Inorg. Chem. **2004**, *43*, 3751–3755

Anion Binding with a Tripodal Amine

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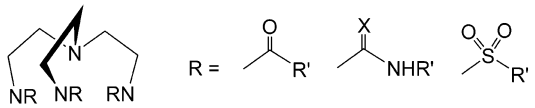
Received February 23, 2004

Binding studies of the tren-based amine, **L** (*N*,*N*′,*N*″-tris(2-benzylaminoethyl)amine), with inorganic anions and two crystal structures, $[H_3\mathbf{L}][H_2PO_4]_3 \cdot H_3PO_4$ and $[H_3\mathbf{L}][Br]_3$, are reported. NMR titration results indicate that the ligand binds $H_2PO_4^-$ and HSO_4^- more strongly than NO_3^- and halides. In the crystal structure of the phosphate complex, the ligand is triprotonated with the three arms pointing outward in a trigonal-planar-like arrangement. Four phosphate species are associated with the receptor, and have been assigned as three $H_2PO_4^-$ counterions located between each of the tren arms, and an additional H_3PO_4 molecule above the quasi-planar tren. The structure of the bromide complex is slightly different, although again the tren receptor is triprotonated and quasi-planar, but in this case C_{2v}-like symmetry is seen with two of the arms pointed in the same direction with a bromide ion in between. The other two bromides lie outside of the tren arms.

Introduction

Because of the amazing impact of anions in many important chemical and biological processes, achieving selective recognition of anionic species by synthetic receptors is a field of intense current interest.[1,2] Among the numerous design choices, trigonal receptors have been especially of interest because of their potential for binding molecules with C_3 rotation axes, such as nitrate, phosphate, and sulfate. An obvious building block for such C_3 topology is tris(aminoethyl)-amine, tren. Hence, a number of simple acyclic tren-derived amide, sulfonamide, urea, and thiourea receptors have been designed, and some have been found to exhibit highly selective binding for different anions.[3−9] The binding ability of these ligands for anions varies with the functional groups attached to the tren unit, with different functional moieties tending to modify the hydrogen bonding capability of the tren NH groups. Furthermore, the presence of an oxygen in the functional group allows for intermolecular hydrogen bonding. Such internal interactions, while potentially blocking the cavity,[6] can also provide a preorganization effect, resulting in an effective clawlike topology for incorporating guest species.



Of the many classes of supramolecular anion receptors, polyamine-based systems were the first[10] and, until recently, probably the most widely studied systems.[11,12] Nonetheless, the tren-based acyclic tripodal amines represent a somewhat missing link in a rather systematic perusal of anion binding with tren-based receptors, although some explorations into the potential of these simple ligands in the extraction of pertechnetate and perrhenate have been reported.[12] Given our interest in main group anions, we decided that further

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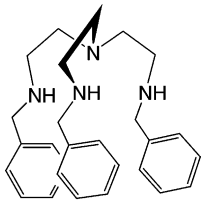
10.1021/ic049762b CCC: $27.50
Published on Web 05/19/2004

examinations of the anion binding capabilities of a substituted tren-based amine, **L**, were in order. It was not anticipated, however, that **L** would necessarily be selective for anions, because, when protonated, the primary amines should be repelled by each other, making the formation of a C_3-symmetric cavity unlikely. Herein we report the crystal structures of **L** with phosphate and bromide and the results of anion binding studies.



L

Experimental Section

General. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM 500 spectrometer at 500 MHz. Chemical shifts for samples were expressed in parts per million and calibrated against TMS as an external reference in a capillary tube. All the chemicals were purchased as reagent grade and were used without further purification. Mass spectra were recorded at the Mass Spectrometry Laboratory at the University of Kansas on a ZAB HS mass spectrometer. Elemental analyses were obtained from Desert Analytics Laboratory, Tucson, AZ.

Synthesis. *N*,*N*′,*N*″-Tris(2-benzylaminoethyl)amine, L. The Schiff base adduct of tren was obtained by dissolving tris(2-aminoethyl)amine (1.00 g, 6.84 mmol) in CH_3OH (100 mL) and slowly adding benzaldehyde (2.18 g, 20.5 mmol). The resulting mixture was stirred at room temperature for 24 h and concentrated to give an oily product, which was dried under vacuum. The Schiff base product was dissolved in CH_3OH (50 mL), and $NaBH_4$ (1.73 g, 45.7 mmol) was added. After stirring at room temperature for 24 h, the solvent was removed in vacuo. The resulting solid yellow residue was dissolved in 1 M aq NaOH solution (100 mL), and the aqueous phase was extracted by CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to give a light yellowish oil. The crude product was purified by column chromatography (silica, 2% CH_3OH in CH_2Cl_2). Yield: 2.0 g, 70%. FAB-MS: *m*/*z* 417.5 [**L**H$^+$]. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.30 (m, 15H, Ar*H*), 3.75 (s, 6H, ArCH_2), 2.70 (t, 6H, NHCH_2), 2.61 (t, 6H, NCH_2). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 140.1 (CH_2CAr), 128.3 (C_{ortho}), 128.0 (C_{meta}), 126.8 (C_{para}), 57.6 (ArCH$_2$), 54.1 (NHCH$_2$), 47.0 (NCH$_2$).

[H$_3$L][OTs]$_3$·3H$_2$O. L (0.50 g, 1.2 mmol) and TsOH·H_2O (0.92 g, 4.8 mmol) were each dissolved in CH_3OH (10 mL) and were mixed with stirring. Et_2O (20 mL) was added to the solution. A white precipitate formed, which was filtered off, washed with Et_2O, and dried in vacuo. Yield: 0.95 g, 80%. Anal. Calcd for $H_3C_{27}H_{36}N_4$·$3C_7H_7SO_3$·$3H_2O$: C, 58.40; H, 6.74; N, 5.68. Found: C, 58.10; H, 6.72; N, 5.54. FAB-MS: *m*/*z* 417.2 [H**L**$^+$], 589.1 [H_2**L**$^{2+}$ + TsO$^-$], 761.1 [H_3**L**$^{3+}$ + 2TsO$^-$]. ^{1}H NMR (500 MHz, D_2O, 3-(trimethylsilyl)propionic acid sodium salt,TSP): δ 7.66 (d, 6H, Ts*H*), 7.45 (m, 15H, Ar*H*), 7.34 (d, 6H, Ts*H*), 4.19 (s, 6H, ArCH_2), 3.10 (t, 6H, NHCH_2), 2.82 (t, 6H, NCH_2), 2.38 (s, 9H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 145.5 (Ts), 142.3 (CH_2CAr), 133.2 (C_{ortho}), 132.9 (C_{meta}), 132.8.8 (C_{para}), 132.4 (Ts), 132.3 (Ts), 128.2 (Ts), 54.1 (ArCH$_2$), 51.5 (NHCH$_2$), 46.4 (NCH$_2$), 23.4 (CH_3).

Table 1. Crystal Data and Structure Refinement for [H$_3$**L**][H_2PO_4]$_3$·H_3PO_4, **1**, and [H$_3$**L**][Br]$_3$, **2**

	1	**2**
empirical formula	$C_{27}H_{48}N_4P_4O_{16}$	$C_{27}H_{39}Br_3N_4$
fw	808.57	659.35
cryst syst	monoclinic	orthorhombic
space group	*Cc*	*Pca*2$_1$
a, Å	15.1148(17)	34.184(10)
b, Å	27.117(3)	5.4758(17)
c, Å	8.9168(10)	15.640(5)
α, deg	90	90
β, deg	95.783(2)	90
γ, deg	90	90
V (Å^3)	3636.1(7)	3286(2)
Z	4	4
d_{calcd} (g/cm^3)	1.477	1.496
λ (Å)	0.71073	0.71073
T (K)	100(2) K	100(2) K
F(000)	1704	1336
abs coeff (mm^{-1})	0.284	4.155
max, min trans	0.9832, 0.8806	0.7886, 0.2509
θ range (deg)	2.63−26.00	2.38−21.97
reflns collected	11104	11742
indep reflns	6294	3540
data/restraints/params	6294/932/598	3540/998/227
R_1,[a] wR_2[b]	0.0771, 0.2371	0.0981, 0.2769
GOF (F^2)	1.033	1.090
obsd data [$I > 2\sigma(I)$]	3832	2662
largest diff peak and hole (e Å^{-3})	0.610 and 0.596	1.993 and −1.190

[a] R1(obsd data) = $\sum||F_o| - |F_o||/\sum|F_o|$. [b] wR2 (all data) = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

[H$_3$L][H_2PO_4]$_3$·H_3PO_4, 1. The phosphate salt of **L** was obtained from dropwise addition of H_3PO_4 (0.1 mL, 48%) to a methanolic solution of **L** (0.10 g, 0.24 mmol), and the mixture was stored at 0 °C. A light yellow precipitate formed after 2 days, was collected by filtration, and was washed with Et_2O. Yield: 0.165 g, 85%. Anal. Calcd for $H_3C_{27}H_{36}N_4$·$3H_2PO_4$·H_3PO_4·H_2O: C, 39.23; H, 6.10; N, 6.78. Found: C, 39.25; H, 6.08; N, 6.85. FAB-MS: *m*/*z* 417.2 [H**L**$^+$], 515.1 [H_2**L**$^{2+}$ + $H_2PO_4^-$], 613.1 [H_3**L**$^{3+}$ + $2H_2PO_4^-$], 711.1 [H_4**L**$^{4+}$ + $3H_2PO_4^-$], 806.0 [H_5**L**$^{5+}$ + $4H_2PO_4^-$]. ^{1}H NMR (500 MHz, D_2O, TSP): δ 7.48 (m, 15H, Ar*H*), 4.20 (s, 6H, ArCH_2), 3.09 (t, 6H, NHCH_2), 2.82 (t, 6H, NCH_2). ^{13}C NMR (125 MHz, D_2O, TSP): δ 130.6 (CH_2CAr), 130.3 (C_{ortho}), 130.1 (C_{meta}), 129.6 (C_{para}), 51.4 (ArCH$_2$), 48.9 (NHCH$_2$), 43.6 (NCH$_2$).

[H$_3$L(Br)][Br]$_2$ ·0.5H$_2$O, 2. L (0.14 g, 0.34 mmol) was dissolved in CH_3OH (2 mL). An aqueous solution of HBr (48%) was added until the pH of the solution was below 1. The resulting cloudy solution was stored in a desiccator containing Et_2O. A yellow precipitate formed the next day, was collected by filtration, and was washed with Et_2O. Yield: 0.170 g, 75%. Anal. Calcd for $H_3C_{27}H_{36}N_4$·$3Br$·$0.5H_2O$: C, 48.52; H, 6.03; N, 8.38. Found: C, 48.99; H, 6.05; N, 8.77. FAB-MS: *m*/*z* 417.2 [H**L**$^+$], 498.0 [H_2**L**$^{2+}$ + Br$^-$]. ^{1}H NMR (500 MHz, D_2O, TSP): δ 7.50 (m, 15H, Ar*H*), 4.23 (s, 6H, ArCH_2), 3.13 (t, 6H, NHCH_2), 2.85 (t, 6H, NCH_2). ^{13}C NMR (125 MHz, D_2O, TSP): δ 130.7 (CH_2CAr), 130.3 (C_{ortho}), 130.2 (C_{meta}), 129.7 (C_{para}), 51.5 (ArCH$_2$), 49.0 (NHCH$_2$), 43.7 (NCH$_2$).

X-ray Crystallography. Attempts to grow crystals of a variety of anions with **L** resulted in the isolation of two salts suitable for X-ray crystallography, the phosphate (**1**) and bromide (**2**) "complexes". Crystals of **1** suitable for X-ray crystallography were obtained by recrystallization from a CH_3OH solution and isolated after 2 days of keeping the solution under Et_2O diffusion in a desiccator. Crystals of **2** were grown by recrystallization from a CH_3OH/H_2O (5:1, v/v) solution under slow diffusion in a desiccator.

The crystallographic data and details of data collection for **1** and **2** are given in Table 1. Intensity data for the crystals were collected

Table 2. P−O Distances (Å) for $[H_3\mathbf{L}][H_2PO_4]_3{\cdot}H_3PO_4$, **1**

atoms	distance	atoms	distance
P(1A)−O(1A)	1.451(7)	P(1A′)−O(1A′)	1.462(7)
P(1A)−O(2A)	1.499(7)	P(1A′)−O(2A′)	1.481(8)
P(1A)−O(3A)	1.448(7)	P(1A′)−O(3A′)	1.462(8)
P(1A)−O(4A)	1.465(7)	P(1A′)−O(4A′)	1.460(8)
P(1B)−O(1B)	1.459(8)	P(1B′)−O(1B′)	1.455(7)
P(1B)−O(2B)	1.470(8)	P(1B′)−O(2B′)	1.495(7)
P(1B)−O(4B)	1.472(8)	P(1B′)−O(3B′)	1.486(7)
P(1B)−O(3B)	1.482(8)	P(1B′)−O(4B′)	1.482(7)
P(1C)−O(1C)	1.462(8)	P(1C′)−O(1C′)	1.459(8)
P(1C)−O(2C)	1.472(8)	P(1C′)−O(2C′)	1.467(8)
P(1C)−O(3C)	1.472(8)	P(1C′)−O(3C′)	1.467(8)
P(1C)−O(4C)	1.458(8)	P(1C′)−O(4C′)	1.471(8)
P(1D)−O(1D)	1.462(7)		
P(1D)−O(2D)	1.467(7)		
P(1D)−O(3D)	1.470(6)		
P(1D)−O(4D)	1.484(8)		

using a Bruker APEX CCD area detector mounted on a Bruker D8 goniometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).[13] The data were collected at 100(2) K, and intensity data were measured as a series of ω and θ oscillation frames. The detector was operated in 512 × 512 mode and was positioned 5.054 cm from the sample. Coverage of unique data was 99.6% complete for **1** to 26.00° in θ and 99.9% complete for **2** to 21.97° in θ. Cell parameters were determined from a least-squares fit of 2483 peaks in the range 2.63° < θ < 20.45° for **1** and 2981 peaks in the range 2.60° < θ < 20.26° for **2**. Virtually no decay was observed, on the basis of data obtained for a number of peaks monitored at both the beginning and end of data collection. The data were corrected for absorption by the semiempirical method.[14] Lorentz and polarization corrections were applied, and the data were merged to form a set of independent data for each sample. Space groups of both the monoclinic, **1**, and orthorhombic, **2**, samples were determined by systematic absences and statistical tests and verified by subsequent refinement. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2.[15]

In the phosphate structure, three of the four phosphate groups were disordered and were modeled in two orientations. The occupancies refined to (A) 0.585(14), 0.415(14); (B) 0.343(11), 0.657(11); and (C) 0.545(11), 0.455(11) for the unprimed and primed atoms, respectively. Restraints on the positional parameters of all phosphate groups and the displacement parameters of the disordered atoms were required. Interatomic P−O distances are shown in Table 2.

In the bromide structure, two of the arms of the cation, C2−C11 and N14−C21, were significantly disordered and were modeled in two orientations with refined occupancies of 0.568(13) and 0.432(13) for the unprimed and primed atoms. The extensive disorder produced a data set that did not scatter to high scattering angles, so it was truncated at 0.95 Å (21.95° in θ).

Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms in the phosphate structure were refined with anisotropic displacement parameters, while only the bromide ions were refined anisotropically in the structure of **2**, because of the truncation of the data. Hydrogens were not placed on the phosphates in structure **1** because of the disorder. Hydrogen atom displacement parameters were set to 1.2 times the displacement parameters of the bonded atoms. Selected hydrogen bonding interactions are shown in Table 3.

Table 3. Hydrogen Bonds Å for $[H_3\mathbf{L}][H_2PO_4]_3{\cdot}H_3PO_4$, **1** and $[H_3\mathbf{L}][Br]_3$, **2**

atoms	distance	atoms	distance
	1		
N(4)−H(4A)···O(1A)	2.86(2)	N(14)−H(14B)···O(1C)	2.916(16)
N(4)−H(4A)···O(1A′)	2.73(3)	N(14)−H(14B)···O(1C′)	2.648(14)
N(4)−H(4B)···O(1B)	3.06(2)	N(24)−H(24A)···O(1A)	2.85(2)
N(4)−H(4B)···O(1B′)	2.669(10)	N(24)−H(24A)···O(1A′)	2.81(3)
N(14)−H(14A)···O(1A)	2.76(2)	N(24)−H(24B)···O(1D)	2.855(12)
N(14)−H(14A)···O(1A′)	2.97(3)		
	2		
N(4)−H(4A)···Br(1)[a]	3.395(19)	N(14)−H(14B)···Br(2)	3.32(3)
N(4)−H(4B)···Br(1)	3.333(19)	N(14′)−H(14C)···Br(1)	3.37(4)
N(4′)−H(4′A)···Br(3)[b]	3.39(2)	N(14′)−H(14D)···Br(1)[a]	3.66(4)
N(4′)−H(4′B)···Br(1)	3.07(2)	N(24)−H(24B)···Br(2)[b]	3.292(13)
N(14)−H(14A)···Br(1)	3.26(3)	N(24)−H(24A)···Br(3)	3.066(13)

[a,b] Symmetry transformations used to generate equivalent atoms: [a] $x, y + 1, z$; [b] $-x + {}^1/_2, y, z - {}^1/_2$.

Binding Constants. Binding constants were obtained by ^{1}H NMR (500 MHz Bruker) titrations of $[H_3\mathbf{L}][OTs]_3$ with $[n\text{-Bu}]_4N^+A^-$ ($A^- = H_2PO_4^-$, HSO_4^-, NO_3^-, Cl^-, and Br^-) in $CDCl_3$. The initial concentration of the ligand was $[H_3\mathbf{L}^{3+}]_0$ = 2 mM. Aliquots of anion were from a stock solution of anion (20 mM). Trimethylsilane (TMS) in $CDCl_3$ was used as an external reference in a capillary tube, and each titration was performed by 20 measurements at room temperature. The association constants, K, were calculated by fitting the change in the NH chemical shift with a 1:1 association model with Sigma Plot software. The equations $\Delta\delta = ([A]_0 + [L]_0 + 1/K - ([A]_0 + [L]_0 + 1/K)^2 - 4[L]_0[A]_0)^{1/2})\Delta\delta_{max}/2[L]_0$ (where L is ligand and A is anion) were used.[16] The error limit in K was less than 10%.

Results and Discussion

Synthesis. The synthesis of **L** is straightforward and involves a simple Schiff base condensation of the amine, tren, with 3 equiv of the aldehyde, benzaldehyde, followed by borohydride reduction of the resulting imines to amines.[17] Purification of the resulting viscous oil is readily accomplished by column chromatography on neutral alumina, using a CH_2Cl_2 solution containing 2% CH_3OH. The free base was protonated by reaction with TsOH. Triprotonation was confirmed by ^{1}H NMR integration and elemental analysis, in addition to the two crystal structures.

Crystallographic Studies. $[H_3\mathbf{L}][H_2PO_4]_3{\cdot}H_3PO_4$ (**1**). The phosphate complex, $[H_3\mathbf{L}][H_2PO_4]_3{\cdot}H_3PO_4$ (**1**), was obtained from reaction of the free base with phosphoric acid in CH_3OH. There are four phosphate "species" for each tren unit (Figure 1A). In the crystal structure alternating tren and phosphate units are stacked in layers along the *c* axis (Figure 2A). Three additional phosphate units are located in the

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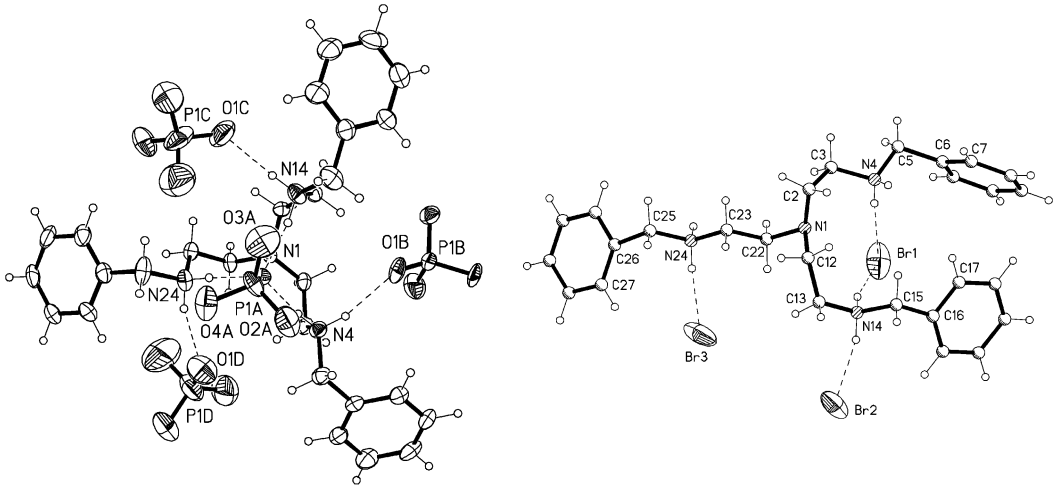
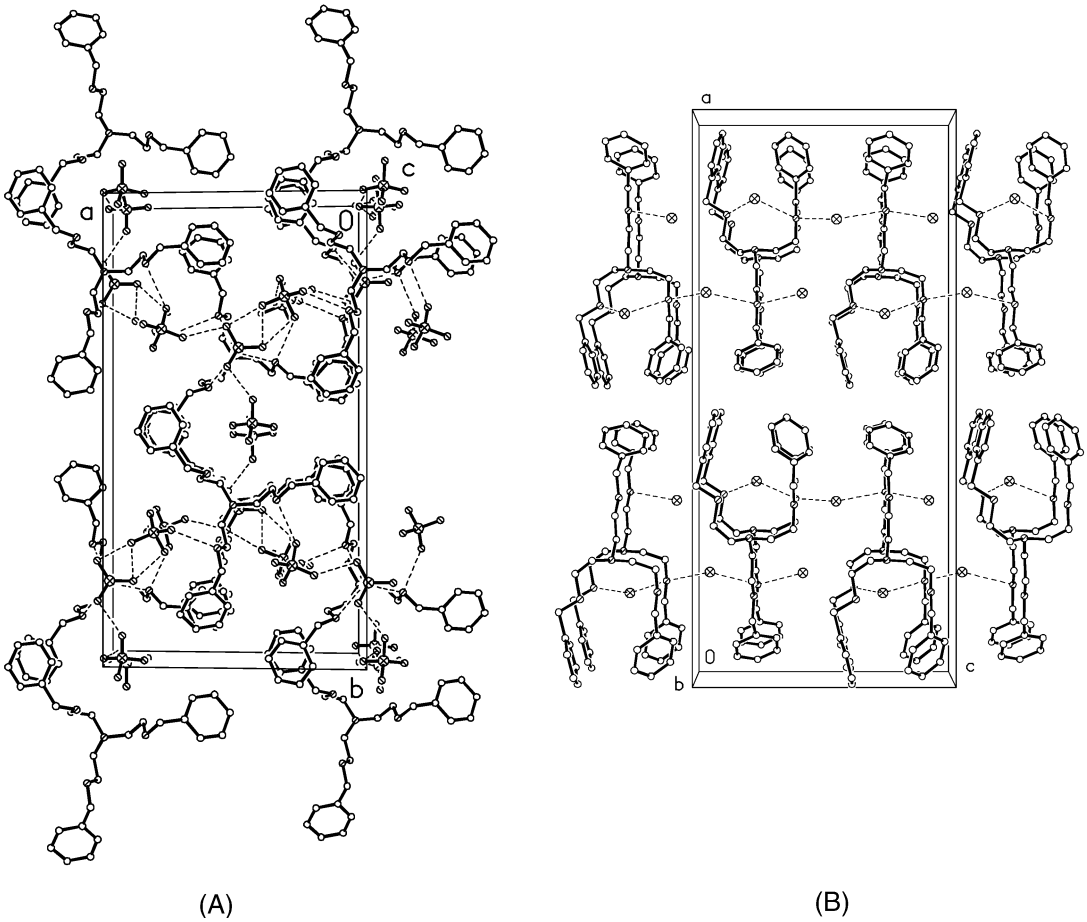


(**A**) (**B**)

Figure 1. ORTEP drawing of $[H_3\mathbf{L}][H_2PO_4]_3{\cdot}H_3PO_4$, **1** (A), and $[H_3\mathbf{L}][Br]_3$, **2** (B). Thermal ellipsoids are at 50% probability.



(A) (B)

Figure 2. Packing diagram of $[H_3\mathbf{L}][H_2PO_4]_3{\cdot}H_3PO_4$, **1** (A) and $[H_3\mathbf{L}][Br]_3$, **2** (B), as viewed down the *a* axis.

channels between the trens. Because of the disorder, it was not possible to locate hydrogens for the phosphates, in order to unambiguously determine their degree of protonation. However, given that the crystals were grown under acidic conditions, it is chemically reasonable to expect three dihydrogen phosphates and one phosphoric acid to be present. A similar finding was reported by us for a macrocyclic complex with phosphate.[18] The most plausible assignment is that the P1A phosphate stacked between the tren units is a molecule of phosphoric acid. This assignment would make sense given that only one of its oxygens (O1A) shows hydrogen bonding contacts with the protonated tren (Table 3). Of the remaining three phosphate groups situated between the arms of the tren unit, each has one hydrogen bond with

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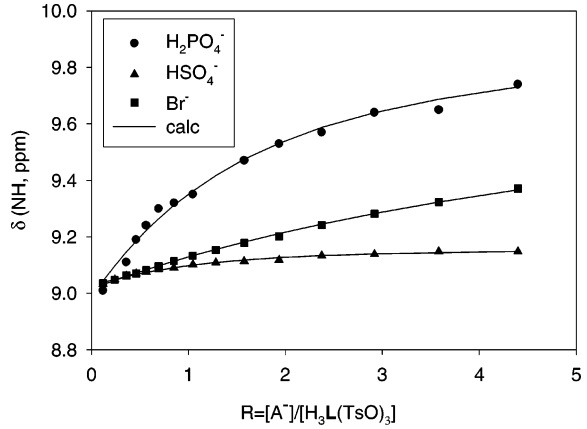

Figure 3. ^{1}H NMR titration curves of $[H_3\mathbf{L}][OTs]_3$ with *n*-$[n\text{-Bu}]_4N^+$ salts of $H_2PO_4^-$, HSO_4^-, and Br^-.

a protonated tren amine. There also are hydrogen bonding interactions between the phosphates.

An interesting comparison can be made with this tren-based receptor and the crystal structure of simple tren with phosphate, $[N\{(CH_2)_2NH_3\}_3]_8[HPO_4]_{12}\cdot 33H_2O$.[19] The structure indicates a large number of anions and ligands held by hydrogen bonding, although in this case the tren exhibits a clawlike conformation, with chelation to HPO_4^{2-} counterions.

The bromide complex, **2**, crystallized as the bromide salt of triprotonated $H_3\mathbf{L}^{3+}$ with three bromide ions (Figure 1B). The tren units stack along the *b* axis, with two of the arms oriented in the same direction, and the third arm extended in the opposite direction (Figure 2B). The two arms pointed in the same direction are hydrogen bonded to one of the bromide ions (Table 3), held between them. These two arms are disordered, and one of the external bromides (Br2) is also hydrogen bonded to N14 of one of the disordered models. The third bromide is hydrogen bonded to N24 of the "extended arm". The hydrogen bonding distances N−H···Br^- range from 3.06 to 3.66 Å.

NMR Studies. The addition of tetrabutylammonium anions salts ($[n\text{-Bu}]_4N^+A^-$: $A^- = H_2PO_4^-$, HSO_4^-, NO_3^-, Br^-, and Cl^-) to the tosylate salt of $H_3\mathbf{L}^{3+}$ in $CDCl_3$ led to downfield shifts of the N−H resonances, which indicates the participation of ligand N−H protons in the binding of anions via hydrogen bonding interactions. Titration data gave the best fit for 1:1 association models of host to guest (see Figure 3). Binding data are presented in Table 4. Results indicate that the receptor $H_3\mathbf{L}^{3+}$ binds both phosphate and sulfate with log $K > 3$, which is considerably higher than that observed for the other anions (log $K < 2$). Both the 1:1 association models and the high affinity for the oxo acid anions at first appear somewhat puzzling and in contradiction to the crystal structure data, which indicates three counteranions. However, it is the two oxo acids, of all the anions examined, that exhibited high affinity, and we have observed a similar binding trend with diamino−tetramido and diamino−tetrathioamido macrocycles.[20,21] The analogy between these latter macrocycles and $H_3\mathbf{L}^{3+}$ is the presence of the amines, which can participate in proton exchange with the oxo acids, leaving either HPO_4^{2-} or PO_4^{3-} as well as SO_4^{2-}. While we were not able to get definitive solution proof of this type of proton equilibria for **L**, we have structural and solution NMR evidence in an amide-based cryptand that the bridgehead amines can become protonated upon binding sequentially one and two chloride ions.[22] Increased affinities with increased anion (and cation) charge have also been observed in binding studies with polyammonium receptors, and may additionally play a role in sulfate and phosphate interactions with **L**.[1,11]

Table 4. Binding Data of $[H_3L][OTs]_3$ with Anions in $CDCl_3$

anions	log K (M^{-1})
$H_2PO_4^-$	3.25
HSO_4^-	3.20
NO_3^-	1.55
Cl^-	1.80
Br^-	1.70

In conclusion, it would certainly be appealing to make an argument that the heightened binding constants for phosphate and sulfate are an indication of selectivity of $H_3\mathbf{L}^{3+}$ for these two anions. However, the crystallographic evidence indicates that the effect is most probably attributed to the aforementioned factors, charge and basicity, rather than true selectivity of this receptor candidate for those anions.

Acknowledgment. The authors thank the National Science Foundation, CHE-0316623, for support of this work, and CHE-0079282 for the purchase of the X-ray instrument.

Supporting Information Available: Two crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049762B

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