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A Triple Anion Helicate Assembled from a Bis(biurea) Ligand and Phosphate Ions[**]

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Helices are ubiquitous in nature, and are also the central structural motif in biological molecules such as the α-helical protein (single helix), DNA (double helix), and collagens (triple helix). Much effort has been made in the design and synthesis of artificial helical molecules, through metal coordination, hydrogen bonding, π-stacking, or salt-bridging interactions, in order to mimic these biomacromolecules both structurally and functionally.[1] Helical metal-coordination compounds (also known as helicates), which are constituted of multidentate ligand strands that intertwine around and coordinate to a series of metal centers, have been extensively investigated.[2,3] In particular, the oligo-2,2′-bipyridine (bpy) ligands can form a number of fascinating double, triple, and circular double helicates with transition metals.[4] These species not only have aesthetically pleasing structures, but also are of importance in biomimics or functional chiral materials.

The field of anion recognition has expanded rapidly in the last two decades because anions play important roles in biology, medicine, and the environment.[5] The anion coordination concept, together with the terms such as coordination geometry and number, which are typical features in transition-metal coordination, have been applied to anion binding because of the similarities of the two processes, although the coordination geometries and coordination number preferences are much less well-defined for anions.[6] Similar to transition metals, anions have also been used to template the formation of a series of novel artificial structures such as macrocycles, catenanes, rotaxanes, and some metal-based helices.[7,8] However, in contrast to the vast amount of metal helicates, anion-based helices (anion helicates) are very rare. A few anion-directed single helices (foldamers) have been synthesized,[1c,9] and there are only four reported examples of double-stranded anion helicates.[10] Sulfate-templated helices with polyguanidinium strands reported by de Mendoza and co-workers[10a] are the first anion-assembled helices. Kruger and co-workers[10b] have synthesized a chloride-induced helix by using pyridinium ligands, and Gale and co-workers[10c] reported a fluoride-directed helix with neutral amide ligands. Haketa and Maeda[10d] recently reported a chloride-directed double helix with pyrrole-based oligomers. To the best of our knowledge, no triple-stranded anion helicates have been reported to date. The paucity of anion helicates, especially triple helicates, is probably due to the complexity of the self-assembly process for these systems. As such, not only high complementarity and affinity for the receptor to bind anions but also appropriate linkers for the formation of a helix are required.

We have been interested in the coordination chemistry of anions, especially the tetrahedral sulfate and phosphate ions, by using oligourea ligands.[11] Inspired by the similarities of metal coordination and anion coordination, a triurea receptor ($\mathbf{L^1}$) for tetrahedral anions has been designed by mimicking the 2,2′:6′,2′′-terpyridine (tpy) scaffold (Scheme 1 a).[11d] The receptor shows an excellent complementarity for PO_4^{3-} ions, and forms a 2:1 anion complex $[PO_4(\mathbf{L^1})_2]^{3-}$ that resembles the $[M(tpy)_2]^{n+}$ metal complexes, in which the phosphate ion is coordinated by (twelve) saturated hydrogen bonds from six urea groups. These results clearly demonstrate the resemblance of oligopyridine and oligourea ligands in the coordination of transition-metal ions and anions, wherein one pyridine donor or one urea group (two NH donors), respectively, serves as a monodentate coordination vector. Herein, this strategy is applied to the construction of anion-induced triple helices. It is known that the 2,2′-bipyridine (bpy) unit tends to form 3:1 complexes with octahedral metal ions, and thus triple helicates can be generated when two bpy fragments are linked by appropriate spacers (to yield the bis(bipyridine) ligands; Scheme 1 b, c, left).[4a] Considering the "coordination saturation" of tetrahedral anions (12 hydrogen bonds), a triple helix could very likely be assembled by using

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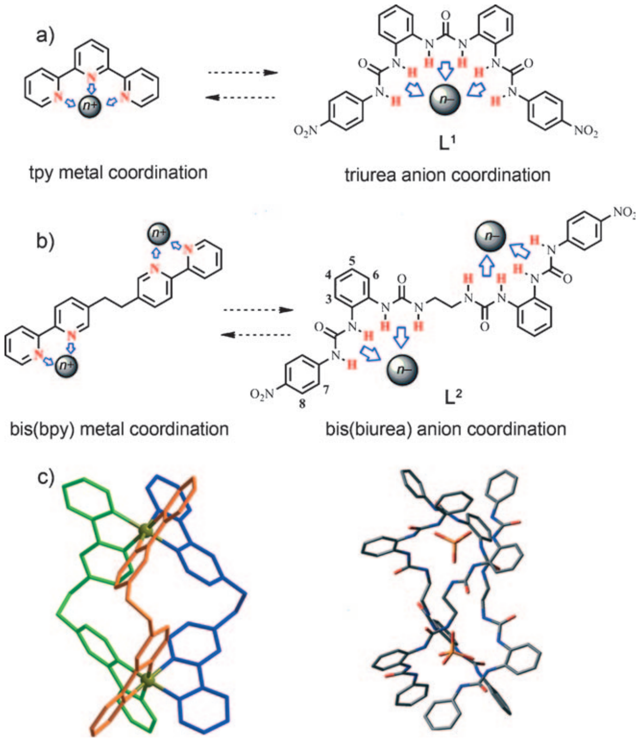

Scheme 1. a, b) Design of the anion receptors $\mathbf{L}^1$ and $\mathbf{L}^2$ by mimicking pyridine–metal coordination; c) triple helices assembled through metal coordination[4a] and anion coordination (DFT model).

three bis(biurea) receptors and two tetrahedral anions (Scheme 1 b, c, right).

For this purpose, the bis(biurea) ligand $\mathbf{L}^2$ was designed based on the following points: Firstly, $\mathbf{L}^2$ features two biurea subunits with the *ortho*-phenyl linker, which has been shown to have an appropriate arrangement for tetrahedral anions as in the triurea, tetraurea, and tripodal hexaurea units.[11d,e,f] Next, the simple ethylene spacer was chosen to connect the two biurea subunits because it has been successfully utilized in the formation of triple metal helicates.[4] Moreover, according to the empirical odd–even rule proposed by Albrecht et al., the ethylene linker favors the chiral helicate conformations.[12] DFT computations were carried out to evaluate the possibility of formatting a triple helix with $\mathbf{L}^2$ and tetrahedral anions.[13] Very encouragingly, the results revealed that the ligand molecules and phosphate ions tend to adopt a stable triple-helical conformation (D_3 symmetry), in which the six urea groups around each phosphate ion fulfill the complementary binding, and the ethylene spacer also satisfies the geometric requirement of the helical structure (Scheme 1 c, right).

The ligand $\mathbf{L}^2$ was thus synthesized by the reaction of *p*-nitro-phenylisocyanate with 1,1′-(ethane-1,2-diyl)bis(3-(2-amino-phenyl)urea) (see the Supporting Information for details). Subsequently, we attempted to obtain the solid-state structure of such a triple helix. Although initial attempts by using $(Bu_4N)H_2PO_4$, Na_3PO_4, or K_3PO_4 have been unsuccessful, we have eventually obtained single crystals of the target triple helix by changing the countercation to $[K([18]crown\text{-}6)]^+$. From the reaction of $\mathbf{L}^2$, K_3PO_4, and [18]crown-6, crystals of complex **1** with the composition $[(PO_4)_2(\mathbf{L}^2)_3][K([18]\text{-crown-6})]_6{\cdot}5\,DMSO{\cdot}3\,H_2O{\cdot}2\,Et_2O$ were isolated in moderate yield.

Complex **1** consists of $[(PO_4)_2(\mathbf{L}^2)_3]^{6-}$ units in which three ligand strands are wrapped around each other and held together by two PO_4^{3-} ions to form a dinuclear triple helix (Figure 1); the experimental structure is in good agreement with the computed structure. The two PO_4^{3-} centers within one helix adopt the same configurations (Δ–Δ or Λ–Λ), but the crystal is racemic (space group *Pbcn*) and contains both *M* and *P* enantiomers. The negative charges are balanced by six solvated $[K([18]crown\text{-}6)]^+$ countercations. Each phosphate ion is bound by six urea groups from three different bis(biurea) ligands through twelve hydrogen bonds (N···O distances range from 2.735(11) to 2.867(11) Å, average 2.802 Å; and N−H···O angles from 140.9 to 177.7°, average 162.8°; Figure 1 and Table S2). The average N···O distance in **1** is slightly shorter than that in the complex of the triurea ligand $(Bu_4N)_3[PO_4(\mathbf{L}^1)_2]$ (2.829 Å) reported by us.[11d] The complementary urea anion binding mode in **1**, wherein each urea group chelates an edge of the phosphate tetrahedron, is similar to that observed in $[PO_4(\mathbf{L}^1)_2]^{3-}$. However, the six coordinating urea groups are supplied by three biurea instead of two triurea units in the latter case.[11d] This is also the difference between the number of ligands in $[M(tpy)_2]^{n+}$ and $[M(bpy)_3]^{n+}$, thus indicating that the match of coordination number and stereochemical preference between the donor and acceptor is also required in anion coordination. In addition, all six terminal aromatic rings interact in a nearly perpendicular orientation (76° on average) to the corresponding *o*-phenyl planes with a CH–plane distance of about 3.5 Å. These T-shaped C−H···π interactions[14] may also have significant contributions to the stabilization of the helix. The helical property of **1** has been characterized by several parameters (e.g., helix pitch and radius, see the Supporting Information for details).

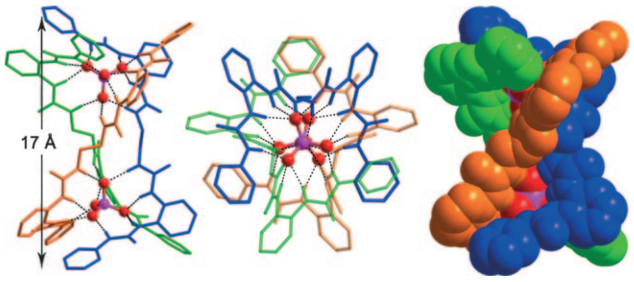

Figure 1. Crystal structure of the triple-helical anion complex $[(PO_4)_2(\mathbf{L}^2)_3]^{6-}$ (**1**). a) Side view; b) top view; c) space-filling representation. Only a *P* enantiomer is shown, and non-acidic hydrogen atoms and nitro groups are omitted for clarity.

The assembly of $\mathbf{L}^2$ and PO_4^{3-} ions in solution was investigated. Both the UV/Vis and ^1H NMR titrations revealed that the 3:2 binding complex formed by $\mathbf{L}^2$ and PO_4^{3-} ions was probably the major species in solution, although minor intermediates might also exist (Figure 2, and Figures S4 and S6 in the Supporting Information). In the ^1H NMR titration, fast exchange occurred that resulted in irresolvable ^1H NMR peaks until addition of 0.66 equivalents

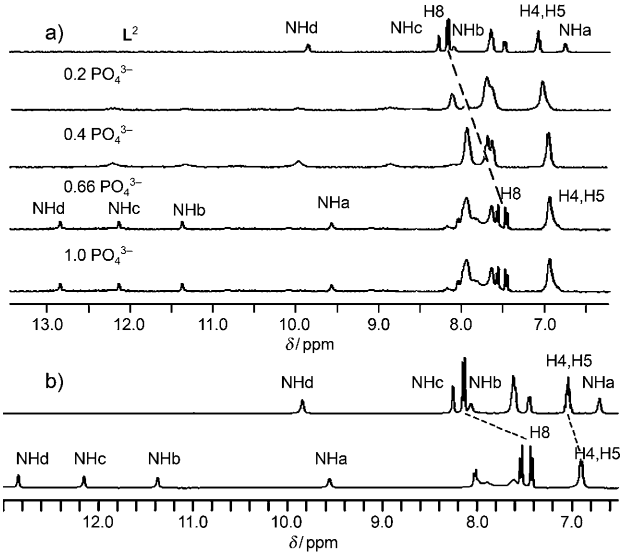

Figure 2. a) ^{1}H NMR titration of $\mathbf{L^2}$ (2.0×10^{-3} M) with [K([18]crown-6)]$_3$PO$_4$ in [D$_6$]DMSO/5% H$_2$O (v/v); b) ^{1}H NMR spectrum of $\mathbf{L^2}$ and complex **1** in [D$_6$]DMSO.

of the anion, at which point the spectrum reached saturation (Figures 2a and S6). The spectral features were identical to those of complex **1** in [D$_6$]DMSO/5% H$_2$O (v/v; Figure S8). Compared with the free ligand, all the urea NH groups in complex **1** showed very large downfield shifts ($\Delta\delta = 2.86$–3.90 ppm; Figure 2b), thus indicating that the PO_4^{3-} ion is tightly hydrogen-bonded by all the urea groups of $\mathbf{L^2}$. An obvious upfield shift of the H8 proton ($\Delta\delta = -0.72$ ppm) was observed because of the strong shielding effects.

In the 1D NOE difference (1D-NOEDIF) experiment, there were distinct responses of the corresponding aromatic protons after the irradiation of H3 + H6, H4 + H5, and H7 + H8 (belonging to *o*- and *p*-phenyl rings; see Scheme 1 for the proton numbering), thus implying the spatial proximity of the terminal aromatic rings and bridging phenyl rings (Figure S7). 2D diffusion ordered spectroscopy (2D-DOSY) in [D$_6$]DMSO at 300 K was also performed. For $\mathbf{L^2}$, the diffusion coefficient (D) was measured to 1.48×10^{-10} m^{2}s^{-1}, which corresponds to a hydrodynamic radius (r_s, calculated from the Stokes–Einstein equation) of 7.5 Å. The DOSY spectrum of complex **1** showed that all the peaks that correlate to the chemical shifts of $\mathbf{L^2}$ are in a horizontal line with a D value of 8.51×10^{-11} m^{2}s^{-1}. The r_s value of this species (13.0 Å) is much larger than the single ligand, but is somewhat smaller than the average dimension of the crystal structure (ca. 17×12 Å^2), which may result from the significant deviation of the structure from spherical (Figures S10, S11). These results suggest that the triple-helical structure may persist in solution. Moreover, ESI-MS studies were carried out; unfortunately, fragmentation occurred during the ionization and the corresponding fragments could not be detected.

The interaction of ligand $\mathbf{L^2}$ and the sulfate ion, another tetrahedral anion, was also investigated. Interestingly, when Na$_2$SO$_4$ was used in the ^{1}H NMR titration under the same conditions ([D$_6$]DMSO/5% H$_2$O), the four NH signals gradually shifted downfield and reached saturation with one equivalent of the anion (Figure S9). However, the saturated downfield shifts ($\Delta\delta = 0.69$–1.01 ppm) were much smaller than those observed with the PO_4^{3-} ion, thus implying weaker interactions between $\mathbf{L^2}$ and the SO_4^{2-} ion than the PO_4^{3-} ion. Moreover, the aromatic H8 proton showed only a slight upfield shift ($\Delta\delta < 0.1$ ppm), which may exclude the presence of a helical conformation as in complex **1**. The solid-state structure of the sulfate complex [(SO$_4$)$_2$$\mathbf{L^2}$]·4Bu$_4$N·2H$_2$O (**2**) was obtained from $\mathbf{L^2}$ and (Bu$_4$N)$_2$SO$_4$, whilst efforts of crystallization using Na$_2$SO$_4$, K$_2$SO$_4$, and [K([18]crown-6)]$_2$SO$_4$ failed. In **2**, the ligand and SO_4^{2-} ions adopt a 1:2 binding mode in the solid state rather than the 1:1 binding mode observed in solution, possibly because **2** was crystallized from a less polar environment. The ligand molecule is S-shaped, with two SO_4^{2-} ions anchored at each side through four hydrogen bonds (Figure 3 and Table S2). The coordination sphere of the SO_4^{2-} ions is completed by two Bu$_4$N$^+$ ions and one water molecule. Notably, even the optimal coordination number (12) and geometry (tetrahedral) of SO_4^{2-} ions are similar to PO_4^{3-} ions, the SO_4^{2-} ion did not template helix formation. This may be attributed to the higher negative charge density and basicity of PO_4^{3-} than SO_4^{2-} ions, which facilitates the phosphate ions to grasp three ligand strands tightly around them. DFT computations also confirmed that the phosphate complex [PO$_4$(biurea)$_3$]$^{3-}$ is more stable than the corresponding sulfate complex [SO$_4$(biurea)$_3$]$^{2-}$ (see the Supporting Information).[13]

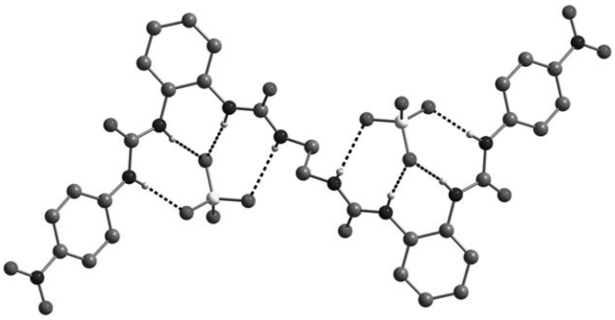

Figure 3. The 1:2 binding mode in the sulfate complex **2** (non-acidic hydrogen atoms, solvents, and countercations are omitted for clarity).

In conclusion, a bis(biurea) anion ligand $\mathbf{L^2}$ assembles with the PO_4^{3-} ion to generate a unique triple anion helicate. The scaffold and binding behavior of $\mathbf{L^2}$ greatly resemble the oligobpy ligands, and the match of coordination number and stereochemical preference between the donor and acceptor is essential in the assembly of the anion complexes. The present work demonstrates that a deep understanding of anion coordination chemistry and anion-based self-assembly can be attained by mimicking metal coordination. Furthermore, our results also provide promising guidelines for the design of new anion ligands: it would be highly desirable to apply the strategies for the assembly of metal-based architectures (e.g., by oligopyridines) to the construction of anion-based structures (e.g., by oligourea units).

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