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A Rational Approach to Selective Recognition of NH_4^+ over K^+[**]

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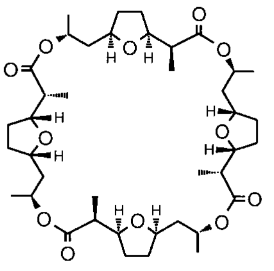
Over the past several decades there has been considerable interest in developing receptors for NH_4^+. Such receptors are desirable as sensors in clinical analysis and in environmental chemistry.[1] For example, concentrations of urea or creatinine in biological samples can be determined indirectly by measuring the amount of NH_4^+ released upon enzyme-catalyzed hydrolysis of the substrates. These receptors are also useful for determining the concentrations of NH_4^+ or ammonia in drinking water and in the air. One of the most effective NH_4^+ receptors is nonactin (**1**), a natural antibiotic agent that is currently used commercially in ion-selective electrodes (ISE).[1, 2] However, a serious drawback of nonactin is that it binds only about ten times more tightly to NH_4^+ than to K^+. Similarly, crown ethers show little or no selectivity for binding NH_4^+ over K^+.[3] Here we report a rationally designed receptor (**2**) that is highly selective for binding NH_4^+ over K^+.



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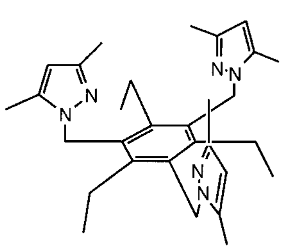

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The main reason why it has been difficult to design receptors that are highly selective for binding NH_4^+ over K^+ is that the sizes of the two monocations are closely matched. However, NH_4^+ and K^+ are clearly distinct in terms of their symmetry. K^+ has a closed valence electron shell with spherical symmetry and prefers ionic bonds with coordination numbers of six or more. In contrast, NH_4^+ has tetrahedral symmetry and allows four specifically positioned hydrogen bonds in addition to ionic interactions. Our goal was thus to develop a receptor with lone pair electrons that are rigidly held at the correct geometry for binding NH_4^+ by hydrogen bonds.[4] We avoided additional functional groups that may stabilize NH_4^+ by dipole interactions since these groups may lower the selectivity.

Molecular mechanics computation[5] showed that the three imine nitrogen atoms in **2** are ideally positioned for hydrogen bonding to NH_4^+ with $N_R \cdots N_A$ distances of about 3 Å and $N_R \cdots N_A \cdots N_R$ angles of about 110° (where N_R represents a receptor imine nitrogen atom, and N_A represents the NH_4^+ nitrogen atom). Whereas this expected bite is perfect for NH_4^+, the bite angle (110°) is too wide to favor higher coordination numbers for metal ions like K^+, and the bite distance (3 Å) is too long for metal ions with a smaller radius.[6] The three ethyl groups in **2** are expected to assist in directing the three pyrazole rings to the same side of the benzene ring by steric interactions (forming *ababab* structures).[7] The three methyl groups in the 5-position of the pyrazole rings were intended to converge the imine nitrogen atoms for binding NH_4^+, and the three methyl groups in the 3-position of the pyrazole rings were intended to block ligands from coordinating to K^+.

Figures 1 and 2 show the crystal structures of **2** and its $NH_4 \cdot PF_6$ complex (**3**), respectively.[8] The structure of **2** reveals that the three pyrazole groups are not all on the same side of the benzene ring. Consistent with the solid-state structure, low-temperature ^1H NMR spectra of **2** in CD_2Cl_2 reveal that the receptor lacks C_3 symmetry in solution.[9] It may be that the repulsion between the three lone pair electrons on the pyrazole imine nitrogen atoms prevents the formation of the above-mentioned *ababab* structure. However, all three pyrazoles of **3** are on the same side of the benzene rings and are hydrogen bonded to NH_4^+ as predicted. Additionally the counterion (PF_6^-) is located close to the NH_4^+ ion with a $N_A \cdots F6$ distance of about 3.0 Å. The $N_R \cdots N_A$ distances range from 2.95 Å to 3.05 Å for **3**, typical of hydrogen bonded N-H-N units.[10] The value of the $N_R \cdots N_A \cdots N_R$ angles range from 105° to 125° for **3**, in good agreement with molecular modeling. It is evident from the crystal structures that the match between the NH_4^+ and the receptors is excellent with no major deformations (Figure 1).[11]

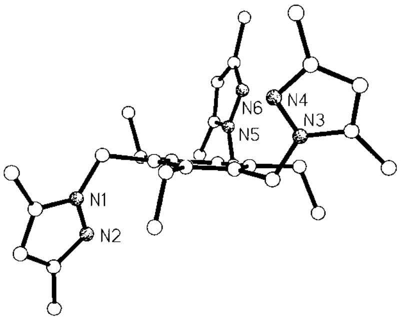

Figure 1. The structure of **2** in the solid state. The asymmetric unit contains two independent molecules with enantiomeric conformations that are related by near noncrystallographic inversion symmetry. Only one of them is depicted.

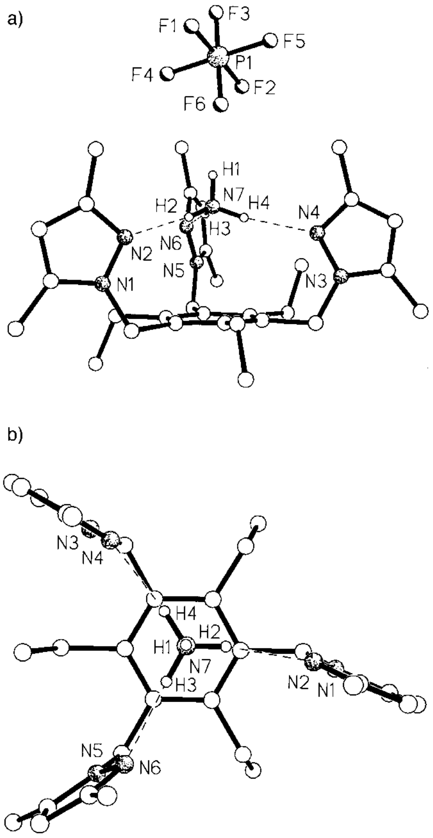

Figure 2. a) Side and b) top views of **3** in the solid state. Except for the four NH_4^+ hydrogen atoms that have been located in the differential Fourier density map and refined without constraints, hydrogen atoms have been omitted for clarity. In (b) the PF_6^- ion has been omitted. Selected interatomic distances [Å] and angles [°]: N2⋯N7 2.949(4), N4⋯N7 3.001(4), N6⋯N7 3.053(4), P6⋯N7 3.031(4); N2-N7-N4 125.2(3), N2-N7-N6 105.8(1), N4-N7-N6 111.9(1).

Figure 3 shows that an ISE based on receptor **2** is highly selective for binding NH_4^+ over K^+ ($\lg K_{NH_4^+/K^+} = -2.6$).[12] In reasonable agreement with this data, the equilibrium constant for binding of the NH_4^+ to **2** ($1.4 \times 10^6\,\mathrm{M}^{-1}$) as determined by the extraction method[3] is over two orders of magnitude greater than that for binding of K^+ to **2** ($8.8 \times 10^3\,\mathrm{M}^{-1}$). The selectivity of the electrode for binding NH_4^+ over Na^+ is even greater ($\lg K_{NH_4^+/Na^+} = -2.8$).[13] By comparison, a nonactin-based ISE, prepared the same way as the **2**-based ISE, is only about ten times more selective for binding NH_4^+ over K^+ ($\lg K_{NH_4^+/K^+} = -1.0$ and $\lg K_{NH_4^+/Na^+} = -2.6$).[14]

Experimental Section

2: 3,5-Dimethyl pyrazole is dissolved in THF, deprotonated with solid NaH, and allowed to react with 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene.[15] The mixture is poured into water, and extracted with $CHCl_3$. The organic phase is washed with aqueous NaOH and evaporated, and the residue is recrystallized from ethanol to give **2** as colorless crystals in 73% yield. Elemental analysis calcd for $C_{30}H_{42}N_6$: C 74.03, H 8.70, N 17.27; found: C

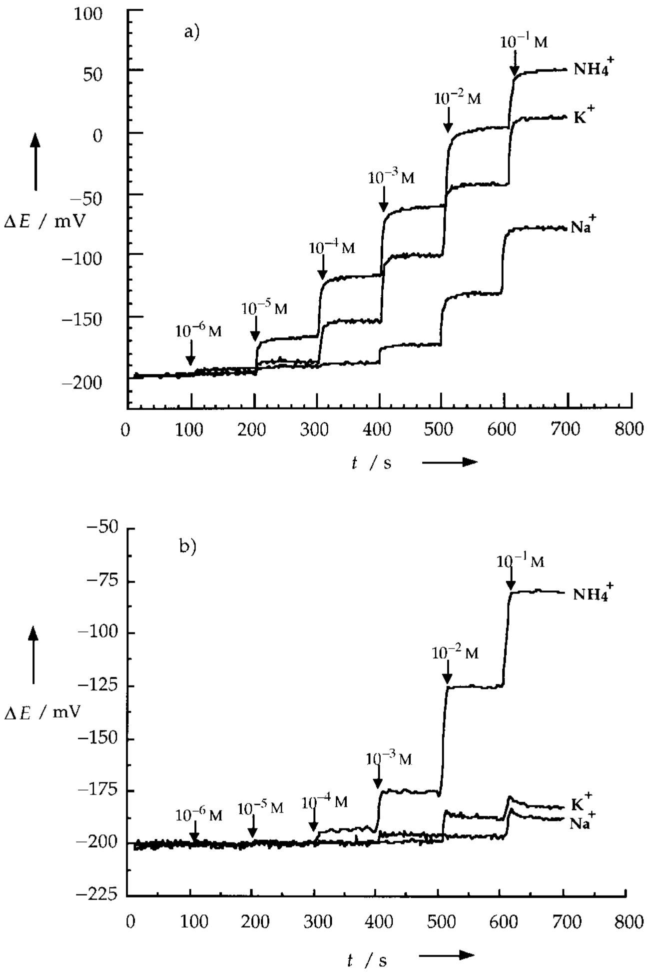

Figure 3. Responses of ISEs to NH_4^+, Na^+ and K^+. a) ISE based on **1**. b) ISE based on **2**.

73.79, H 8.71, N 17.04; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.86$ (9H, t, Me), 2.14 (9H, s, Me), 2.15 (9H, s, Me), 2.77 (6H, q, CH_2), 5.18 (6H, s, CH_2), 5.76 (3H, s, pyrazol-4-yl-H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 11.85$, 13.75, 15.09, 24.12, 47.59, 106.03, 130.83, 139.85, 145.62, 147.38.

3: Colorless crystals of [**2**·NH_4]PF_6 (**3**) were obtained by recrystallizing stoichiometric amounts of **2** and NH_4PF_6 from hot ethanol in 70% yield. Elemental analysis calcd for $C_{30}H_{46}F_6N_7P$: C 55.46, H 7.14, N 15.09; found: C 55.83, H 7.26, N 15.29; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.11$ (9H, t, Me), 2.11 (9H, s, Me), 2.38 (9H, s, Me), 2.47 (6H, q, CH_2), 5.05 (6H, s, CH_2), 5.85 (3H, s, pyrazol-4-yl-H), 6.79 (3 or 4H, somewhat broad, NH_4).

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[4] Cation–π interaction between the benzene ring of the receptor and NH_4^+ may also contribute to the overall binding energy. However, this is not expected to affect the selectivity. Experimental $\Delta H°$ values for the complexation of K^+ and NH_4^+ to a benzene ring are −19.2 and −19.3 kcal mol^{-1}, respectively: J. Sunner, K. Nishizawa, P. Kebarle, *J. Phys. Chem.* **1981**, *85*, 1814–1820; C. A. Deakyne, M. Meot-Ner, *J. Am. Chem. Soc.* **1985**, *107*, 474–479.

[5] The energy minimum of the NH_4^+-bound receptor was obtained by molecular mechanics computation using Quantum Cache (version 3.11) from the Oxford Molecular Group. Preliminary ab initio computation also shows that the minimized structure is in good agreement with that obtained from X-ray crystallography.

[6] Tris(pyrazol-1-ylmethyl)benzenes have been studied in metal-coordination chemistry. In line with our argument they do not act as mononucleating tridentate ligands of a single metal each, but rather bridge different metal centers: a) W.-K. Chang, S.-C. Sheu, G.-H. Lee, Y. Wang, T.-I. Ho, Y.-C. Lin, *J. Chem. Soc. Dalton Trans.* **1993**, 687–694; b) C. M. Hartshorn, P. J. Steel, *Chem. Commun.* **1997**, 541–542. An exception is found in a complex with ruthenium that is η^6-bound to the benzene ring and further coordinated by the three pyrazole nitrogen atoms. The benzene ring is deformed and the pyrazolylmethyl units are bent inwards: c) C. M. Hartshorn, P. J. Steel, *Angew. Chem.* **1996**, *108*, 2818–2820, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2655–2657. However, such a mode is hardly expected with alkaline metals.

[7] D. J. Iverson, G. Hunter, J. F. Blount, J. R. Damewood, Jr., K. Mislow *J. Am. Chem. Soc.* **1981**, *103*, 6073–6083; for other interesting examples, see T. D. P. Stack, J. A. Weigel, R. H. Holm, *Inorg. Chem.* **1990**, *29*, 3745–3760; C. Walsdorff, W. Saak, S. Pohl, *J. Chem. Soc. Dalton Trans.* **1997**, 1857–1861; C. Walsdorff, W. Saak, D. Haase, S. Pohl, *Chem. Commun.* **1997**, 1931–1932; Z. Hou, T. D. P. Stack, C. J. Sunderland, K. N. Raymond, *Inorg. Chim. Acta* **1997**, *263*, 341–355; A. Metzger, V. M. Lynch, E. V. Anslyn, *Angew. Chem.* **1997**, *109*, 911–914, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 862–865; A. P. Bisson, V. M. Lynch, M.-C. K. Monahan, E. V. Anslyn, *Angew. Chem.* **1997**, *109*, 2435–2437, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2340–2342; B. F. Hoskins, R. Robson, D. A. Slizys, *Angew. Chem.* **1997**, *109*, 2861–2863, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2752–2755; T. Szabo, B. M. O'Leary, J. Rebek, Jr., *Angew. Chem.* **1998**, *110*, 3606–3609, *Angew. Chem. Int. Ed.* **1998**, *37*, 3410–3413; C. Walsdorff, S. Park, J. Kim, J. Heo, K.-M. Park, J. Oh, K. Kim, *J. Chem. Soc. Dalton Trans.* **1999**, 923–929.

[8] Crystal data for **2**: $0.3 \times 0.3 \times 0.2$ mm, $C_{30}H_{42}N_6$, $M_r = 486.70$, monoclinic, space group Cc, $a = 11.2859(2)$, $b = 20.8673(4)$, $c = 24.1688(5)$ Å, $\beta = 97.303(1)°$, $V = 5645.7(2)$ Å^3, $Z = 8$, $T = 296$ K, $\rho_{calcd} = 1.145$ g cm^{-3}, Siemens SMART CCCD diffractometer, $Mo_{K\alpha}$ radiation, 11730 reflections collected, 5567 independent reflections, $R1 = 0.0592$, $wR2 = 0.1525$ $[I > 2\sigma(I)]$, $R1 = 0.0732$, $wR2 = 0.1697$ (all data), GOF = 1.105. Crystal data for **3**: $0.7 \times 0.3 \times 0.3$ mm, $C_{30}H_{46}F_6N_7P$, $M_r = 649.71$, triclinic, space group $P\bar{1}$, $a = 10.927(4)$, $b = 11.302(3)$, $c = 15.464(4)$ Å, $\alpha = 95.27$, $\beta = 95.99(3)$, $\gamma = 112.66(3)°$, $V = 1734.5(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.244$ g cm^{-3}, 5198 independent reflections, $R1 = 0.0631$, $wR2 = 0.1709$ $[I > 2\sigma(I)]$, $R1 = 0.0729$, $wR2 = 0.1822$ (all data), GOF = 1.062. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115195 (**2**) and CCDC-115196 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] For example, the ^{1}H NMR signals due to the three methyl groups ($\delta = 0.8$, t, 9H) of the ethyl groups in **2** are equivalent at 297 °K. However, this signal splits into two ($\delta = 1.2$, br, 3H; $\delta = 0.3$, br, 6H) at 180 °K.

[10] L. N. Kuleshova, P. M. Zorkii, *Acta Crystallogr. Sect. B* **1981**, *37*, 1363–1366.

[11] We expected the three ethyl groups in ammonium-bound **2** to point away from the three pyrazole groups. It appears that crystal packing between two molecules of the complex within the unit cell forces one of the ethyl groups to point in the direction of the pyrazole rings: C. Walsdorff, K.-M. Park, J. Oh, K. Kim, *Acta Crystallogr. Sect. C* **1999**, *55*, 108–110.

[12] The ion-selective membranes were prepared by slow evaporation of a solution in THF containing 1% ionophore, 33% polyvinyl chloride, and 66% bis(2-ethylhexyl)adipate (by weight). A 0.10 M NH_4Cl solution was used as filling solution with an AgCl-coated silver wire in the standard compartment of the ISE. Selectivity constants for each electrode were determined by the two solution method at 0.010 M

concentrations of NH_4^+ (pH 7.2 with 0.10 M Tris buffer): Y. Umezawa, K. Umezawa, H. Sato, *Pure. Appl. Chem.* **1965**, *67*, 507–518.

[13] An elegantly designed cryptand that is highly sensitive and selective for binding NH_4^+ has been reported. However, the crytand is much too basic (more basic than ammonia) and hydrophilic for use as an ISE: E. Graf, J.-P. Kintzinger, J.-M. Lehn, J. LeMoigne, *J. Am. Chem. Soc.* **1982**, *104*, 1672–1678.

[14] However, nonactin binds more tightly to NH_4^+ than does **2**.

[15] 1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene was prepared as previously described: C. Walsdorff, W. Saak, S. Pohl, *J. Chem. Res. (S)* **1996**, 282–283, *J. Chem. Res. (M)* **1996**, 1601–1618.

The Sting of the Scorpion: A Metallaboratrane[**]

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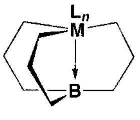
Andrew J. P. White, and David J. Williams

Bis(azolyl)borate chelates are often referred to as "scorpionates" because their coordination geometry can place a hydrogen substituent on boron in close proximity to a metal center constrained within the claws.[1] This arrangement leads in some cases to agostic interactions, however to date none of these situations have involved direct formation of a metal–boron bond (B–H oxidative addition). By extending this conceptual arthropomorphism and in deference to the parable, we confirm that it is indeed "in the nature of the scorpion to sting". Herein we report the first example of a poly(azolyl)borate ligand that undergoes B–H activation (stinging) at one metal center to provide the unprecedented metallaboratrane structural motif (**A**), akin to the more familiar boratrane cages (**B**).[2]



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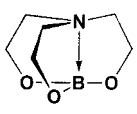
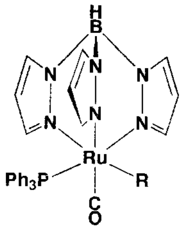


B

We have previously described the chemistry of the isoelectronic σ-organyl complexes [Ru(R)(CO){HB(pz)$_3$}(PPh$_3$)] (**1**, pz = pyrazol-1-yl; R = vinyl, aryl),[3] and [Ru(R)(CO)(PPh$_3$)([9]aneS$_3$)]$^+$ (**2**, [9]aneS$_3$ = 1,4,7-trithiacyclononane),[4] which feature facially tridentate triaza-scorpionate or trithia macrocyclic coligands. The recent report of the new ligand "HB(mt)$_3$" (mt = 2-sulfanyl-1-methylimidazole)[5] suggested to us that the complexes [Ru(R)(CO)(PPh$_3$){HB(mt)$_3$}] (**3**) should be readily accessible, and that the HB(mt)$_3$ ligand in such complexes would effectively serve as a hybrid of the HB(pz)$_3$ and [9]aneS$_3$ ligands. In our initial attempts to prepare the complexes **3** we have encountered an unprecedented class of reaction for tris(azolyl)borates, namely the intramolecular activation of the bridgehead B–H bond to provide the first example **4** of a metallaboratrane.



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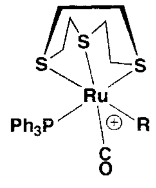
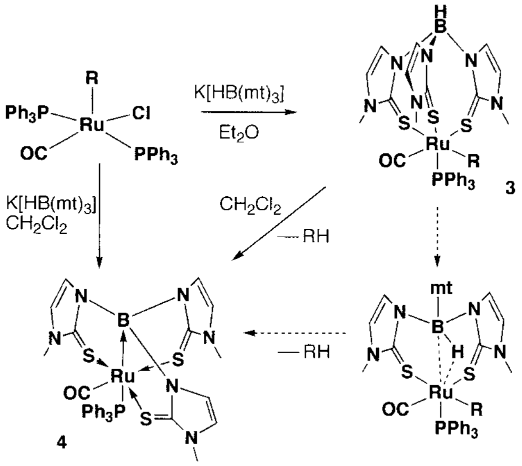


2

The treatment of the complex [Ru(CH=CHCPh$_2$OH)Cl(CO)(PPh$_3$)$_2$][6] with Na[HB(mt)$_3$] (dichloromethane, room temperature) provides high yields of the novel ruthenaboratrane complex [Ru{B(mt)$_3$}(CO)(PPh$_3$)] (**4**, Scheme 1). The formulation of the yellow complex follows from spectroscopic data and was confirmed by a crystallographic study.[7] The gross composition is reflected in the positive-ion FAB mass spectrum, which includes a molecular ion as the base peak and fragmentations arising from the loss of the carbonyl and phosphane ligands. One singlet resonance ($\delta = 17.1$) is observed for the bridgehead boron atom in the ^{11}B NMR spectrum. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra are solvent dependent: Thus in CDCl$_3$ a static structure is suggested by the appearance of sharp peaks arising from two mt environments. However, the operation of a fluxional process is apparent in C$_6$D$_6$ at room temperature. The infrared spectrum reveals one carbonyl absorption at $\tilde{\nu} = 1888$ cm^{-1} (Nujol), a frequency which is suggestive of zero-valent ruthenium (see below).



Scheme 1. Synthesis of **4**. R = CH=CH$_2$, CH=CHCPh$_2$OH, CH=CH(4-MeC$_6$H$_4$), C$_6$H$_5$.

The structure of the complex **4**, as revealed from an X-ray diffraction study, is shown in Figure 1.[7] The ruthenium atom adopts a distorted octahedral coordination despite the constraints of bis-chelation, with *cis*-interligand angles in the

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