b2/b209331f/ for crystallographic data in CIF or other electronic format.

Electrochemical characterization of anion complexes

Since the H_3TPA^{3+} receptor cannot be isolated in free form, the anion exchange process as described below was considered using $[H_3TPA(PF_6)]^{2+}$ as a starting complex.



The ΔE values (indicated in Table 3) were ratios

$$\frac{K_x^{ox}/K_x^{red}}{K_{PF_6}^{ox}/K_{PF_6}^{red}}$$

for two complexes derived as follows:

$$\Delta E = E_2 - E_1$$
$$= E_0 + 0.059 \log\left(K_x^{ox} / K_x^{red}\right)$$
$$-\left(E_0 + 0.059 \log\left(K_{PF_6}^{ox} / K_{PF_6}^{red}\right)\right)$$

Other measurements

Cyclic voltammetry was performed with a Hokuto HA-501 potentiostat and a Hokuto HB-105 function generator equipped with a Graphtec WX2400 X-Y recorder or Hokuto HZ-3000. The working and the counter electrodes were a glassy-carbon disk and a platinum wire, respectively. Cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1}. The sample solutions (*ca.* 1.0 mM) containing 0.1 M TBAX-acetonitrile [TBA = tetra(n-butyl)ammonium; X = PF_6, CF_3SO_3, Br, or Cl] were deoxygenated with a stream of nitrogen gas. The reference electrode was Ag/Ag^+ and the half-wave potential of Fc^+/Fc ($E_{1/2}(Fc^{+/0})$) *vs.* Ag/Ag^+ was 0.015 V in CH_3CN. Electronic spectra were recorded on a Shimadzu 2550 or HP 5254A spectrophotometer at 20 °C. IR spectra were recorded on a Perkin Elmer Spectrum GX infrared spectrophotometer. ^1H NMR spectra were measured on a JEOL-Lambda 300 (300 MHz) or Bruker AVANCE 600 (600 MHz) spectrometer.

Results and discussion

Crystal structural studies of $[H_3TPA(CF_3SO_3)](CF_3SO_3)(PF_6)$, $[H_3TPA(Br)](PF_6)_2$, and $[H_3TPA(Cl)](PF_6)_2$ complexes

Crystal structures of cationic moieties in the anion complexes $[H_3TPA(CF_3SO_3)](CF_3SO_3)(PF_6)$, $[H_3TPA(Br)](PF_6)_2$, and $[H_3TPA(Cl)](PF_6)_2$ are shown in Fig. 1, while their structural parameters are summarized in Table 2. The anion receptor complex $[H_3TPA(CF_3SO_3)]^{2+}$ consists of one H_3TPA^{3+} cation and one $CF_3SO_3^-$ anion, while other $CF_3SO_3^-$ and PF_6^- anions are located apart. The $CF_3SO_3^-$ anion is bound with two pyridiniumylmethyl groups through two hydrogen bonds between one oxygen atom O1 of $CF_3SO_3^-$ and two nitrogen atoms N2 and N3 of H_3TPA^{3+}. The remaining pyridiniumylmethyl group containing N4 does not participate in the hydrogen bonding formation. The distances of O1–N2 and O1–N3 were estimated as 2.874(3) and 2.813(3) Å which are similar to those of common N–O hydrogen bonds.[2-4] The distance S1–O1 [1.453(3) Å] is longer than those of S1–O2 [1.432(3) Å] and S1–O3 [1.439(3) Å]. As reported in the $[H_3TPA(SO_4)](NO_3)$ complex,[29] only the O1 atom of the $CF_3SO_3^-$ anion was involved in the hydrogen bonding with the H_3TPA^{3+} receptor. A number of guest anions have been bound with polyammonium receptors *via* electrostatic interaction and hydrogen bonding, but this is the first example of a structurally characterized complex with the $CF_3SO_3^-$ anion. Although this anion has a less symmetrical structure and is larger in size, our H_3TPA^{3+} receptor effectively covered one face of this anion keeping the opposite face exposed.

In contrast to $[H_3TPA(CF_3SO_3)](CF_3SO_3)(PF_6)$, $[H_3TPA(Br)](PF_6)_2$ has two crystallographically independent chiral structures which are included per unit cell but whose overall structures have similar characteristics. In this complex, one Br^- anion forms a hydrogen bond with three pyridiniumylmethyl groups and is nicely accommodated in the H_3TPA^{3+} cavity. The bond distances of Br–N2, –N3, and –N4 are estimated as 3.369(6), 3.304(5), and 3.280(5) Å, respectively. These are significantly shorter than the sum of van der Waals radii of N and Br atoms (3.45 Å). $[H_3TPA(Cl)](PF_6)_2$ also has two crystallographically independent chiral structures in one unit cell, though its space group is different from that of $[H_3TPA(Br)](PF_6)_2$. Based on the three hydrogen bonds with pyridinium

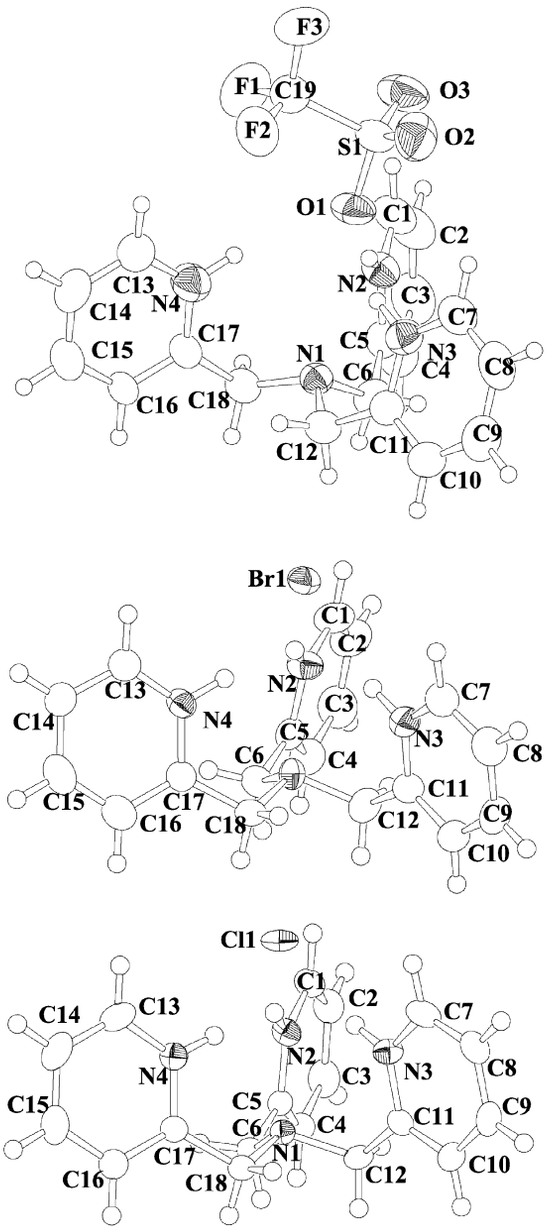


Fig. 1 Molecular structures of complex cations of $[(H_3TPA)(CF_3SO_3)]$-$PF_6{\cdot}CF_3SO_3$ (upper), $[(H_3TPA)(Br)](PF_6)_2$ (middle), and $[(H_3TPA)$-$(Cl)](PF_6)_2$ (lower) with the atomic numbering scheme showing 40 (upper), 50% (middle and lower) probability thermal ellipsoids.

groups of the H_3TPA^{3+} receptor, one Cl^- anion is nicely trapped in the three-dimensional receptor cavity. The bond distances of Cl–N2, –N3, and –N4 are observed as 3.061(3), 3.034(3), and 3.094(3) Å, respectively, and are also shorter than the sum of van der Waals radii of N and Cl atoms (3.30 Å). The observed distances are comparable to those of hydrotris(3-*tert*-butyl-pyrazolin-2-ium)borate $[HB(3\text{-}^tBupzH)_3]$,[28] in which the Cl^- anion is similarly trapped in the tripodal cavity by forming three hydrogen bonds.

The crystal structures of the three complexes obtained clearly indicate that H_3TPA^{3+} offers versatile anion coordination modes, which depended on the anion geometry. Table 2 shows that the bond distance of nitrogen–nitrogen (N2–N3, 4.14 Å) is somewhat shorter than those of N3–N4 (4.29 Å) and N2–N4 (4.27 Å) in the $[H_3TPA(CF_3SO_3)]^{2+}$ complex. Since these distances relate well with the hydrogen bonding strength with the anion, two pyridinium rings containing N2 and N3 are situated in close proximity *via* complexation, though N4 nitrogen does not participate in the hydrogen bond formation. In contrast, the distances of N2–N3, N3–N4 and N2–N4 are similar to each

Table 2 Selected bond lengths (Å) for $[(H_3TPA)(CF_3SO_3)]CF_3SO_3{\cdot}PF_6$, $\{[(H_3TPA)Br](PF_6)_2\}_2{\cdot}CH_3CN{\cdot}CH_3OH$, and $\{[(H_3TPA)Cl](PF_6)_2\}_2$

Bond lengths(Å)	$[(H_3TPA)(CF_3SO_3)]CF_3SO_3{\cdot}PF_6$	$\{[(H_3TPA)Br](PF_6)_2\}_2{\cdot}CH_3CN{\cdot}CH_3OH$	$\{[(H_3TPA)Cl](PF_6)_2\}_2$
X–N2	2.874(3)	3.369(6)	3.061(3)
X–N3	2.813(3)	3.304(5)	3.034(3)
X–N4	3.262(3)	3.280(5)	3.094(3)
X–N2N3N4[a]	1.709(4)	2.2469(9)	1.965(1)
S1–O1	1.453(3)		
S1–O2	1.432(3)		
S1–O3	1.439(3)		
N2–N3	4.14	4.24	4.03
N3–N4	4.29	4.19	3.96
N2–N4	4.27	4.22	4.11

Hydrogen bonding values (Å and °) for $[(H_3TPA)(CF_3SO_3)]CF_3SO_3{\cdot}PF_6$

	N–H	H–O1	N–O1	N–H–O1
N2–H ··· O1	0.94	1.97	2.874(3)	160.3
N3–H ··· O1	0.94	1.89	2.813(3)	164.5
N4–H ··· O1	0.94	2.36	3.262(3)	161.2

Hydrogen bonding values (Å and °) for $\{[(H_3TPA)Br](PF_6)_2\}_2{\cdot}CH_3CN{\cdot}CH_3OH$

	N–H	H–Br	N–Br	N–H–Br
N2–H ··· Br	0.95	2.47	3.369(6)	158.8
N3–H ··· Br	0.95	2.41	3.304(5)	158.5
N4–H ··· Br	0.95	2.37	3.280(5)	158.7

Hydrogen bonding values (Å and °) for $[(H_3TPA)Cl](PF_6)_2$

	N–H	H–Cl	N–Cl	N–H–Cl
N2–H ··· Cl	0.92	2.19	3.061(3)	158.2
N3–H ··· Cl	0.93	2.15	3.034(3)	159.0
N4–H ··· Cl	0.91	2.25	3.094(3)	153.4

[a] Distance from X to a plane consisting of N2, N3, and N4.

Table 3 Redox potentials of the complexes and pK_b values of the anions in CH_3CN

	E_{pc}/V[a] ($[M]^{2+}/[M]^+$)	ΔE/mV[b]	pK_b[c]
$[H_3TPA(PF_6)]^{2+}$	−1.31	0	> 30
$[H_3TPA(CF_3SO_3)]^{2+}$	−1.37	60	29.6
$[H_3TPA(Br)]^{2+}$	−1.40	90	26.7
$[H_3TPA(Cl)]^{2+}$	−1.44	130	23.3

[a] E_{pc} *vs.* Ag/Ag^+. [b] $\Delta E = E_{pc}(PF_6) - E_{pc}(X)$. [c] See refs. 36 and 40.

other in $[H_3TPA(Br)]^{2+}$ and $[H_3TPA(Cl)]^{2+}$ complexes: averaged distances were estimated as 4.22 Å in $[H_3TPA(Br)]^{2+}$ and 4.03 Å in $[H_3TPA(Cl)]^{2+}$. A similar trend was confirmed when bond angles of Br–H–N and Cl–H–N were compared.

IR spectral studies of $[H_3TPA(PF_6)](PF_6)_2$, $[H_3TPA(CF_3SO_3)](PF_6)_2$, $[H_3TPA(Br)](PF_6)_2$, and $[H_3TPA(Cl)](PF_6)_2$ complexes

The strength of hydrogen bonding between the anion and pyridinium group reflects on IR absorptions observed in the region from 2600 to 3400 cm^{-1}. Fig. 2 shows IR spectra of the four anion receptor complexes, $[H_3TPA(PF_6)](PF_6)_2$, $[H_3TPA(CF_3SO_3)](PF_6)_2$, $[H_3TPA(Br)](PF_6)_2$, and $[H_3TPA(Cl)](PF_6)_2$, which were measured as KBr pellets after mixing each anion complex (*ca.* 2–3 mg) with a large excess of KBr (200 mg).

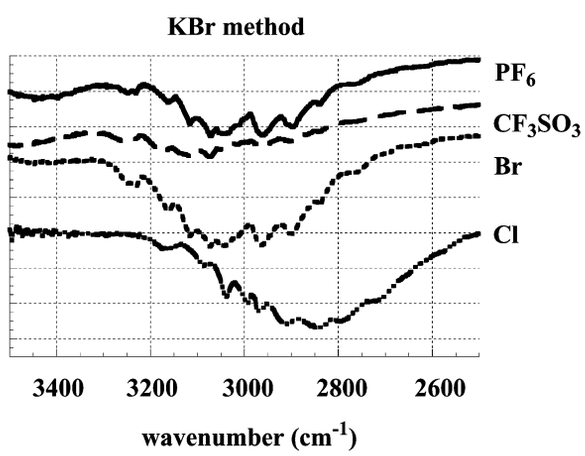


Fig. 2 IR spectral changes of $[H_3TPA(PF_6)](PF_6)_2$, $[H_3TPA(CF_3SO_3)](PF_6)_2$, $[H_3TPA(Br)](PF_6)_2$, and $[H_3TPA(Cl)](PF_6)_2$ complexes.

Some peaks assigned in connection with N ··· H ··· X hydrogen bonding appeared in the range 2600–3400 cm^{-1} in each spectrum.

When the complex $[H_3TPA(PF_6)](PF_6)_2$, $[H_3TPA(CF_3SO_3)](PF_6)_2$, or $[H_3TPA(Br)](PF_6)_2$ is mixed with an excess of KBr in the solid state, several peaks concerning N ··· H ··· X hydrogen bonds for $[H_3TPA(PF_6)](PF_6)_2$, $[H_3TPA(CF_3SO_3)]$-

$(PF_6)_2$, and $[H_3TPA(Br)](PF_6)_2$ appeared at the same wavenumbers of 3254, 3160, 3111, 3074, 3051, 2964, and 2904 cm^{-1}. These mean that PF_6^- in $[H_3TPA(PF_6)]^{2+}$ or $CF_3SO_3^-$ in $[H_3TPA(CF_3SO_3)]^{2+}$ is easily replaced with Br^- in KBr to form $[H_3TPA(Br)]^{2+}$. Although the crystal structure of $[H_3TPA(PF_6)](PF_6)_2$ is not indicated (see Fig. S1 in ESI †), its preliminary structural analysis indicated that one PF_6^- anion was contained within the H_3TPA^{3+} cavity by forming hydrogen bonds as found in the other three complexes. In contrast, peaks of $[H_3TPA(Cl)](PF_6)_2$ appeared at different positions compared with those obtained in the above three complexes, suggesting that Cl^- anions have a basicity high enough not to be replaced with the large excess Br^- ion.

^{1}H NMR titration studies

Since the PF_6^- anion is weakly bound in the $[H_3TPA(PF_6)]^{2+}$ complex and easily exchanged by $CF_3SO_3^-$, Br^-, and Cl^- anions, we can monitor anion exchange processes using ^{1}H NMR spectroscopy. Fig. 3 shows the ^{1}H NMR spectral changes obtained by addition of $^nBu_4NX$ (X = Cl or Br) to $[H_3TPA(PF_6)](PF_6)_2$ in CD_3CN, while Fig. 4 plots the chemical shifts of the protons on the 4- and 6-positions on the pyridinium ring

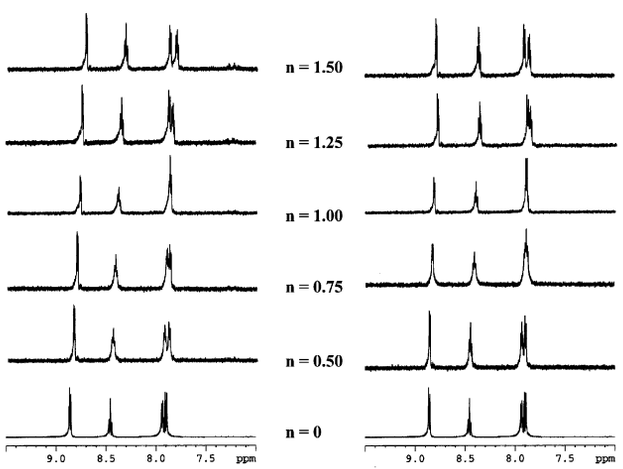


Fig. 3 ^{1}H NMR spectra obtained by addition of $^nBu_4NX$ [X = Cl (left), and Br (right)] to $[H_3TPA](PF_6)_3$ in CD_3CN.

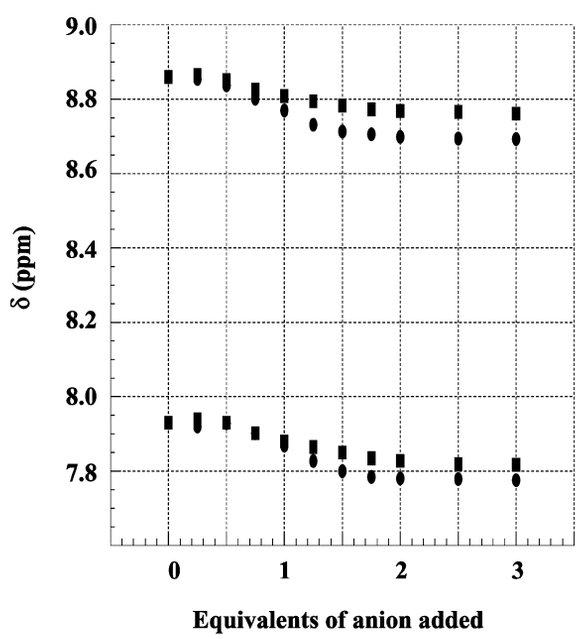


Fig. 4 ^{1}H NMR titration curves of $[H_3TPA(PF_6)](PF_6)_2$ and Cl^- (●) or Br^- (■) in CD_3CN; δ is the shift value of the 4- (lower) and 6-positioned (upper) protons on the pyridinium cations.

against the equivalent of Cl^- and Br^- anions added to the PF_6^- anion.

The addition of the Cl^- or Br^- anion to the solution of $[H_3TPA(PF_6)](PF_6)_2$ significantly shifted signals for four pyridinium ring protons to the high field side. The separated signals did not appear, indicating that the exchange of the PF_6^- with the guest anion (Cl^- or Br^-) in the H_3TPA^{3+} receptor cavity occurs dynamically faster than the NMR time scale. Since Z-shaped titration curves were obtained (Fig. 4), both PF_6^- anions located in and out of the H_3TPA^{3+} cavity are replaced stepwise with the added anions (Cl^- or Br^-) as described below.

$$[H_3TPA(PF_6)](PF_6)_2 + 3X^- \rightleftarrows [H_3TPA(X)](X)_2 + 3PF_6^-$$

Interestingly, the Cl^- anion induced larger shift values than the Br^- anion, supporting the opinion that the Cl^- anion was more tightly bound with the H_3TPA^{3+} receptor. We have tried to determine the stability constant of each anion exchange process, but the observed ^{1}H NMR spectral changes were too small to be able to analyze these processes quantitatively.

Cyclic voltammometric studies

The cyclic voltammogram (CV) of the CH_3CN solution containing the 0.5 mM $[H_3TPA(PF_6)](PF_6)_2$, $[H_3TPA(CF_3SO_3)](CF_3SO_3)(PF_6)$, $[H_3TPA(Br)](PF_6)_2$, or $[H_3TPA(Cl)](PF_6)_2$ was measured in the presence of 0.05 M TBAX {X = PF_6 for $[H_3TPA(PF_6)](PF_6)_2$, CF_3SO_3 for $[H_3TPA(CF_3SO_3)](CF_3SO_3)(PF_6)$, Br for $[H_3TPA(Br)](PF_6)_2$, or Cl for $[H_3TPA(Cl)](PF_6)_2$} as the supporting electrolyte. These anion receptor complexes have redox-active pyridinium groups, and showed three irreversible reduction waves based on the three pyridinium moieties in H_3TPA assigned to $[H_3TPA(X)]^{3+}/[H_2TPA(X)]^{2+}$, $[H_2TPA(X)]^{2+}/[HTPA(X)]^+$, and $[HTPA(X)]^+/[TPA(X)]^0$.[35] The E_{pc} values assigned to $[M]^{2+}/[M]^+$ of the $[H_3TPA(PF_6)]^{2+}$, $[H_3TPA(CF_3SO_3)]^{2+}$, $[H_3TPA(Br)]^{2+}$, and $[H_3TPA(Cl)]^{2+}$ are −1.31, −1.37, −1.40, and −1.44 V *vs.* Ag/Ag^+, respectively (Table 3). From the differences in reduction potentials of the four examined complexes, the ratios of the binding constants in the oxidized and reduced states

$$\frac{K_x^{ox} / K_x^{red}}{K_{PF_6}^{ox} / K_{PF_6}^{red}}$$

of the following equation are determined using the E_{pc} of $[H_3TPA(PF_6)]^{2+}$ as a reference (see the Experimental section).

Since the H_3TPA^{3+} receptor has a +3 charge and its reduced H_2TPA^{2+} form should have a significantly decreased affinity to the guest anion, it is possible to interpret that the potential shift (ΔE) depends largely on the ratio of K^{ox} and K^{red}.[37–39] The H_3TPA^{3+} similarly bound PF_6^-, Br^- and Cl^- anions *via* three hydrogen bonds, but its reduced form should have two pyridinium groups as anion binding sites. This indicates that the strength of the single hydrogen bond significantly influences the ΔE value in each anion complex system. Table 3 indicates that the potential shifted values (ΔE) drastically increase from 60 $\{[H_3TPA(CF_3SO_3)]^{2+}\}$, to 90 $\{[H_3TPA(Br)]^{2+}\}$, to 130 mV $\{[H_3TPA(Cl)]^{2+}\}$. Although the degree of the hydrogen bonding between the pyridinium hydrogen and the guest anion is probably proportional to the pK_b value of the anion,[40] the H_3TPA^{3+} receptor was confirmed as exhibiting similar anion selectivity under electrochemical conditions to those observed in the X-ray, IR, or NMR studies for anions in the series $Cl^- > Br^- > CF_3SO_3^- > PF_6^-$.

The present study shows that the H_3TPA^{3+} receptor, having three pyridinium groups, has an excellent binding ability for a variety of anions such as PF_6^-, $CF_3SO_3^-$, Br^-, and Cl^- anions. Since their guest anions have different sizes, symmetries, and pK_b values, this tripode can be viewed as a versatile anion

receptor. Interestingly, its anion selectivity was controlled by the nature of hydrogen bonding between the pyridinium hydrogen and the guest anion.

Acknowledgements

The authors are grateful to Professor Shinobu Itoh and Professor Akio Ichimura of Osaka City University for valuable comments on X-ray measurement of $[H_3TPA(Cl)](PF_6)_2$ and on cyclic voltammetry of anion-receptor complexes. They also thank Dr Satoshi Shinoda for valuable suggestions of NMR characterizations.

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