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Chloride Coordination by Oligoureas: From Mononuclear Crescents to Dinuclear Foldamers

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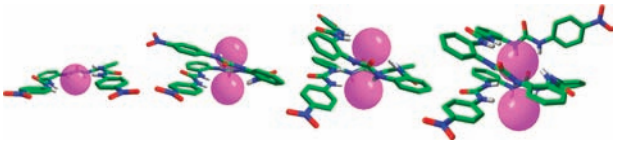
ABSTRACT



A series of acyclic oligourea receptors which closely resemble the scaffolds and coordination behavior of oligopyridines have been synthesized. Assembly of the receptors with chloride ions afforded mononuclear anion complexes or dinuclear foldamers depending on the number of the urea groups.

Foldamers are "artificial folded molecular architectures" which are stabilized by a collection of noncovalent interactions between nonadjacent monomeric units and/or host−guest interactions.[1] In nature, folding of the primary sequences is a common structural feature of many biological molecules such as proteins, peptides and oligonucleotides.[2] Foldamers have found applications in many fields, such as molecular recognition, catalysis, and materials science. To gain deeper understanding of folding and the functions of the folded molecules, many artificial foldamers have been developed. Most of the synthetic molecules studied so far resemble more or less intramolecular H-bonds between repetitive amide units.[3] Alternatively, foldamers can also form by host−guest interactions.[4] While metal ions are the most widely used guests for this purpose,[5] neutral molecule-[6] and anion-directed[7] foldamers are also known. Among these

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systems, the anion binding foldamers are of great biological significance because they may potentially mimic the functions of natural anion channels[8] or anion transporters.[9] There are a few examples that fall into this category;[7,10−12] yet, information of the exact folding dimensions and other structural features of most anion-binding foldamers remains rare due to the lack of crystal structures.[13]

We have recently developed a class of oligourea receptors[14] by mimicking the scaffolds of the well-known transition-metal ligands, oligopyridines. Inspired by the similarities of metal coordination and anion coordination,[15] we designed a bis-bisurea ligand and obtained the first triple anion helicate from this ligand and phosphate ions.[14b] As a further step to the anion-binding helical structures, we synthesized a series of *o*-phenyl bridged oligoureas with gradually increasing chain length (tris(urea) **L**^{1}, tetrakis(urea) **L**^{2}, pentakis(urea) **L**^{3}, and hexakis(urea) **L**^{4}; Schemes S1−S3, Supporting Information (SI)). The *o*-phenyl group has proven to be a proper bridge to connect two urea groups for effective anion binding,[14a−d,16] and these molecules are expected to show folding conformations when coordinating to anions. The phosphate and sulfate binding properties of the two shorter receptors (**L**^{1} and **L**^{2}) have been reported by us, and the tetrakis(urea) **L**^{2} shows a tendency of folding when binding a sulfate ion.[14c,d]

In this work, the longer analogues **L**^{3} and **L**^{4} were synthesized (SI) and the binding of **L**^{1}−**L**^{4} with the chloride anion was investigated. We now report four dinuclear foldamers as well as two mononuclear crescents resulted from chloride coordination with these oligoureas. All anion complexes were structurally characterized, and the existence of the foldamers in solution has also been confirmed by 1D and 2D (^{1}H, COSY, and NOESY) NMR spectroscopy.

Crystals of the six anion complexes were obtained by slow diffusion of diethyl ether to the chloroform (for **L**^{1}, **L**^{2}, **L**^{4}) or chloroform/acetone (10:1 v/v; for **L**^{3}) solutions of the ligands in the presence of excess (TEA)Cl, (TPA)Cl, or (TBA)Cl (TEA = tetraethylammonium, TPA = tetrapropylammonium, and TBA = tetrabutylammonium). The shortest ligand **L**^{1} forms two isomeric mononuclear crescents with a chloride ion ((TBA)[**L**^{1}Cl], **1a** and **1b**), while the longer ones, **L**^{2}−**L**^{4}, form dinuclear foldamers $(TBA)_2[\mathbf{L}^2Cl_2]$ (**2**), $(TEA)_2[\mathbf{L}^3Cl_2]\cdot CH_3COCH_3$ (**3**), $(TBA)_2[\mathbf{L}^4Cl_2]\cdot 0.5Et_2O$ (**4a**), and $(TPA)_2[\mathbf{L}^4Cl_2]$ (**4b**) (Figure 1). All the complexes (except the planar molecule **1b**) are racemic, containing equimolar *M*- and *P*-helices. Each chloride ion is bound by three to seven H-bonds with the N···Cl distances ranging from 3.260 to 3.385 Å and N−H···Cl angles from 144.3° to 160.5° (Tables 1 and S1, SI).

Treatment of the tris(urea) **L**^{1} with (TBA)Cl afforded two isomeric mononuclear crescents (**1a** and **1b**). **1a** adopts such a conformation that one of the terminal urea subunits lies out of the plane defined by the other two urea groups (Figure 1a). The two terminal urea groups bind a chloride ion by four H-bonds, while the middle urea forms two intermolecular H-bonds which connect adjacent molecules into an infinite ribbon. In contrast, complex **1b** adopts a nearly planar conformation where the three ureas occupy three edges of a square, binding a chloride ion in the center with five H-bonds (Figure 1b). The remaining NH binding site is involved in an intermolecular H-bond with the urea carbonyl of another molecule, thus linking two planar crescents to a dimer (Figure S1). The electronic energies of the two isomers were evaluated by DFT calculations, which revealed that **1b** is much more stable than **1a** (by 80.3 kcal mol^{-1}) in the gas phase. Complex **1b** has one more N−H···Cl contact than **1a**, and the solid-state structure of **1a** may be stabilized by the formation of the infinite chain of intermolecular urea···urea H-bonds.

The tetrakis(urea) **L**^{2} forms a dinuclear foldamer (complex **2**) with two chloride ions, in which the four urea units are arranged along a square (Figure 1c). Notably, single-stranded dinuclear foldamers are relatively rare in anion coordination.[11c,d,12] In complex **2**, the two anions are located on the axis of the helix and each is bound by four H-bonds from two alternating urea groups, with a Cl···Cl distance of 3.613(9) Å. Considering that the sum of their ionic radii is only 3.62 Å,[17] such a

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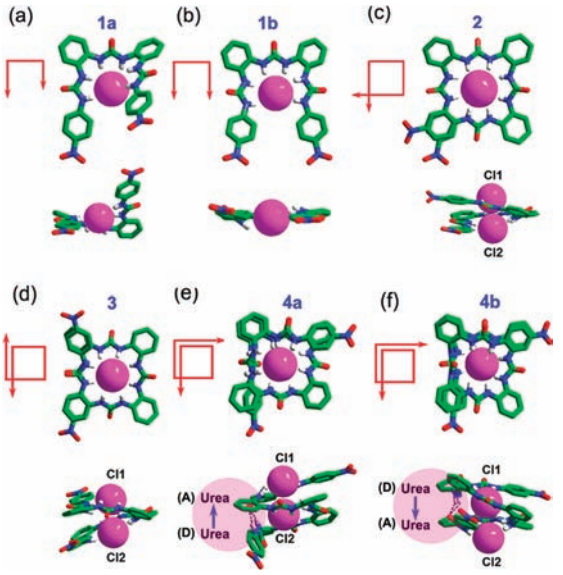

Figure 1. Crystal structures of (a) **1a**, (b) **1b**, (c) **2**, (d) **3**, (e) **4a**, and (f) **4b** in top and side views (only the *M*-helices are shown; shadows in **4a** and **4b** highlight the intramolecular H-bonds; chloride ions are shown with the radius of 1.81 Å; solvent molecules, nonacidic H-atoms, and countercations are omitted for clarity). Red lines: representative illustrations of the folding conformations.

distance is quite unusual which has to overcome severe electrostatic repulsion between the two ionic guests. In the related oligopyrrole-based dinuclear foldamer, the Cl···Cl distance is 4.638(2)/4.632(2) Å.[12] In the present case, the repulsion is possibly compensated by the eight cooperative H-bonds as well as a strong $\pi\cdots\pi$ stacking interaction between the two terminal aryl groups (Table S2 and Figure S2).

The square-like arrangement is maintained in the dinuclear foldamers of the pentakis(urea) $\mathbf{L^3}$, $(TEA)_2[\mathbf{L^3}Cl_2]$ (**3**), and hexakis(urea) $\mathbf{L^4}$, $(TBA)_2[\mathbf{L^4}Cl_2]\cdot 0.5Et_2O$ (**4a**) and $(TPA)_2[\mathbf{L^4}Cl_2]$ (**4b**), which form 1.25 and 1.5 helical turns, respectively (Figure 1d–f). Compared with **2**, the electrostatic repulsion is released partially in the longer analogues since the Cl···Cl separation increases gradually from 3.613(9) Å in **2** to 4.024(5) Å in **4b**. On the other hand, all NH sites in **3** participate in the binding with the two chloride ions (each by five H-bonds), while only ten of the twelve NH donors in **4a** and **4b** are involved in anion binding. In **4a**, the two chloride ions are bound by three and seven H-bonds, while in **4b** they are bound by six and four H-bonds, respectively. The remaining two NH binding sites in **4a** and **4b** form intramolecular H-bonds with the oxygen atom of another urea. In both cases, the urea···urea interactions occur with one terminal urea unit, and the difference lies in its role as the H-bond donor (**4a**) or acceptor (**4b**). DFT calculations showed that the two isomers have almost the same energy (differing by 2.0 kcal mol^{-1}).

Table 1. Hydrogen Bonds (Å and deg) Involved in Chloride Binding and Cl···Cl Separations in the Crystal Structures of the Six Complexes

	Cl1		Cl2		
	H-bond number	average d(N···Cl) and ∠NHCl [Å, deg]	H-bond number	average d(N···Cl) and ∠NHCl [Å, deg]	Cl1···Cl2 separation [Å]
1a	4	3.260, 160.5	–	–	–
1b	5	3.262, 144.3	–	–	–
2	4	3.340, 158.4	4	3.331, 160.1	3.613(9)
3	5	3.349, 153.9	5	3.325, 153.2	3.826(6)
4a	3	3.322, 154.7	7	3.385, 146.4	3.881(8)
4b	6	3.322, 156.6	4	3.298, 153.1	4.024(5)

Theoretical calculations (Hartree–Fock method) were performed to optimize the structures of the free ligands. The results revealed that the shorter $\mathbf{L^1}$ and $\mathbf{L^2}$ adopt the expanded conformations without a preference of folding. For the pentakis(urea) $\mathbf{L^3}$, four of the urea subunits converge to a compact conformation through intramolecular H-bonds, but the remaining terminal urea arm is oriented away. The longest ligand $\mathbf{L^4}$ displays a folding conformation similar to its chloride complex **4b**. These results imply that there is an increasing tendency of self-folding as the number of the urea groups extends (Figure S3). While $\mathbf{L^2}$ and $\mathbf{L^3}$ form foldamers only with the templation of chloride ions, the hexakis(urea) $\mathbf{L^4}$ tends to fold itself.

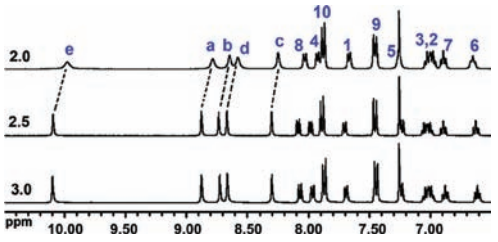

Figure 2. Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectra of $\mathbf{L^3}$ in the presence of various equivalents of (TBA)Cl (5 mM) (indicated by black numbers).

The chloride binding properties of $\mathbf{L^1}$–$\mathbf{L^4}$ were investigated by ^{1}H NMR experiments conducted in $CDCl_3$. For parallel comparison, the tetrabutyl ammonium chloride (TBA)Cl was used in all cases. Interestingly, though the ligands alone are hardly soluble in $CDCl_3$, they can dissolve in the presence of Cl^- due to the formation of the discrete chloride complexes. To completely dissolve the receptor (5 mM), at least 1 equiv of Cl^- is needed for $\mathbf{L^1}$ and $\mathbf{L^2}$ and 2 equiv for $\mathbf{L^3}$ and $\mathbf{L^4}$. These solutions were used for further NMR titrations. Figure 2 shows the spectra of $\mathbf{L^3}/2Cl^-$ which are well-resolved, and the spectra of other receptors are given in Figure S4. For $\mathbf{L^1}/Cl^-$, when more anions were added, all NH signals showed continuous downfield shifts which were not

finished even after 25 equiv of Cl^- ions were added. The NH signals of $\mathbf{L^2}/Cl^-$ also showed downfield shifts, but the main changes were completed with 2 equiv of Cl^- ions and a sharp, saturated spectrum appeared after adding 2.5 equiv of chloride ions. Similarly, saturated spectra of $\mathbf{L^3}$ (Figure 2) and $\mathbf{L^4}$ were achieved with approximately 2.5 and 2.0 equiv of Cl^- ions, respectively. Based on these results, it may be concluded that, in the $CDCl_3$ solution with an excess of Cl^- (> 2.5 equiv), $\mathbf{L^2}$, $\mathbf{L^3}$, and $\mathbf{L^4}$ show a 1:2 binding mode, while $\mathbf{L^1}$ may form multiple complexes of higher order. In the anion binding by analogous acyclic receptors, coexistence of multiple equilibria was also observed.[18] ESI-MS experiments in $CHCl_3$ were performed. Both the 1:1 and 1:2 (host/guest) chloride complexes of $\mathbf{L^4}$ were observed, while only the 1:1 complex of $\mathbf{L^1}$, $\mathbf{L^2}$, and $\mathbf{L^3}$ was detected (Figure S5).

Partial conformational information of the complexes can be obtained by comparing the NMR spectra of $\mathbf{L^1}$–$\mathbf{L^4}$ alone and in the presence of Cl^- ions. The spectra of free $\mathbf{L^1}$–$\mathbf{L^4}$ determined in DMSO-d_6 displayed very similar, highly overlapped signals (Figure S6), indicating that the free ligands possibly adopt similar expanded conformations. After 2 equiv of Cl^- ions were added, the CH protons on the terminal *p*-nitrophenyl groups of $\mathbf{L^1}$ shifted slightly downfield ($\Delta\delta$: 0.05, 0.08 ppm). In contrast, these CH protons of $\mathbf{L^2}$–$\mathbf{L^4}$ showed upfield shifts (0.05–0.18 ppm) (Figure S7). The differences were also observed in the spectra of $\mathbf{L}/2Cl^-$ recorded in $CDCl_3$. We suppose that $\mathbf{L^2}$–$\mathbf{L^4}$ might adopt folded conformations on binding chloride ions, which can result in shielding effects on the terminal CH protons. However, there is no such shielding in the crescent complexes of $\mathbf{L^1}$. On the other hand, the chemical shifts in both DMSO and $CDCl_3$ are better resolved in the presence of chloride ions. A high dispersion of ^1H NMR signals is usually thought to be typically characteristic of a well-ordered solution conformation.[5b] Thus these observations are consistent with the putative folding conformations of the complexes **2**, **3**, and **4** in solution.

For further evidence of the folding in solution, 2D NMR (in $CDCl_3$) investigations have been performed. In the case of $\mathbf{L^3}/3Cl^-$ (an excess of chloride ions was added to ensure the formation of the dinuclear foldamer) the spectrum is well-resolved, but the signals for other ligands and 3 equiv of Cl^- are not dispersed enough to allow clear assignment of the protons. We have also tested other anions (F^-, Br^-, NO_3^-, AcO^-, SO_4^{2-}, 3 equiv, as TBA salts), which could aid the dissolution of the ligands ($\mathbf{L^3}$ and $\mathbf{L^4}$) in $CDCl_3$ but showed poor dispersion of the spectra (Figure S8). Hence, the system $\mathbf{L^3}/3Cl^-$ was used for 2D NMR (600 MHz, COSY and NOESY, in $CDCl_3$) studies. In the NOESY spectrum, cross-peaks are formed between all adjacent NH protons, which is consistent with the crystal structure of complex **4**, wherein all NH protons point to the inside of the foldamer. Additional supports for the foldamer are the cross-peaks between NHe-NHc, NHb-CH9, and NHc-CH9 which are caused by the through-space coupling. These cross-peaks are not found in the COSY spectrum, thus confirming that they result from the spatial effect (Figures S9 and S10).

Efforts were made to determine the binding affinity as well as the binding stoichiometry (by the Job's plot) by UV/vis titrations in $CHCl_3$-0.5% DMSO (DMSO was used to dissolve the ligands, Figure S11). Unfortunately, the colorimetric changes in DMSO are not large enough to allow accurate determination. Nevertheless, the two-step changes of UV–vis spectra provided evidence for the 1:2 (host/guest) binding mode between $\mathbf{L^2}$–$\mathbf{L^4}$ and Cl^-. Upon addition of Cl^-, the charge transfer bands showed a continuous bathochromic shift until 2 equiv of Cl^- were added. During the addition of 1 equiv of Cl^-, clear isosbestic points were formed indicating the formation of only one single complex, possibly the 1:1 binding mode. As more Cl^- ions were added, the newly emerged band shifted away gradually from the isosbestic points and reached saturation after addition of 2 equiv of Cl^-.

In summary, a series of dinuclear chloride-binding foldamers have been obtained based on *o*-phenyl-bridged oligoureas. A growing tendency for dinuclear foldamers was elucidated with the increasing number of urea units. This current work further proves the strategy for designing anion ligands by simply translating the well developed transition-metal ligands to anion binding scaffolds, which have been successful in the construction of novel anion-based architectures.

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Supporting Information Available. Experimental details, X-ray data, NMR and UV–vis titrations, and DFT computations. This material is available free of charge via the Internet at http://pubs.acs.org.

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