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Metal-Controlled Assembly and Selectivity of a Urea-Based Anion Receptor

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1-(3-[1,10]phenanthrolin-2-yl-phenyl)-3-(4-trifluoromethyl-phenyl)-urea (**1**) forms a solution-stable 1:2 complex with copper(I), $[Cu^{I}(\mathbf{1})_2]^+$, which behaves as an anion receptor in aprotic media. The $[Cu^{I}(\mathbf{1})_2]^+$ receptor may adopt a geometrical arrangement in which the two facing urea subunits give tetrafurcate H-bond interaction with a spherical anion (halides and $H_2PO_4^-$). In the presence of the Y-shaped acetate, the $[Cu^{I}(\mathbf{1})_2]^+$ receptor rearranges to interact with two CH_3COO^- ions, according to two stepwise equilibria. Thus, in the presence of substoichiometric amounts of the anions, $[Cu^{I}(\mathbf{1})_2]^+$ discriminates $H_2PO_4^-$ over CH_3COO^-, inverting the basicity trend.

Introduction

Since the pioneering works of Wilcox[1] and Hamilton,[2] urea has become a widely used fragment for the design of neutral receptors and sensors for anions.[3] The single urea subunit typically behaves as a donor of two H-bonds and establishes complementary interactions with two oxygen atoms of a given oxoanion, e.g., the Y-shaped acetate.[4] However, the normally observed selectivity pattern ($CH_3COO^- > H_2PO_4^- > NO_2^- > HSO_4^- > NO_3^- > ClO_4^-$) does not rely on structural features (e.g., the more or less favorable matching of the urea NH fragments and anion oxygen atoms) but simply reflects the decreasing basicity of the anion, expressed, for instance, by the value of the partial negative charge on its oxygen atoms.[4] On the other hand, urea establishes with spherical halide ions bifurcate hydrogen bonding interactions whose intensity decreases with the charge density of the anion ($Cl^- > Br^- > I^-$). Fluoride exhibits a unique behavior; it establishes a monofurcate interaction with one NH fragment of urea, giving the rather stable H-bonded complex $[LH\cdots F]^-$, which, on addition of a second equivalent of F^-, may release a HF molecule to give the deprotonated form of the receptor, L^-, and the self complex $[HF_2]^-$.[5] H-bond donor tendencies of receptors on the basis of a single urea subunit can be enhanced through the covalent linking to electron-withdrawing substituents (e.g., nitrophenyl, cyanophenyl, trifluoromethylphenyl), but the increased acidity does not alter the affinity pattern, which is ultimately determined by the basicity of the anion. Thus, selectivity can be achieved only by positioning two or more urea subunits on a rigid platform that has been designed by taking into account the geometrical binding preferences of the anion (e.g., a calix[6]arene,[6] a 1,3-xylyl fragment,[7] a 1,2-cyclohexane subunit).[8]

According to a different approach, metals can be used to properly assemble H-bond donor subunits (e.g., urea derivatives) and to generate binding sites suitable for selective anion binding.[9] In particular, the H-bond donor subunit must be covalently linked to a ligand for metal ions. Then, when two or more molecules of the functionalized ligand react with a chosen metal, a coordination complex forms, which may properly orientate the H-bond donor subunits and offer a convenient binding site for anions. The shape and size of

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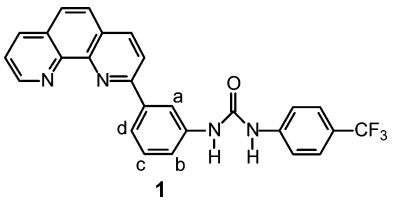
the binding site are determined by the coordinative preferences of the metal (toward a tetrahedral, square, or octahedral geometry) and by the nature and length of the spacer connecting the ligand to the H-bond donor subunit. For instance, a Pt^{II} center coordinated four urea functionalized isoquinolines at the corners of a square, giving a substitutionally inert complex; the four urea subunits formed a H-bond donor cavity suitable for interaction with $H_2PO_4^-$ and HSO_4^- in a DMSO solution.[10] Because of the extreme kinetic stability of the d^8 (low-spin) metal center, the $[Pt^{II}(isoquinoline)_4]^{2+}$ moiety provides a rigid platform that has been compared to the purely organic scaffold of calix[4]arenes. Other inert metal centers (e.g. Ru^{II}, d^8 low-spin, which imposes an octahedral coordination geometry)[11] have been utilized to build molecular cavities that are capable of accommodating anions through interaction with H-bond donors appended to the ligand(s). On the other hand, substitutionally labile d^{10} metal centers allow for reversible assembling of functionalized ligands, a feature which may impart a higher versatility in anion recognition. A first report refers to the 1:2 tetrahedral Cu^I complex of a 1,10-phenanthroline ligand linked to an acylaminopyridine moiety (H-bond donor through the amide NH fragment and H-bond acceptor through the pyridine nitrogen atom) that has been shown to form H-bond complexes with dicarboxylic acids in chloroform.[12] More recently, it has been shown that a $[Ag^IL_2]^+$ complex, in which L is a pyridine covalently linked to a urea subunit, forms a stable adduct with the nitrate ion, which is H-bonded to both urea fragments. The $[Ag^IL_2\cdots NO_3]$ ternary complex has been characterized both in the solid state[13] and in acetone solution.[14] In particular, the coordination to the metal induced a 30-fold enhancement of the affinity of the urea-based receptor toward NO_3^-.



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We report here on the anion binding tendencies of the 1:2 Cu^I complex with the urea-functionalized 1,10-phenanthroline **1**, 1-(3-[1,10]phenanthrolin-2-yl-phenyl)-3-(4-trifluoromethyl-phenyl)-urea. The linking positions in the phenylurea fragment and in the phenanthroline moiety have been chosen in order to favor the formation of a not-too-large anion binding site following metal complex assembly, as suggested by modeling studies. A trifluoromethylphenyl group has been appended to the other phenyl ring to enhance the H-bond donor tendencies of the urea moiety and induce an optical charge-transfer transition, which is useful for reporting purposes. Binding studies have been carried out in a DMSO solution and in a 4:1 v/v THF:MeCN mixture, and pertinent association constants have been determined through the nonlinear least-squares analysis of data from UV−vis spectrophotometric titration experiments. The crystal structure of the $Cu^I(\mathbf{1})_2Cl$ salt is reported.

Experimental Section

Materials and Methods. All reagents for syntheses were purchased from Aldrich/Fluka and used without further purification. 2-Chloro-1,10-phenanthroline (**2**) was prepared in three steps from commercial 1,10-phenanthroline according to the literature procedure.[15] UV−vis spectra were recorded on a Varian CARY 100 spectrophotometer with a quartz cuvette (path length 0.1−1.0 cm). In the titrations with anions, UV−vis spectra of the samples were recorded after the addition of aliquots of an alkylammonium salt solution of the envisaged anion ($[Bu_4N]^+$ for CH_3COO^-, $H_2PO_4^-$, NO_2^-, HSO_4^-, F^-, Br^-, and I^-; $[BzMe_3N]^+$ for Cl^-). All spectrophotometric titration curves were processed with the HyperQuad program.[16] ^1H NMR spectra were obtained on a Bruker AVANCE 400 spectrometer (400 MHz) operating at 9.37 T.

Syntheses. 2-(3-Nitro-phenyl)-1,10-phenanthroline (3). 2-chloro-1,10-phenanthroline **(2)** (362 mg, 1.69 mmol) was dissolved in toluene (10 mL). While the solution was degassed with bubbling nitrogen, 3-nitrophenylboronic acid (295 mg, 1.77 mmol) was added, followed by $Pd(PPh_3)_4$ (97 mg, 0.084 mmol). Finally, 10 mL of a degassed aqueous solution of Na_2CO_3 (2 M) was added. The solution was then heated at reflux under nitrogen for 15 h. A spot-to-spot conversion is observed on TLC (Al_2O_3, CH_2Cl_2/MeOH (1%)). The solution was cooled, and 30 mL of CH_2Cl_2 and 30 mL of water were added. After the first separation of the two phases, the aqueous phase was extracted with 2 × 50 mL of CH_2Cl_2. The organic phase was filtered through a plug of Celite, dried with Na_2SO_4. After filtration, the solvent was removed to yield 530 mg of crude product. This crude material was purified by chromatography over alumina, eluting with CH_2Cl_2/MeOH (2%) to yield pure **2** (500 mg, 97% yield). ^1H NMR (400 MHz, $CDCl_3$): 9.27 (d, 1H), 9.05 (s, 1H), 8.81 (d, 1H), 8.47 (d, 1H), 8.30 (d, 1H), 8.27 (d, 1H), 8.20 (d, 1H), 7.83 (s, 2H), 7.73 (t, 1H), 7.68 (t, 1H). ES-MS *m*/*z*: 302.1 $[M + H]^+$, calcd 302.1. Anal. Calcd for $C_{18}H_{11}N_3O_2$: C, 71.75; H, 3.68; N, 13.95. Found: C, 71.89; H, 3.67; N, 14.25.

3-[1,10]Phenanthrolin-2-yl-phenylamine (4). 2-(3-Nitro-phenyl)-1,10-phenanthroline (**3**) (322 mg, 1.07 mmol) was dissolved in 30 mL of ethanol. $SnCl_2 \cdot 2H_2O$ (1.6 g, 7.1 mmol) was added, and the resulting mixture was heated at reflux for 3 h under nitrogen. The reaction was monitored by TLC (Al_2O_3, CH_2Cl_2/MeOH (2%)), and a clean spot-to-spot conversion was observed. Ethanol was removed under vacuum. The solid was taken up in CH_2Cl_2/H_2O (pH was adjusted to 12 with NaOH). The aqueous phase was extracted twice with CH_2Cl_2 (30 mL). The combined organic phase was washed twice with basic water (pH 12) and once with distilled water. After being dried over Na_2SO_4 and filtered, the solvent was removed to yield 3-[1,10]phenanthrolin-2-yl-phenylamine (**7**). This isolated yellow oil turned rapidly into a black oil, indicating that decomposition was taking place. Nevertheless, a good mass of a

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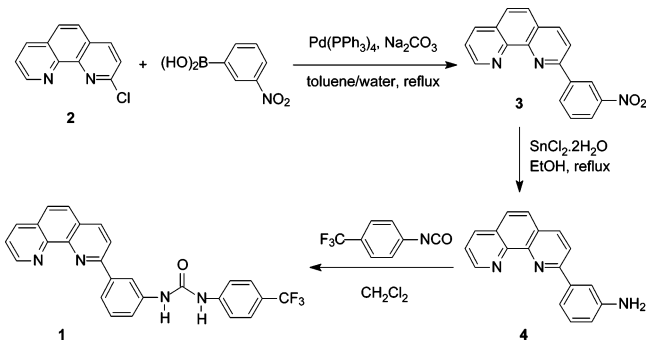
Scheme 1



fraction that was kept in solution could be obtained (ES-MS *m*/*z*: 272.4 $[M + H]^+$, calcd 272.3). TLC of this sample indicated that no decomposition was observed when **4** was kept in solution. For the following step (i.e., the formation of the urea−phenanthroline conjugate (**1**)), after filtration, the solution of CH_2Cl_2 containing **4** was concentrated under vacuum and used immediately.

1-(3-[1,10]Phenanthrolin-2-yl-phenyl)-3-(4-(trifluoromethyl-phenyl)-urea (1). To a CH_2Cl_2 solution of 3-[1,10]phenanthrolin-2-yl-phenylamine (1.07 mmol on the basis of a 100% conversion of **3**) was added 1.1 equiv of α,α,α-trifluoro-*p*-tolylisocyanate (165 μL). The solution was stirred at room temperature for 2 h. The white precipitate that appeared in the course of the reaction was filtered and washed with CH_2Cl_2. The urea−phenanthroline conjugate **1** was obtained as a white solid (305 mg, 62% yield). For a visual depiction of the total synthesis, see Scheme 1

. ^{1}H NMR (400 MHz, d_6-DMSO): 9.17 (d, 3H), 8.60 (d, 1H), 8.53 (dd, 1H), 8.45 (s, 1H), 8.35 (d, 1H), 8.05 (m, 3H), 7.80 (m, 2H), 7.52 (d, 1H), 7.48 (d, 1H), 7.55 (t, 1H). ES-MS *m*/*z*: 459.1 $[M + H]^+$, calcd 459.1. Anal. Calcd for $C_{26}H_{17}N_4F_3O$: C, 68.12; H, 3.74; N, 12.22. Found: C, 68.66; H, 3.77; N, 13.06.

$[Cu(1)_2](ClO_4)$. 1 (24.1 mg, 2 equiv) was dissolved in a CH_2Cl_2/MeOH mixture (10:3 mL). The solution was degassed, and $[Cu(CH_3CN)_4](ClO_4)$ (8.6 mg, 1 equiv) in a degassed solution of CH_3CN was added. The solution immediately turned red. It was allowed to stir at room temperature for 1 h. The solvent was then removed under vacuum to quantitatively yield $[Cu(\mathbf{1})_2](ClO_4)$ (29 mg) as a red solid. ES-MS *m*/*z*: 979.2 $[M - ClO_4]^+$, calcd 979.3. Once this complex was isolated, it was very difficult to dissolve it in any solvent except DMSO. For the titration in the THF/CH_3CN mixture, the complex was prepared in situ. ***Caution**: perchlorate salts are potentially explosive and must be handled with care. In particular, they should never be heated as solids.*

X-ray Crystallographic Studies. Diffraction data of the $[Cu^I(\mathbf{1})_2]Cl$ complex salt were collected at ambient temperature on a Bruker-AXS Smart-Apex CCD-based diffractometer. Omega rotation frames (scan width 0.3°, scan time 50 s, sample-to-detector distance 7 cm) were processed with the SAINT software (Bruker-AXS Inc.), and intensities were corrected for Lorentz and polarization effects. Absorption effects were analytically evaluated by the SADABS software,[17] and correction was applied to the data (0.72 and 0.98 minimum and maximum transmission factors). Crystal data for [Cu(I)**L**]Cl complex: $C_{52}H_{34}ClCuF_6N_8O_2$, $M_r = 1015.87$, $T = 293$ K, crystal dimensions 0.13 × 0.08 × 0.04 mm^3, monoclinic, $P2_1/c$ (No. 14), $a = 15.412(5)$, $b = 25.957(5)$, $c = 25.514(3)$ Å, $\beta = 107.58(1)$, $V = 9730(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.387$, $F(000) = 4144$, $\mu = 0.576$ mm^{-1}, Mo Kα X-radiation ($\lambda = 0.7107$ Å), $2\theta_{max} = 46°$, 46 463 measured reflections, 13 t778 independent reflections ($R_{int} = 0.049$), 11 693 strong reflections [$I_o > 2\sigma(I_o)$], 1262 refined parameters, R1 = 0.0928 (strong data) and 0.1078 (all data), wR2 = 0.2240 (strong data) and 0.2341 (all data), GOF = 1.150, 0.87 and −0.38 maximum and minimum residual electron density.

Single crystals suitable for X-ray diffraction study were always characterized by diffracted intensities corresponding to the $P2_1$ space group. In particular, the systematic extinctions due to the *c* glide plane were not obeyed. Several attempts to solve the structure by direct methods (SIR-97)[18] in the $P2_1$ space group produced a first partial atomic model, which exhibited the symmetry of the $P2_1/c$ space group. The presence of the forbidden reflections in the diffraction pattern was thus ascribed to merohedral twinning. Refinement by full-matrix least-squares procedures on F^2 using all reflections (SHELXL-97)[19] was performed assuming a second component in the crystal, rotated by 180° about [100]. The agreement index strongly improved, and the atomic model was completed by analyzing the Δ*F* map. The refined twin ratio result was 0.52(1):0.48(1). All non-hydrogen atoms were refined with anisotropic temperature factors; hydrogen atoms were placed using the appropriate AFIX instructions. CCDC 289232 contains the supplementary crystallographic data for this paper.

Results and Discussion

1. Design of the Receptor. The Cu^I ion gives with 1,10-phenanthroline a tetrahedral complex $[Cu^I(phen)_2]^+$. However, the coordination geometry is not exactly tetrahedral (N−Cu−N bond angles differ from the canonic value of 109.5°) because of steric constraints imposed by the rigid phenanthroline framework.[20] Steric effects exerted by small substituents on the 2,9 positions (e.g., methyl[21] and trifluoromethyl)[22] force the phenanthrolines to lie perpendicular each other, minimizing the interligand repulsions. However, aromatic substituents on the heterocyclic rings may induce variable distortions; for instance, in the symmetric 2,9-diphenyl-1,10-phenanthroline complex of Cu^I, the angle between phen planes is ca. 59°,[23] whereas in the monosubstituted 2-dimethylaminophenyl-phenanthroline, the angle is ca. 68°.[24]

Notice that in ligand **1**, the linking positions in the phenylurea fragment and in the heterocyclic ring have been judiciously selected, generating a rather small and strictly defined binding site that is suitable for interaction with a single anion. In this regard, modeling studies where carried out using a semiempirical method (PM3) for the H-bond complex $[Cu^I(\mathbf{1})_2\cdots Cl]^+$. The pertinent calculated structure is shown in Figure 1.

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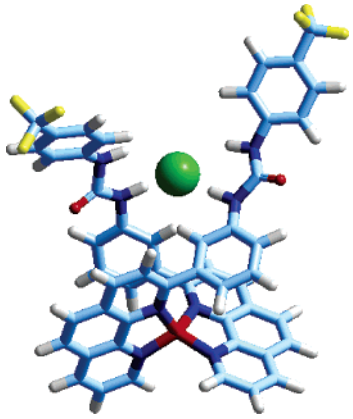

Figure 1. Hypothesized structure of the $[Cu^{I}(\mathbf{1})_2\cdots Cl]^+$ complex, which has been modeled through a semiempirical method (PM3).

In the model, the chloride ion receives four H-bond from the two facing urea subunits, according to a rather distorted tetrahedral geometry (the angle between the two NH−Cu−NH planes is 60.8°). On the other hand, the Cu^{I} center experiences a regular tetrahedral coordination; in particular, the angle between the phenanthroline planes is 89.2°. In any case, the model suggests that the $[Cu^{I}(\mathbf{1})_2]^+$ complex may act as a receptor for a single spherical anion.

2. Crystal and Molecular Structure of the $Cu^{I}(1)_2Cl$ Salt. On diffusion of *n*-hexane on a 4:1 v/v THF:MeCN solution containing $[Cu^{I}(CH_3CN)_4]ClO_4$, **1** (2 equiv), and Et_3-BzNCl (1 equiv), red-purple crystals of a salt of formula $Cu^{I}(\mathbf{1})_2Cl$ that were suitable for X-ray diffraction studies formed. The corresponding ORTEP plot of the complex salt is shown in Figure 2.

The crystal structure consists of two nonsymmetrically equivalent $[Cu^{I}(\mathbf{1})_2]Cl$ molecules with similar features, in which each Cu atom is coordinated by four nitrogen atoms of two phenanthroline subunits. However, in contrast to what is suggested by modeling studies, the diarylurea pendant arms of each metal complex do not converge to provide a tetrahedral tetrafurcate binding site for chloride, but point toward opposite directions, each one establishing bifurcate hydrogen bonds with different Cl^- ions. Moreover, it appears that the two nonsymmetrically equivalent $[Cu^{I}(\mathbf{1})_2]^+$ molecules are held together by $\pi-\pi$ interactions between two phenanthroline subunits, which are arranged in an offset manner, exhibiting a dihedral angle between the phenanthroline rings of 2.0(1)° and a centroid−centroid distance of 3.67(1) Å.

Noticeably, similar interactions occur in the whole crystal between the phenanthroline fragments of symmetrically related molecules (as shown in the stick model in Figure 3). In particular, $\pi-\pi$ stacking interactions are established between $[Cu(1)L_2]^+-[Cu(1)L_2]^+$ and $[Cu(2)L_2]^+-[Cu(2)L_2]^+$ couples (L = **1**), the separation between the centroids of overlapping phenanthrolines being 3.62(1) and 4.03(1) Å, respectively. Further face-to-face π-stacking interactions are also in place between adjacent diarylurea groups still arranged according to an offset manner: the centroid−centroid distances between superimposed diarylureas are in the range 3.77(1)−3.92(1) Å. All these $\pi-\pi$ interactions are responsible for the array of infinite molecular layers placed normal to the *c* axis. Quite interestingly, chloride ions play an important role in stabilizing such an ordered crystalline arrangement. In particular, each Cl^- ion is H-bonded to two urea fragments belonging to the copper(I) complexes of two different cells. In particular, each chloride ion receives four H-bonds, according to a rather distorted tetrahedron, with the angles between the two NH−Cl−NH planes being 52.9(3) and 53.5(3)°. The hydrogen-bond motif results in infinite chains formed by $Cl(1)^-\cdots[Cu(1)L]^+\cdots Cl(2)^-\cdots[Cu(2)]L^+\cdots Cl(1)^-$. Relevant structural parameters of the N−H···Cl interactions are reported in Table 1.

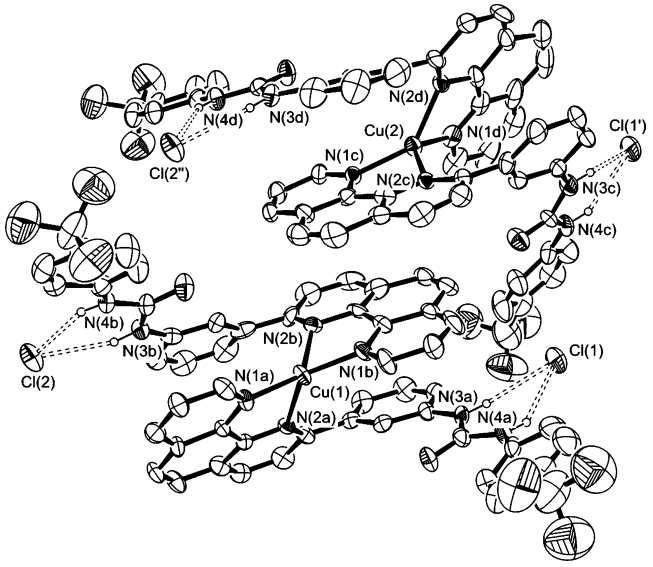

Figure 2. Ortep view of the $[Cu^{I}(\mathbf{1})_2]Cl$ complex salt (names are only show for Cu, N. and Cl atoms; thermal ellipsoids are drawn at the 30% probability level; only hydrogen atoms bonded to the N_{urea} atoms are reported). The crystal contains two nonsymmetrically equivalent $[Cu^{I}(\mathbf{1})_2]^+$ molecules and their counterions; each Cl^- ion interacts with four NHCONH (urea) groups as a proton acceptor of weak hydrogen bonds (drawn with dashed lines).

Extended $\pi-\pi$ interactions and hydrogen bonds induce severe distortions on the coordination geometry of both Cu^{I} centers; in particular, each Cu^{I} center is placed out of the best plane of both the chelate phenanthroline fragments: displacements are 0.35(1) and 0.46(1) Å for Cu(1) and 0.27(1) and 0.35(1) Å for Cu(2). Therefore, the angles between the two CuN_2 planes (65.3(2)° for Cu(1) and 67.5(2)° for Cu(2)) are different than those between the two phenathroline rings bound to the same metal (52.2(1)° for Cu(1) and 56.8(1)° for Cu(2)). Both features are to be compared to the value of 90° of an ideal tetrahedral $[Cu^{I}(phen)_2]^+$ complex (with Cu in the plane of both ligands and the phenanthrolines normal to each other) and to the value of 89.2° from the structural modeling study.

For both metal centers, the bond distances with respect to the two N atoms of the ortho-substituted aromatic rings (2.187(7) Å for Cu(1) and 2.136(6) Å for Cu(2)) are longer than those observed for the nitrogen atoms of the unsubsti-

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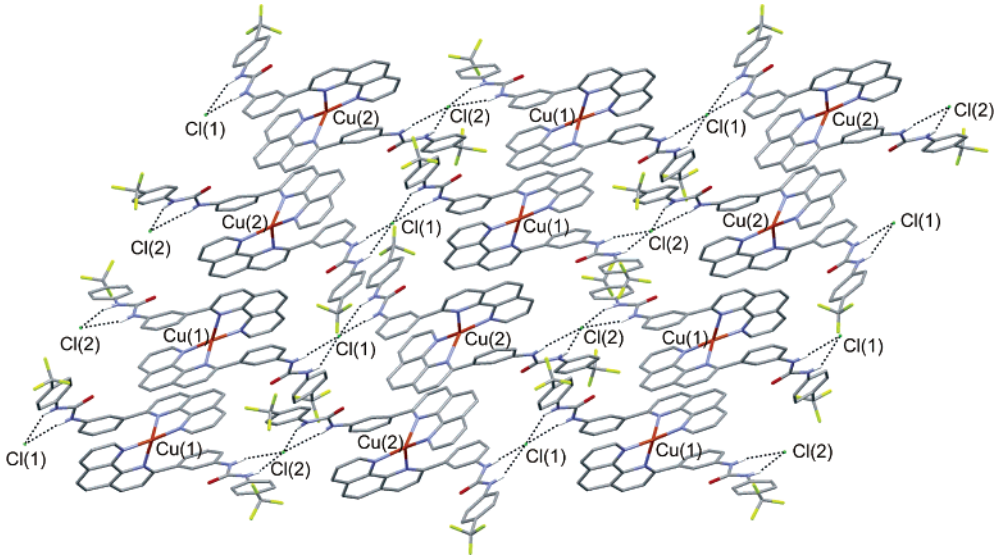


Figure 3. Simplified sketch of the molecular layer normal to the *c* axis; the extensive face-to-face π-stacking interactions between the aromatic groups of the $[Cu^{I}(\mathbf{1})_2]^+$ molecules are observed. Only H atoms bonded to the urea groups are shown, and the hydrogen-bond motifs involving NHCONH groups and Cl^- ions are drawn with dashed lines. Each of the chloride ions, Cl(1) and Cl(2), receives four hydrogen bonds.

Table 1. Structural Parameters of the N−H···Cl Interactions[a]

donor group	D···A (Å)	H···A (Å)	D−H···A (deg)	acceptor atom
N(3a)−H(1Na)	3.256(7)	2.460(7)	154.3(4)	Cl(1)
N(4a)−H(4Na)	3.212(8)	2.447(8)	148.6(5)	Cl(1)
N(3b)−H(3Nb)	3.258(7)	2.432(7)	161.4(5)	Cl(2)
N(4b)−H(4Nb)	3.268(7)	2.451(7)	158.9(5)	Cl(2)
N(3c)−H(3Nc)	3.330(8)	2.535(8)	154.1(5)	Cl(1′)
N(4c)−H(4Nc)	3.184(8)	2.387(8)	154.5(5)	Cl(1′)
N(3d)−H(4Nd)	3.368(8)	2.551(8)	159.1(5)	Cl(2″)
N(4d)−H(4Nd)	3.243(7)	2.420(7)	160.5(5)	Cl(2″)

[a] Symmetry codes: (′) = 1 − *x*, 2 − *y*, 1 − *z*; (″) = 2 − *x*, 1 − *y*, 1 − *x*.

Table 2. Bond Distances (Å) and Angles (deg) around the Two Metal Centers

Cu(1)−N(1a)	1.964(6)	Cu(2)−N(1c)	2.009(6)
Cu(1)−N(2a)	2.187(7)	Cu(2)−N(2c)	2.136(6)
Cu(1)−N(1b)	2.029(7)	Cu(2)−N(1d)	2.001(8)
Cu(1)−N(2b)	2.111(7)	Cu(2)−N(2d)	2.127(8)
N(1a)−Cu(1)−N(2a)	81.30(24)	N(1c)−Cu(2)−N(2c)	80.74(25)
N(1a)−Cu(1)−N(1b)	134.72(25)	N(1c)−Cu(2)−N(1d)	134.40(27)
N(1a)−Cu(1)−N(2b)	132.30(25)	N(1c)−Cu(2)−N(2d)	133.44(27)
N(2a)−Cu(1)−N(1b)	131.73(26)	N(2c)−Cu(2)−N(1d)	130.82(28)
N(2a)−Cu(1)−N(2b)	93.16(27)	N(2c)−Cu(2)−N(2d)	96.21(27)
N(1b)−Cu(1)−N(2b)	82.56(27)	N(1d)−Cu(2)−N(2d)	81.54(29)

tuted rings (1.964(6) for Cu(1) and 2.009(6)). Structural parameters pertinent to metal−ligand interactions are shown in Table 2.

3. Anion Binding in Solution: Poorly Polar Medium. Solid-state results seem to indicate unfavorable arrangement for selective anion binding, which requires face-to-face juxtaposition of the two urea moieties, within the same metal complex. However, geometrical features in the solid state are determined by intermolecular interactions ($\pi-\pi$ stacking and Cl^- bridging through H-bonds), which, in a diluted liquid solution, can be disrupted in favor of solute−solvent interactions. In any case, anion-binding studies were carried out in a 4:1 v/v THF:MeCN solution. Such a medium was chosen in order to maximize the solubility of **1** and of its copper(I) complex.

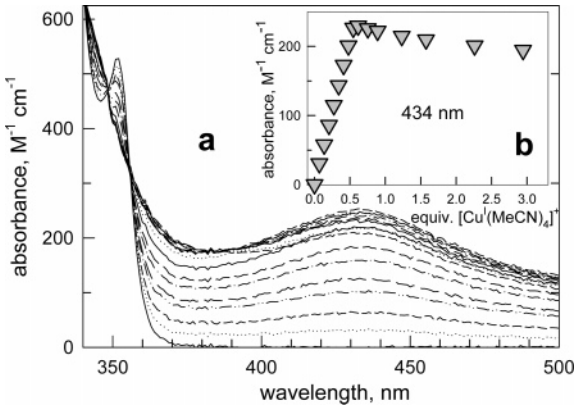


Figure 4. (a) Family of spectra obtained over the course of the titration of a solution 3×10^{-4} M in **1** with a standard solution of $[Cu^{I}(CH_3CN)_4]ClO_4$ in a 4:1 v/v THF:MeCN medium; (b) titration profile based on the absorbance of the band growing at 434 nm.

The formation and stability of the $[Cu^{I}(\mathbf{1})_2]^+$ complex in the THF/MeCN mixture were investigated by titrating a solution of $[Cu^{I}(CH_3CN)_4]ClO_4$ with a standard solution of **1**. On addition of the phenanthroline derivative, the solution took a red-purple color and an absorption band, centered at 434 nm, appeared. The family of spectra recorded over the course of the titration is shown in Figure 4a. The band, which derives from a metal-to-ligand charge-transfer (MLCT) transition within the $[Cu^{I}(\text{phenanthroline})_2]^+$ complex, reaches its maximum on addition of 0.5 equiv of Cu^{I}, indicating the quantitative formation of the $[Cu^{I}(\text{phenanthroline})_2]^+$ complex (see the titration profile in Figure 4b). The absence of any curvature suggests that the constant β_2 of the $Cu^+ + 2L \rightleftarrows [Cu^{I}L_2]^+$ complex formation equilibrium is too large to be determined through a spectrophotometric titration experiment. In any case, it can be assumed that in a THF/MeCN solution, 1×10^{-6} to 1×10^{-4} M in $[Cu^{I}(CH_3CN)_4]ClO_4$ and 2×10^{-6} to 2×10^{-4} M in **1**, the conditions used in this study, the $[Cu^{I}L_2]^+$ complex forms quantitatively. Titration experiments were then carried out by adding a

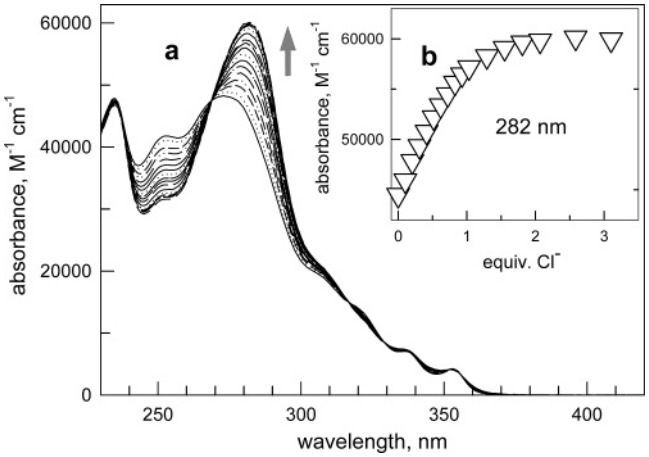


Figure 5. (a) Family of spectra obtained over the course of the titration of a solution 7.5×10^{-6} M in **1** with a standard solution of $[Bu_3BzN]Cl$ in a 4:1 v/v THF:MeCN medium; (b) titration profile based on the absorbance at 282 nm.

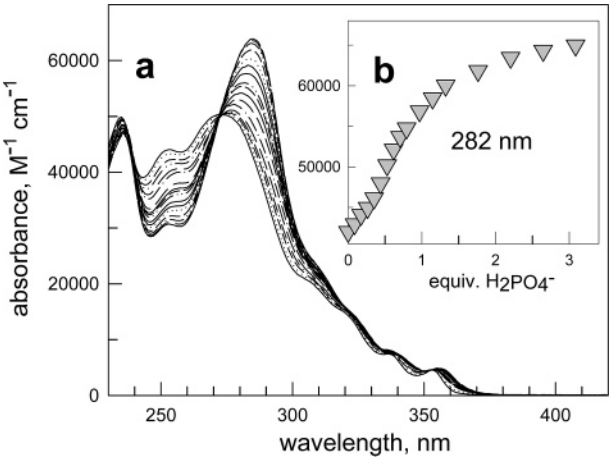


Figure 6. (a) Family of spectra obtained over the course of the titration of a solution 7.5×10^{-6} M in **1** with a standard solution of $[Bu_4N]H_2PO_4$ in a 4:1 v/v THF:MeCN medium; (b) titration profile based on the absorbance at 282 nm.

standard solution of the tetrabutylammonium salt of the envisaged anion, $[Bu_4N]X$, to a solution of the receptor (either **1** or the $[Cu^I(\mathbf{1})_2]^+$ complex).

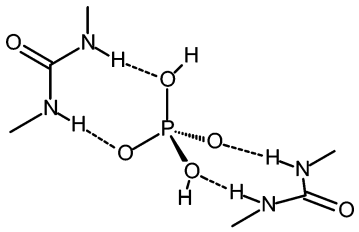
Figure 5a shows the family of spectra obtained over the course of the titration of a solution 7.5×10^{-6} M in **1** with a standard solution of $[Bu_3BzN]Cl$. System **1** shows a band centered at 270 nm, to be associated to a charge-transfer transition along the NH-to-CF_3 dipole, across the benzene ring. On chloride addition, the band at 270 nm undergoes a red shift to the limiting value of 282 nm, while its absorbance increases, a behavior that is ascribed to the formation of the $[L\cdots Cl]^-$ H-bond complex. In particular, on complex formation, negative charge is transferred from the anion to the nitrogen atom of the urea fragment, which increases the intensity of the dipole and accounts for the red shift of the band. Multiwavelength least-squares analysis of spectral data, using the HyperQuad program,[17] indicated the occurrence of the equilibrium $L + Cl^- \rightleftarrows [L\cdots Cl]^-$, with $\log K = 4.46 \pm 0.01$. Formation of a 1:1 H-bond complex was also observed for Br^- ($\log K = 3.75 \pm 0.01$). In the case of I^-, even at a 1×10^{-4} M concentration level, very moderate spectral modifications were observed, and it can be assessed only that $\log K \leq 2$. On the other hand, on titration with the strongly basic acetate anion, the titration profile clearly indicated the formation of a 1:1 H-bond complex, but the absence of any curvature even at a receptor concentration of 1×10^{-6} M pointed toward an association constant $\log K > 7$.

$H_2PO_4^-$ and F^- anions displayed a different behavior. In particular, Figure 6a shows the family of spectra obtained over the course of the titration of a solution 7.5×10^{-6} M in **1** with a solution of $[Bu_4N]H_2PO_4$. Nonlinear least-squares fitting of the titration data over the 250−350 nm wavelength interval indicated the occurrence of two consecutive equilibria ($X^- = H_2PO_4^-$)

$$L + X^- \leftrightarrows [L\cdots X]^-; \log K_{11} = 5.35 \pm 0.04 \quad (1)$$

$$L + [L\cdots X]^- \leftrightarrows [L\cdots X\cdots L]^-; \log K_{21} = 5.11 \pm 0.12 \quad (2)$$

The occurrence of the two stepwise equilibria can be visually perceived in the titration profile in Figure 6b. In fact, a flex point is observed that corresponds to the addition of 0.5 equiv of $H_2PO_4^-$. In particular, during the addition of the first 0.5 equiv, the $[L\cdots X\cdots L]^-$ complex forms; then, on further anion addition, the $[L\cdots X\cdots L]^-$ complex decomposes to give two 1:1 $[L\cdots X]^-$ complexes. The formation of a rather stable 2:1 complex is ascribed to the ability of the $H_2PO_4^-$ ion to receive four H-bonds from two urea subunits, as tentatively shown in structural sketch **5**.



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Note that such an opportunity is not allowed by the more-basic Y-shaped CH_3COO^- anion, which can only establish a bifurcate interaction with a single urea receptor. A similar two-step interaction has been observed for the spherical fluoride ion (see pertinent $\log K$ values in Table 3). At this point, one could ask why spherical chloride and iodide ions do not form the $[L\cdots X\cdots L]^-$ complex in the early stages of the titration. In this instance, it can be suggested that both Cl^- and Br^- are too poorly basic to give a stable H-bond interaction with a second molecule of the urea receptor.

Similar titration experiments were then carried out on solutions of the $[Cu^I(\mathbf{1})_2]^+$ complex. Figure 7a shows the family of spectra obtained over the course of the titration of a solution 1.3×10^{-4} M in the $[Cu^I(\mathbf{1})_2]^+$ receptor with $[Me_3BzN]Cl$. Also in this case, on chloride addition, a red shift of the charge-transfer band was observed, whereas the titration profile (Figure 7b) clearly indicated the formation of a 1:1 receptor:anion adduct. It is therefore suggested that the following association equilibrium occurs: $[Cu^I(\mathbf{1})_2]^+ + Cl^- \leftrightarrows [Cu^I(\mathbf{1})_2\cdots Cl]$. However, the titration profile does not

Table 3. Association Constants (log K values) for the Interaction of Receptors L and $[Cu^{I}(L)_2]^+$ (L = 1), in a 4:1 v/v THF:MeCN Mixture at 25 °C, with Anions

anion	$L + X^- \leftrightarrows [L\cdots X]^-$	$L + [L\cdots X]^- \leftrightarrows [L\cdots X\cdots L]^-$	$[Cu^{I}(L)_2]^+ + X^- \leftrightarrows [Cu^{I}(L)_2\cdots X]$
F^-	5.20 ± 0.03	4.36 ± 0.12	>7
Cl^-	4.46 ± 0.01		>7
Br^-	3.75 ± 0.01		6.15 ± 0.06
I^-	<2		4.52 ± 0.01
CH_3COO^-	>7		>7
$H_2PO_4^-$	5.35 ± 0.04	5.15 ± 0.12	>7

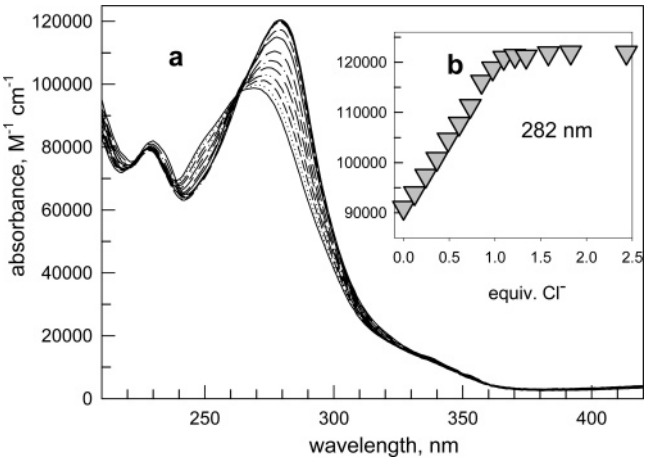
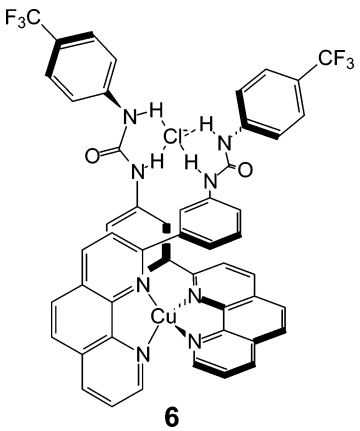


Figure 7. (a) Family of spectra obtained over the course of the titration of a solution 1.3×10^{-4} M in $[Cu^{I}(\mathbf{1})_2]^+$ with a standard solution of $[Bu_4N]Cl$ in a 4:1 v/v THF:MeCN medium; (b) titration profile based on the absorbance at 282 nm.

show any curvature, which prevents the determination of a reliable association constant. No curvature was observed on titration of a 50-fold diluted solution of the $[Cu^{I}(\mathbf{1})_2]^+$ complex (2.6×10^{-6} M) either, which indicates that log K > 7. Thus, the binding constant of chloride to the $[Cu^{I}(\mathbf{1})_2]^+$ receptor is at least 350-fold higher than that of the simple receptor **1**. Such a difference can hardly be ascribed to the favorable electrostatic effect exerted by the Cu^+ ion toward the incoming anion, in view of relatively high distance and ligand shielding effects. Rather, it is suggested that the $[Cu^{I}(\mathbf{1})_2]^+$ receptor, whatever its geometrical arrangement before complexation, reorganizes to chelate the chloride ion with the two urea pendant arms.

A tentative sketch of the 1:1 H-bond complex is shown below, as structural formula **6**, which reflects the calculated structure in Figure 1.



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Formation of a $[Cu^{I}(\mathbf{1})_2\cdots X]$ complex was observed for all the other investigated anions. In particular, remarkable enhancement of the association constant was observed for bromide (log $K = 6.15 \pm 0.06$) and iodide (log $K = 4.52 \pm 0.01$). In the case of $H_2PO_4^-$ and F^- ions, very steep titration profiles were observed, which set log K values beyond the detectable limit under the experimental conditions (log K > 7).

Thus, it appears that the preorientation effect exerted by the Cu^{I} center allows for tetrafurcate H-bond formation with the poorly basic chloride and bromide anions. On the other hand, $H_2PO_4^-$ and F^- ions are able to establish tetrafurcate interaction with two urea subunits even in absence of the templating metal center (vide supra). However, the $[L\cdots X\cdots L]^-$ complex is not especially stable and decomposes on addition of an excess of X^-, giving two 1:1 complexes. This is not the case of the corresponding $[Cu^{I}(L)_2\cdots X]$ complexes, which maintain their integrity even after the addition of a large excess of X^-. Only in the case of Cl^- was decomposition observed, but it was of a different nature. In particular, excess addition of chloride caused the decrease and disappearance of the MLCT band centered at 434 nm. This indicates the occurrence of decomposition of the $[Cu^{I}(phenanthroline_2]^+$ complex, probably due to metal extrusion and formation of the especially stable $[Cu^{I}Cl_2]^-$ species. On the other hand, excess addition of other investigated anions did not modify the MLCT band.

In the case of acetate, the effect of the metal on anion binding could not be investigated, because even metal-free receptor **1** formed a 1:1 H-bond complex $[L\cdots CH_3COO]^-$ with a log K > 7. Thus, we decided to study the interaction of CH_3COO^- and $H_2PO_4^-$ with **1** and $[Cu^{I}(\mathbf{1})_2]^+$ in the more-polar and competing solvent DMSO. In fact, because of the higher solvating tendencies of DMSO, the anion desolvation term in this medium is especially endergonic, which reduces the values of association constants. This circumstance would permit us to discriminate the behavior of more-basic anions and to evaluate their recognition selectivity.

4. Anion Binding in Solution: Highly Polar Medium. DMSO played an effective discriminating role in anion recognition by receptors **1** and $[Cu^{I}(\mathbf{1})_2]^+$. In particular, addition of even a large excess of tetraalkylammonium halides, including F^-, did not cause any modification of the absorption spectra of both **1** and $[Cu^{I}(\mathbf{1})_2]^+$. Also, on titration of a solution 2.6×10^{-4} M in **1** with a standard solution of $[Bu_4N]H_2PO_4$, no detectable shift of the charge-transfer band centered at 270 nm was observed, indicating a very low solution stability of the H-bond complex (log K < 2). However, on titrating a solution containing the $[Cu^{I}(\mathbf{1})_2]^+$

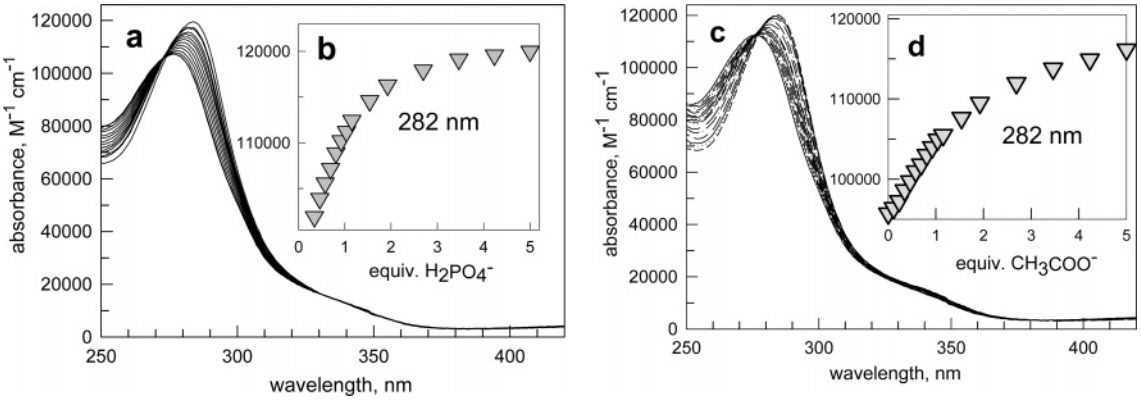


Figure 8. (a) Family of spectraobtained over the course of the titration of a solution 1.3×10^{-4} M in $[Cu^I(\mathbf{1})_2]^+$ with a standard solution of $[Bu_4N]H_2PO_4$ in a DMSO medium; (b) titration profile based on the absorbance at 282 nm; (c) family of spectra obtained over the course of the titration of a solution 1.3×10^{-4} M in $[Cu^I(\mathbf{1})_2]^+$ with a standard solution of $[Bu_4N]CH_3COO$; (d) titration profile based on the absorbance at 282 nm.

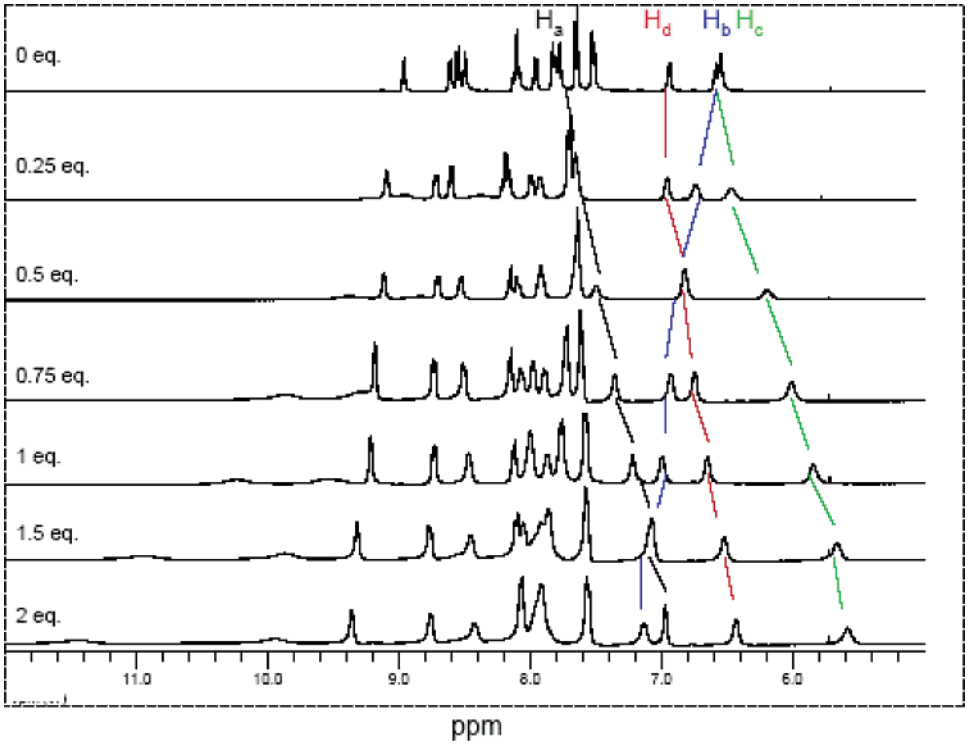


Figure 9. Family of spectra obtained over the course of the titration of a solution 6.0×10^{-3} M in $[Cu^I(\mathbf{1})_2]^+$ with $[Bu_4N]H_2PO_4]$ in a 4:1 v/v DMSO-d_6:CD_3CN medium.

receptor with $[Bu_4N]H_2PO_4$, a pronounced red shift of the charge-transfer band and substantial modifications of the spectral pattern were observed, as shown in Figure 8a. The titration profile, shown in Figure 8b, indicates the formation of a H-bond complex of 1:1 stoichiometry, for which an association constant log $K = 4.15 \pm 0.01$ was calculated through nonlinear least-squares treatment of spectral data. The metal-induced enhancement of the association constant suggests that in the $[Cu^I(\mathbf{1})_2 \cdots H_2PO_4]$ complex, the dihydrogenphosphate ion is chelated by two facing urea subunits, as sketched in structural formula **6**.

Such a hypothesis has been corroborated by a ^{1}H NMR titration experiment. Figure 9 shows the spectra obtained over the course of the titration of a 4:1 v/v DMSO-d_6:CD_3CN solution of $[Cu(\mathbf{1})_2](ClO_4)$ (6×10^{-3} M) with $[Bu_4N](H_2PO_4)$. Spectra indicate that anion binding is responsible for the broadening of the signals, indicating a fluxional process on the NMR time scale, together with important structural changes characterized by large shifts ($\Delta\delta$) of H_a, H_b, H_c, and H_d. Protons of the urea groups are shifted downfield, indicating the formation of a H-bonded adduct with the anion $H_2PO_4^-$. Meanwhile, the protons located on the *m*-phenylene linker undergo upfield shifts ($\Delta\delta(H_a) = -0.81$, $\Delta\delta(H_c) = -1.01$, $\Delta\delta(H_d) = -0.52$) and a downfield shift ($\Delta\delta(H_b) = 0.57$). This behavior is reminiscent of the shifts observed during the formation of helices in other *m*-phenylene-bridged phenanthroline systems[25] and can be attributed to the chelation of $H_2PO_4^-$ by the two urea fragments (in agreement with the UV−vis titration), leading to a helical structure in the ion pair−receptor adduct in solution.

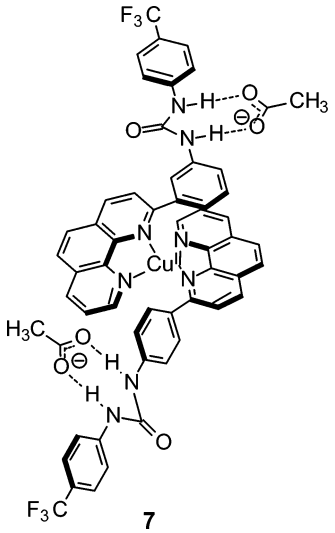
A quite different behavior was observed when the interaction of receptors **1** and $[Cu^I(\mathbf{1})_2]^+$ with acetate was studied.

Following the spectrophotometric titration of plain receptor **1**, an association constant log $K = 3.30 \pm 0.01$ was calculated for H-bond complex $[L\cdots CH_3COO]^-$. On the other hand, Figure 8c shows the family of spectra obtained during the titration with $[Bu_4N]CH_3COO$ of a solution of the $[Cu^I(\mathbf{1})_2]^+$ receptor. The spectral pattern is qualitatively similar to that obtained on titration with dihydrogenphosphate (in Figure 8a), but the titration profile displayed in Figure 8d is distinctly less steep. In particular, a best fitting of the spectral data was obtained on assuming the occurrence of two consecutive equilibria (3) and (4), characterized by stepwise association constants of a rather similar magnitude.

$$[Cu^I(\mathbf{1})_2]^+ + CH_3COO^- \leftrightarrows [Cu^I(\mathbf{1})_2\cdots CH_3COO] \text{ (3); } \log K_1 = 3.50 \pm 0.01$$

$$[Cu^I(\mathbf{1})_2\cdots CH_3COO] + CH_3COO^- \leftrightarrows [Cu^I(\mathbf{1})_2\cdots (CH_3COO)_2]^- \text{ (4); } \log K_2 = 3.24 \pm 0.04$$

It should be noted that the CH_3COO^- ion can establish bifurcate hydrogen bonding interaction with only one urea subunit and cannot profit from the tetrafurcate binding site made by two facing urea subunits offered by the $[Cu^I(\mathbf{1})_2]^+$ receptor, as $H_2PO_4^-$ and spherical halide anions do. Thus, it is suggested that each acetate ion goes to interact with a urea moiety oriented toward the outside. The arrangement of the 1:2 H-bonded complex, $[Cu^I(\mathbf{1})_2\cdots(CH_3COO)_2]^-$, is tentatively sketched as formula **7**. Notice that the log K_1 and log K_2 values are rather close to the log K value determined for acetate interaction with metal-free receptor **1** (log $K = 3.30$) and that the [log K_1 − log K_2] difference is close to the value expected on pure statistical bases ($\Delta\log K = \log 4 = 0.6$). This suggests independent binding of each CH_3COO^- ion at remote and noninterfering urea subunits, as tentatively illustrated by formula **7**.



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Thus, it appears that the $[Cu^I(\mathbf{1})_2]^+$ receptor, at least in the presence of a stoichiometric amount of anion, inverts the selectivity trend on the basis of basicity and chooses to bind $H_2PO_4^-$ in the presence of the more-basic CH_3COO^-. As an example, Figure 10 shows how the percent concentrations of the phosphate and acetate complexes vary over the course of the titration of solutions 1×10^{-4} M in the $[Cu^I(\mathbf{1})_2]^+$ receptor.

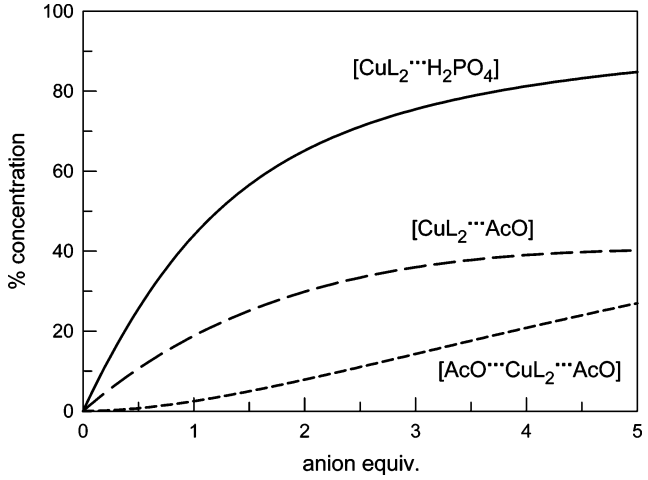

Figure 10. Medium: DMSO, 1×10^{-4} M in $[Cu^I(\mathbf{1})_2]^+$. Solid line: percent concentration of the $[Cu^I(\mathbf{1})_2\cdots H_2PO_4]$ complex over the course of the titration with $H_2PO_4^-$. Dashed lines: percent concentration of the $[Cu^I(\mathbf{1})_2\cdots CH_3COO]$ complex (long dashes) and the $[CH_3COO\cdots Cu^I(\mathbf{1})_2\cdots CH_3COO]^-$ complex (short dashes) over the course of the titration with CH_3COO^-. Percent concentration is given by the ratio of the current concentration of the receptor−anion complex $[Cu^I(\mathbf{1})_2]^+$ over the total concentration of the $[Cu^I(\mathbf{1})_2]^+$ receptor.

It is observed that in the titration with phosphate, on addition of 1 equiv of anion, 49.9% of $H_2PO_4^-$ has been taken by the $[Cu^I(\mathbf{1})_2]^+$ receptor. On the other hand, in the titration with acetate, after 1 equiv addition, only 23.7% of the total CH_3COO^- has been removed from the solution (18.8% as $[Cu^I(\mathbf{1})_2\cdots CH_3COO]$ and $2 \times 2.5\%$ as $[CH_3COO\cdots Cu^I(\mathbf{1})_2\cdots CH_3COO]^-$). Recognition selectivity of $H_2PO_4^-$ over CH_3COO^- increases as the concentration of the $[Cu^I(\mathbf{1})_2]^+$ receptor further decreases.

Conclusion

As recently pointed out,[26] the young discipline of anion coordination chemistry[27] has learned some useful tricks from its older and more-experienced sister, metal coordination chemistry,[28] which includes the chelate effect.[29] The neutral bifurcate H-bond donor urea, L, binds a spherical anion X^-, just as the neutral bidentate ligand ethylenediamine (en) forms two coordinative bonds with a transition-metal ion M^{n+}. However, whereas a second en molecule can further coordinate the metal without any substantial reduction of affinity, giving a $[M(en)_2]^{n+}$ complex with a variety of transition metals in solvents of different polarity, including water, a second molecule of urea is able to establish hydrogen-bonding interactions with the anion, giving the $[L\cdots X\cdots L]^-$ H-bond adduct, only with especially basic ions

(25) (a) Dietrich-Buchecker, C. O.; Colasson, B.; Jouvenot, D.; Sauvage, J.-P. *Chem.—Eur. J.* **2005**, *11*, 4374. (b) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Commun.* **1999**, 615. (c) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; De Cian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2231.
(26) Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671.
(27) Graf, E.; Lehn, J.-M. *J. Am. Chem. Soc.* **1976**, *98*, 6403.
(28) Werner, A. *Z. Anorg. Allg.* **1893**, *3*, 267.
(29) Schwarzenbach, G. *Helv. Chim. Acta* **1952**, *35*, 2344.

(e.g., F^- and $H_2PO_4^-$) and in poorly polar media. Such a failing behavior is to be ascribed to the intrinsic weakness of hydrogen-bonding interactions compared to metal−ligand interactions. However, if two urea subunits are linked together by a spacer of suitable length, anion chelation may occur, essentially because of a favorable entropy contribution. In previously quoted examples,[6−8] the urea subunits have been linked covalently through a spacer or a platform whose nature defines the geometrical features of the receptor's donor set. Alternatively, as shown here, the urea subunits are allowed to assemble together, through coordination to a metal center, which acts as a template. The coordinative geometrical requirements of the metal as well as the design of the urea−ligand conjugate determine size and orientation of the H-bond binding site and help to define the selectivity of anion recognition. Moreover, the use of a kinetically labile metal ion (e.g., Cu^I) imparts versatility to the receptor, which can switch from a locked arrangement, suitable to the recognition of spherical anions, including dihydrogenphosphate, to an unlocked arrangement, which favors the interaction with nonspherical anions, such as the Y-shaped acetate.

Finally, it should be observed that there exists a current and increasing interest on ion-pair recognition,[30] i.e., the simultaneous selective complexation of a metal ion and an anion by a heteroditopic receptor. For instance, Smith has designed rigid polycyclic receptors containing amide N−H fragments that are capable of accommodating a cation (e.g., K^+) and an anion (e.g., Cl^-) in close contact; in the presence of K^+, the receptor's affinity toward Cl^-, in a DMSO solution, was 13-fold enhanced because of a cooperative electrostatic effect.[31] On the other hand, Beer has shown that, in a ditopic receptor containing oxa-crown and amide binding sites, the presence of K^+ inverts the selectivity toward Cl^- and $H_2PO_4^-$ because of the different inference of cooperative electrostatic and conformational allosteric effects.[32] The conjugate urea−phenanthroline system described here is an example of a self-assembling heteroditopic receptor for d^{10} metal salts, e.g., Cu^IX. The metal-induced enhancement of the affinity toward anions, which excludes any electrostatic contribution and is simply related to conformational effects, varies over 2−3 orders of magnitude and is much higher than that observed in previously reported examples.

Acknowledgment. The financial support of the European Union (RTN Contract HPRN-CT-2000-00029) and the Italian Ministry of University and Research (PRIN−Dispositivi Supramolecolari; FIRB−Project RBNE019H9K) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format for the $[Cu^I(\mathbf{1})_2]Cl$ complex salt. This material is available free of charge via the Internet at http://pubs.acs.org.

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