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New *N*,*N*,*N*-Heteroscorpionates Based on 2,2′-Bis(pyrazolyl)ethanamine and Its Derivatives. Ligands Designed for Probing Supramolecular Interactions

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The successful design and synthesis of the new bis(pyrazolyl)ethanamine ligand and its copper(I) triphenylphosphine complex is reported. The ligand coordinates to the copper(I) center in a *fac* tridentate fashion, through both the pyrazolyl rings and the nitrogen atom from the NH_2 group. In the solid state, the compound is organized in a 2D noncovalent network by N–H$\cdots\pi$ and C–H$\cdots\pi$ interactions and hydrogen bonds. The analogous ligand with a benzyl group substituted on the amine forms a complex with the same copper(I) center that has a similar 2D supramolecular structure and, in addition, is organized by the benzyl synthon into a 3D architecture.

Crystal engineering is a topic of intense research interest and holds promise for revolutionizing materials design and synthesis.[1] An essential step along the path to predicting solid structures from the substituent groups on the chemical species of interest is to more clearly elucidate the factors that govern the noncovalent assembly of molecules or ions into their ultimate solid-state architectures. Remarkable strides have been made with both common organic and inorganic systems.[1] Our research focuses on the syntheses and supramolecular aspects of the metal complexes of the ubiquitous scorpionate ligands, first introduced by Trofimenko nearly 40 years ago.[2] We have developed synthetic routes to controllably impart substitution along the scorpionate periphery, an advancement that is essential for further probing the role of noncovalent forces in supramolecular organization involving these ligands.[3] Of note is the synthesis of the alcohol-appended derivative $HOCH_2C(pz)_3$, which has allowed the preparation of the multitopic $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$ ($n = 2$, 3, 4, and 6; pz = pyrazolyl ring) family of semirigid ligands[3] as well as other types[4] of systems. Metal complexes of these ligands have remarkable topologies that maximize noncovalent interactions of the groups in the ligand backbone. We named these ligands "structurally adaptive" because they are ideal candidates for studying the self-assembly process and the various factors that might have an influence over such processes.[3b,d,5]

It would be highly desirable to prepare amine-appended poly(pyrazolyl)methanes such as either $H_2NCH_2C(pz)_3$ or $H_2NCH_2CH(pz)_2$ to take advantage of the useful hydrogen-bonding capabilities, the Schiff-base condensation reactions, and nucleophilic substitution reactions involving this new functionality or even for derivatization to potentially water-soluble ammonium derivatives. Unfortunately, the seemingly straightforward preparative reactions (conversion of the alcohol to the halide, followed by nucleophilic displacement with an amine) do not work as expected, and these appended scorpionates have thus far remained elusive. We now communicate our successful strategy at preparing the amine-appended bis(pyrazolyl)methane compound, $NH_2CH_2CH(pz)_2$, introduce a derivatization route, and take a first look at the role that the amine (including the relatively acidic NH)

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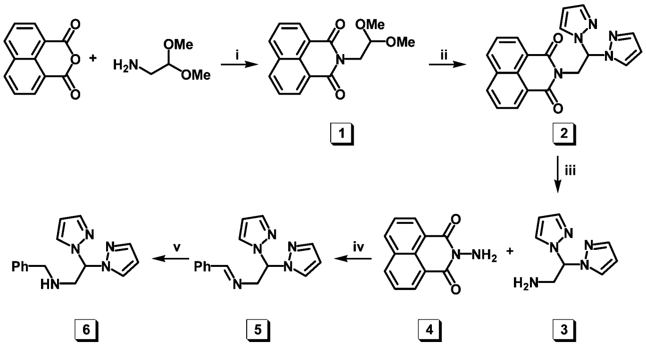
10.1021/ic060347o CCC: $33.50

Scheme 1. Synthesis and Functionalization of 2,2′-Bis(pyrazolyl)ethanamine[a]



[a] (i) Ethanol, reflux, 12 h. (ii) Hpz, neat, 220 °C. (iii) $N_2H_4 \cdot H_2O$ toluene, reflux, 12 h. (iv) PhCHO, ethanol, reflux, 12 h. (v) $NaBH_4$, methanol, 12 h.

has in the supramolecular organization of some model copper(I) triphenylphosphine complexes.

The full synthetic pathway to $NH_2CH_2CH(pz)_2$ and some derivatives is depicted in Scheme 1 (for experimental details, see the Supporting Information). We have previously described the synthesis of *N*-[2,2-bis(pyrazolyl)ethane]-1,8-naphthalimide (**2**) and the remarkable ability of this ligand to form robust $\pi-\pi$-stacked dimers in its $Re(CO)_3Br$ complexes[3a] that survive both in solution and under electrospray mass spectral conditions. We found that the reaction of the free ligand **2** with hydrazine hydrate liberates the desired bis(pyrazolyl)ethanamine (**3**), along with *N*-aminonaphthalimide (**4**) as the byproduct. The amine is soluble in water and almost all organic solvents. Condensation of **3** with benzaldehyde followed by reduction with $NaBH_4$ produced the secondary amine **6**.[6] This indirect route to the monobenzylated product avoids the difficulties in separating the dibenzylated derivative, a potential byproduct of the more direct S_N2 reaction between the amine and benzyl bromide.

The equimolar reaction of $H_2NCH_2CH(pz)_2$ and $[Cu(PPh_3)_2]NO_3$ yielded a pale-yellow powder with the composition $\{(PPh_3)Cu[(pz)_2CHCH_2NH_2]\}(NO_3)$ (**7**). The structure of **7**, depicted in Figure 1, shows that the ligand is tridentate, coordinated to the copper(I) center with both the pyrazolyl rings and the NH_2 group. The fourth coordination site of the pseudotetrahedral copper(I) atom is occupied by a triphenylphosphine ligand. The bond lengths and angles are those expected for a compound of this nature.[7] As can also be seen in Figure 1, the presence of the acidic NH directly influences the crystal packing, as was originally intended in the design of this ligand system. Here, two concerted $D-H\cdots\pi$ interactions (D = N and C; blue dotted lines in Figure 1) result in the assembly of the cationic building blocks into chains.

One hydrogen atom from the NH_2 group is oriented toward one of the phenyl rings from the triphenylphosphine moiety containing C(51)−C(56), from another building block. The H−centroid and N−centroid distances are 2.59 and 3.50 Å, respectively, with a N−H−centroid angle of 171°. The hydrogen atom is positioned almost above the center of the ring, as demonstrated by the H−perpendicular distance to the ring of 2.53 Å and the small slip angle of 11.8°. The phenyl ring that serves as the proton acceptor also acts as a proton donor in the second $D-H\cdots\pi$ interaction: one hydrogen atom is oriented toward a second phenyl ring from the triphenylphosphine moiety, which is coordinated to the copper(I) center within the first building block. The H−centroid and C−centroid distances are 2.69 and 3.47 Å, respectively, with a C−H−centroid angle of 140°. The hydrogen atom is positioned exactly above the center of the ring, as demonstrated by the H−perpendicular distance to the ring of 2.68 Å and the very small slip angle of 4.8°.

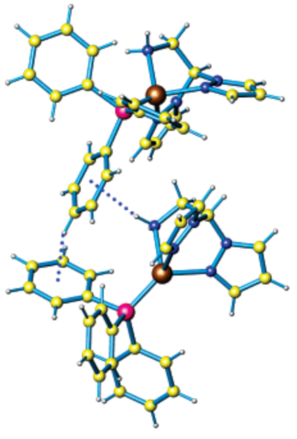


Figure 1. Structure of the $\{(PPh_3)Cu[(pz)_2CHCH_2NH_2]\}^+$ building block in **7** and its self-assembly into chains through $C-H\cdots\pi$ and $N-H\cdots\pi$ interactions (blue dotted lines). Color code: copper, light brown; carbon, yellow; nitrogen, blue; phosphorus, purple; hydrogen, gray.

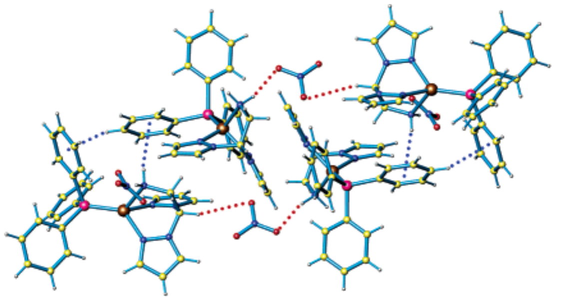


Figure 2. 2D organization of **7** via $D-H\cdots\pi$ interactions (D = C, N; blue dotted lines) and $D-H\cdots O$ hydrogen bonds (red dotted lines).

These chains are further connected into a 2D sheet, by hydrogen bonds involving bridging NO_3^- counterions and the acidic NH and CH groups on the scorpionate periphery (Figure 2). Specifically, the second hydrogen atom from the NH_2 group is involved in a $N-H\cdots O$ hydrogen bond; the H−O and N−O distances are 2.18 and 3.08 Å, respectively, with an N−H−O angle of 165°. The second hydrogen bond in which the NO_3^- anion is engaged involves the methine hydrogen from the $-CH(pz)_2$ moiety. The H−O and C−O distances are 2.38 and 3.29 Å, respectively, with an N−H−O angle of 151°. These two $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds build up the 2D, sheetlike structure of **7**.

The benzyl-functionalized amine ligand **6** reacted with the same copper(I) starting material to yield $\{(PPh_3)Cu[(pz)_2$-

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(6) A very recent publication has reported the synthesis and metal complexes of a related, sterically hindered anilide ligand via a different synthetic pathway: Adhikari, D.; Zhao, G.; Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chem.* **2006**, *45*, 1604.

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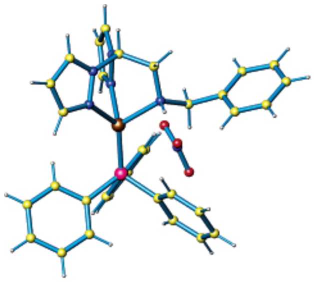

Figure 3. Structure of the $\{(PPh_3)Cu[(pz)_2CHCH_2NHCH_2Ph]\}^+$ building block in **8**. The color code is the same as that in Figure 1.

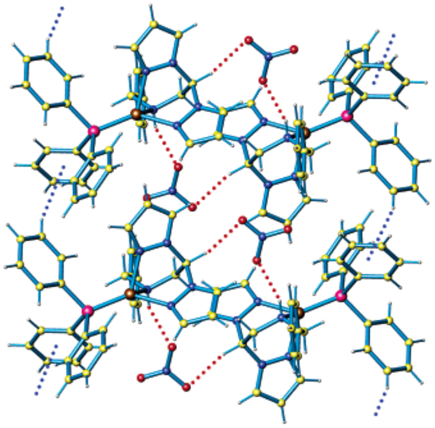

Figure 4. 2D supramolecular organization of **8** via C−H···π interactions and N−H···O and C−H···O hydrogen bonds.

$CHCH_2NHCH_2Ph]\}(NO_3)$ (**8**). The local cation structure of **8** is similar to that of **7**, with a tridentate scorpionate and a triphenylphosphine ligand completing a pseudotetrahedral copper(I) coordination sphere (see Figure 3). The benzyl group is oriented away from both the copper center and the phenyl rings of the triphenylphosphine ligand.

While the replacement of one hydrogen atom from the amine group with the benzyl group did not change the immediate environment around copper(I), it did have a major influence on the supramolecular structure compared to **7**. One major difference between **7** and **8** is a change in the 1D chain structure where the N−H···π interaction is not present in the case of **8**. As can be seen in Figure 4, the cationic building blocks are still arranged in chains, but these chains are held together by only C−H···π interactions.

One of the phenyl rings from the triphenylphosphine group acts as a proton donor, and another one from an adjacent triphenylphosphine group serves as a proton acceptor. The H−centroid and C−centroid distances are, in this case, 2.97 and 3.86 Å, respectively, with a C−H−centroid angle of 159°. The hydrogen atom is positioned above the C(53) atom, therefore imposing a H−perpendicular distance to the ring of 2.84 Å and a slip angle of 16.6°. As in the case of **7**, the NO_3^- anions link the chains into a 2D network. The association pattern is the same as that with **7**; the hydrogen atom from the NH group is involved in a N−H···O hydrogen bond; the H−O and N−O distances are 2.21 and 2.97 Å, respectively, with an N−H−O angle of 157°. The second hydrogen bond in which the counterion is engaged, with the methine hydrogen from the $-CH(pz)_2$ moiety, has the following geometrical characteristics: the H−O and C−O distances are 2.36 and 3.31 Å, respectively, with a C−H−O angle of 156°.

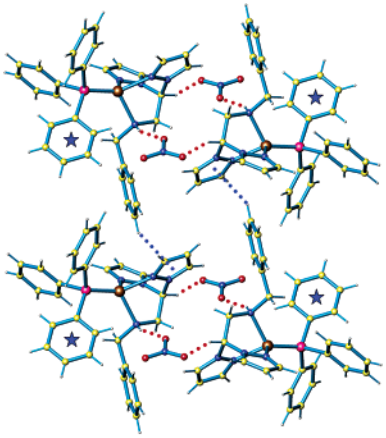

Figure 5. 3D architecture of **8**, based on a C−H···π interaction between the benzyl group and a pyrazolyl ring. The phenyls marked with a star are those that act as proton receptors in the chain formation shown in Figure 4.

A more substantial difference caused by the introduction of the benzyl functional group is an increase in the dimensionality of the noncovalent network of the copper(I) compound, from a 2D sheet structure in **7** to a 3D structure in **8**. The added benzyl group acts as a donor and the pyrazolyl ring as an acceptor in a CH−π interaction, as pictured in Figure 5. The H−centroid and C−centroid distances are, in this case, 2.99 and 3.73 Å, respectively, with a C−H−centroid angle of 137°.

In summary, we have successfully prepared a new amine-appended heteroscorpionate synthon $H_2NCH_2CH(pz)_2$ that can be easily derivatized for use as a supramolecular probe or that can be potentially used for a broad range of other interests, from catalysis, through crystal engineering, and ending with the rational design of compounds with special spin-crossover properties.[8] Our endeavors to use **3** to prepare ligands of the general formula $C_6H_{6-n}[CH_2NRCH_2CH(pz)_2]_n$ and covalent networks thereof will be forthcoming.

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Supporting Information Available: Synthetic details and crystallographic data for **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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