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Anion Recognition and Sensing by a New Macrocyclic Dinuclear Copper(II) Complex: A Selective Receptor for Iodide

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A macrocyclic dinuclear copper complex, $[Cu_2^{II}(\mathbf{1})Br_3(H_2O)]Br$, has been synthesized and characterized by X-ray crystallography, in which the macrocycle is folded to form a bowl-shaped cavity. The sensing ability of the receptor has been studied for halides by UV−vis spectroscopy in water−acetonitrile (1:3, v/v) and water. The results indicate that the new receptor exhibits a strong affinity and selectivity for iodide.

The field of anion coordination chemistry continues to expand with new synthetic molecules capable of recognizing anions with environmental and biomedical relevance.[1] Various types of synthetic receptors have been developed that employ hydrogen bonds offered by specific binding sites as in azamacrocycles,[2] amides,[3] thioamide,[4] urea,[5] and pyrroles[6] to bind anions with size and shape selectivity in various media. Without the involvement of hydrogen bonds, quaternized ammonium hosts by electrostatic forces,[7] and azamacrocycles[8a] and phosphonium hosts[8b] by ion pairing (in an aqueous medium where hydrogen bonding is weak)[8] are known to form anion complexes in an aqueous medium. An alternative approach is to use dinuclear metal complexes[9] as shown in seminal papers by Nelson[10] and Fabbrizzi[11] with two copper ions in cryptand-based receptors, providing vacant axial sites that are available to coordinate an anion through Lewis acid−base interactions. The presence of two metal ions further increases the rigidity of a cryptand, and the metal−metal distance within the cavity determines the binding strength, displaying selectivity for an anion with the correct *bite length*. For example, the dicopper(II) complex of *m*-xylyl-based cryptand ($Cu^{II}-Cu^{II}$ = 6.10 Å) showed a strong affinity for an anion of comparable size such as N_3^- or NCS^- but failed to bind small halides.[10] However, the dicopper(II) complex of furan-based cryptand in which the two metal centers are separated by 3.87 Å formed complexes with halides showing a strong selectivity for chloride.[11] This approach was further employed recently in the dinuclear copper(II) complex of an expanded cryptand binding nucleotide with a high selectivity for guanosine 5′-monophosphate[12] and in the cobalt(II) complex of *m*-xylyl-based cryptand [$Co^{II}-Co^{II}$ = 4.866(3) Å] binding chloride.[13]

Although transition-metal complexes with monocyclic analogues are well documented and a high level of understanding has been achieved on physicochemical and structural aspects,[14] their application as anion receptors is comparatively little known.[15] Monocycle-based dinuclear complexes

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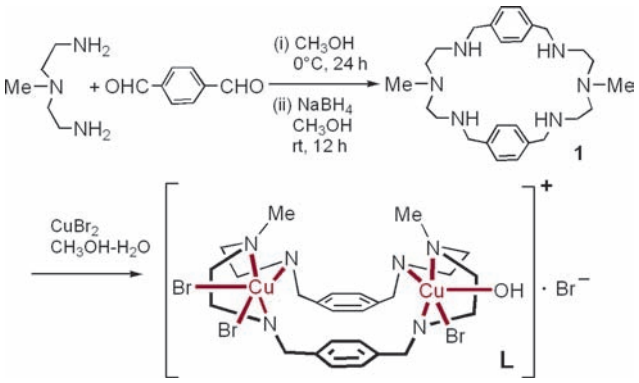
Scheme 1. Synthesis of $[Cu_2^{II}(\mathbf{1})Br_3(H_2O)]Br$



are expected to be more rigid than their precursors but would be less rigid than their bicyclic analogues, thereby expecting not to be restricted only for an anion with a specific *bite length*. In our continuing effort to design anion binding hosts,[16] we synthesized a macrocycle-based compound **1**, whose central nitrogen atoms are attached with methyl groups to provide an additional rigidity, and obtained the square-pyramidal dinuclear copper(II) complex $[Cu_2^{II}(\mathbf{1})Br_3(H_2O)]^+$, which is suitable for recognizing an anion. Herein, we report the synthesis and crystal structure of the new dinuclear complex, and its halide-binding properties in acetonitrile−water (CH_3CN-H_2O) mixture (3:1) and water, showing a strong affinity for iodide.

The free macrocycle **1** was prepared as reported previously.[17] The synthesis of a macrocyclic dinuclear copper complex was accomplished from the reaction of **1** with 2 equiv of anhydrous $CuBr_2$ in a H_2O-CH_3OH mixture. Crystals suitable for X-ray analysis were obtained by the slow evaporation of a water solution of the complex.

X-ray analysis[18] reveals that the complex is crystallized in the space group *Pn* to yield a molecular formula $C_{26}H_{44}Br_3Cu_2N_6O\cdot Br$ (**R**), in which two Cu^{II} ions reside at both N_3 sites in the macrocycle. Each Cu^{II} ion is coordinated with three macrocyclic nitrogen atoms and one bromide at the equatorial plane, but one has an axial bromide, while the other has an axial water, thus forming a square-pyramidal geometry. Such an effect leads to the macrocycle adopting a bowl-shaped cavity (Scheme 1 and Figure 1) with a Cu−Cu distance of 7.101 (4) Å. The Cu−N distances are 2.025(4)−2.056(4) Å, which are comparable to the corresponding Cu−N distances [1.973(5)−2.056(5) Å] observed in an *m*-xylyl-based macrocycle.[10] The $Cu-Br_{axial}$ distance, 2.959(4) Å, is significantly longer than the $Cu-Br_{equatorial}$ distances [Cu2−Br2 = 2.3890(7) Å and Cu1−Br1 = 2.4171(7) Å], a phenomenon that is known as Jahn−Teller distortion.[15a] One bromide remains outside the cavity, interacting with the

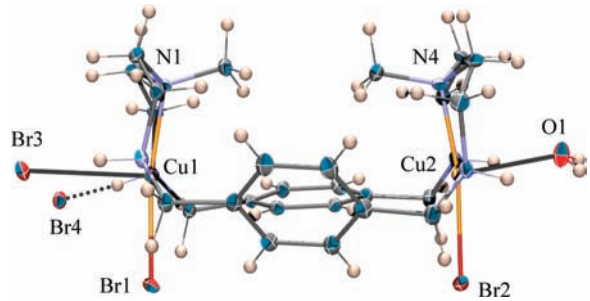


Figure 1. Crystal structure of $[Cu_2^{II}(\mathbf{1})Br_3(H_2O)]Br$.

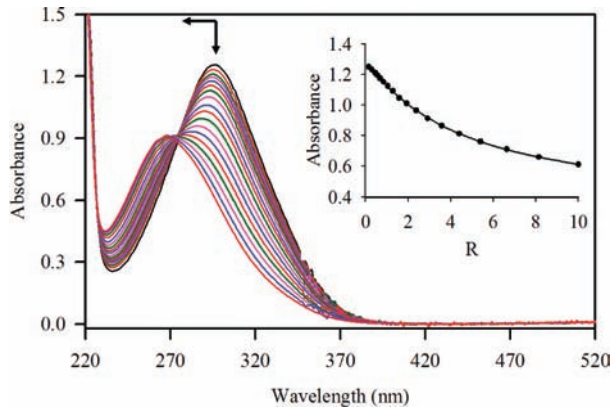


Figure 2. Changes in the absorption spectra of **R** (1×10^{-4} M) with an increasing amount of F^- ($R = [F^-]_0/[\mathbf{R}]_0 = 0-10$) in CH_3CN-H_2O (3:1, v/v). The titration curve is shown in the inset.

secondary nitrogen atom (N2) through NH [N2···Br4 = 3.261(3) Å] to satisfy the charge requirement of the complex. We also isolated crystals from **L** in the presence of two equivalents of tetrabutyl ammonium bromide, showing the same structure.

The receptor was found to be insoluble in aprotic solvents like CH_3CN or $CHCl_3$ but soluble in a CH_3CN-H_2O mixture. Therefore, a solution of CH_3CN containing 25% H_2O was used for the titration experiments of **R** (1×10^{-4} M) performed by a UV−vis spectroscopic method using tetrabutylammonium halides (1×10^{-2} M) at room temperature. The receptor showed an absorption band at 296 nm in the absence of an anion. The addition of F^- to the receptor solution resulted in a gradual decrease in the intensity while shortening the wavelength (blue shift), showing an isosbestic point at 277 nm (Figure 2). A similar trend was observed when Cl^- was added to **R**, whereas the addition of Br^- did not result in any appreciable change in λ_{max} or the intensity. This observation is consistent with our crystallographic evidence showing one outer-sphere Br^- outside the cavity (Br4 in Figure 1).

The response of **R** to I^- was quite different than other halides studied showing a remarkable enhancement of the absorption (Figure 3) while λ_{max} shifted slightly (blue shift of 3 nm) as compared with chloride (13 nm) and fluoride (29 nm). The absorption was significantly affected upon interaction with iodide, displaying a new band at 360 nm. The addition of iodide to **R** (1×10^{-3} M) in CH_3CN-H_2O also resulted in a visual color change (blue to green), as demonstrated in Figure 4. The blue color of the receptor solution was changed to light blue for fluoride or chloride; however, no color change was seen for bromide. The relative changes

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(18) Crystal data for **R**: $C_{26}H_{44}Br_3Cu_2N_6O\cdot Br$, $M = 903.39$, monoclinic, $a = 7.9327(10)$ Å, $b = 9.1110(11)$ Å, $c = 22.667(2)$ Å, $\alpha = 90°$, $\beta = 99.465(6)°$, $\gamma = 90°$, $V = 1616.0(3)$ Å^3, $T = 90.0(5)$ K, space group *Pn*, $Z = 2$, μ(Mo Kα) = 6.292 mm^{-1}, 30 150 reflections measured, 9778 independent reflections ($R_{int} = 0.023$). The final R1 was 0.038 [$I > 2\sigma(I)$]. The final R1 was 0.049 (all data). The goodness of fit on F^2 was 1.027. Flack parameter = 0.484(8). CCDC 764942.

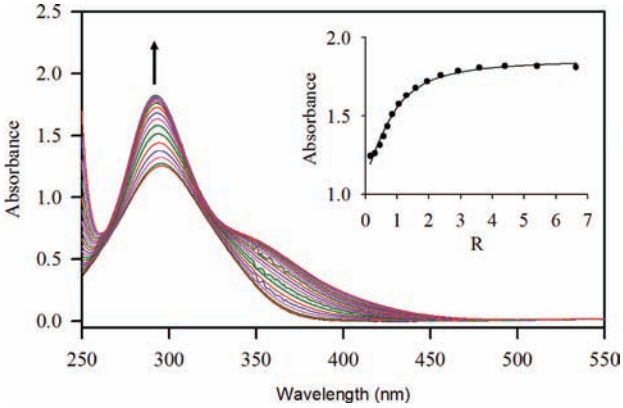

Figure 3. Changes in the absorption spectra of **R** (1×10^{-4} M) with an increasing amount of I^- ($R = [I^-]_0/[\mathbf{R}]_0 = 0-10$) in CH_3CN-H_2O (3:1, v/v). The titration curve is shown in the inset.

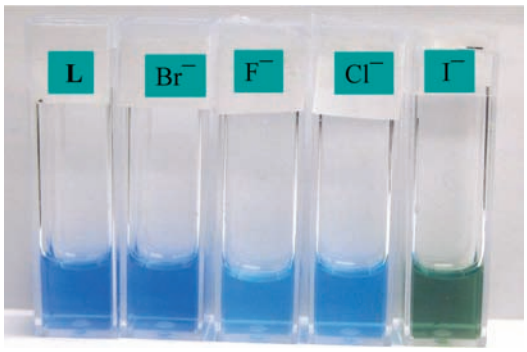

Figure 4. Color changes observed upon the addition of different halides (10 equiv) to **R** (1×10^{-3} M) in CH_3CN-H_2O (3:1, v/v).

Table 1. Equilibrium Constants (K, M^{-1}) of **R** for Anions As Determined from UV−Vis Titrations in CH_3CN-H_2O (3:1, v/v)

	K_a (M^{-1})	
anion	CH_3CN-H_2O (3:1, v/v)	H_2O
bromide	no binding	no binding
fluoride	2270	20
chloride	3200	25
iodide	23 900	125

in the wavelength or intensity as a function of the anion concentration satisfied 1:1 equilibrium isotherms as calculated from the nonlinear regression analysis,[19] showing a strong affinity for I^- (Table 1). The observed selectivity pattern of **R** for halides ($I^- > Cl^- > F^- > Br^-$) is different from that of the dicopper(II) complex of the *m*-xylyl-based cryptand ($Cl^- > F^- > Br^- > I^-$) reported earlier.[11] In our study, the selectivity roughly correlates with the size of the halides. The spectral changes are perhaps due to the replacement of attached groups linked to copper ions by an added anion. We also performed UV−vis binding studies in water under neutral conditions (pH = 7.0); however, the receptor displayed negligible changes in the absorption spectra in the presence of halide, showing a weak affinity for

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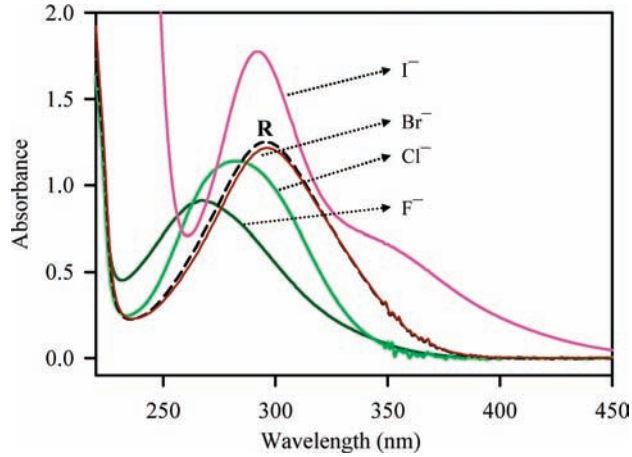

Figure 5. Changes in the absorbance of **R** (1×10^{-4} M) in the presence of 10 equiv of different anions in CH_3CN-H_2O (3:1, v/v) at room temperature. λ_{max}: **R** = 296 nm, I^- = 293 nm, Cl^- = 283 nm, and F^- = 267 nm.

I^- (125 M^{-1} compared to 23 900 M^{-1} in CH_3CN-H_2O) and almost no affinity for F^-, Br^-, or Cl^-.

The receptor exhibited different responses to different halides in terms of the absorption intensity and band (λ_{max}; Figure 5). The opposite trend in the absorbance with fluoride and iodide could be related to the charge-transfer complexes between **R** and X^-. At the end of the titrations, the absorption band (λ_{max}) of **R** at 296 nm was shifted to 267, 283, and 293 nm for F^-, Cl^-, and I^-, respectively, suggesting that the magnitude of $\Delta\lambda_{max}$ is primarily dependent on their relative basicity ($F^- > Cl^- > I^-$).

In conclusion, we have synthesized and structurally characterized a new macrocycle-based dinuclear copper complex, as an ideal receptor for iodide. The receptor binds iodide strongly, showing good selectivity for it over other halides. The new receptor is capable of discriminating anions that can be monitored from their λ_{max}, absorption intensity, or even visual color change. An appreciable variation of the magnitude of λ_{max} with different anions allows the receptor to be useful for the direct identification of halides in solution. We are currently pursuing further work in this direction.

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Supporting Information Available: Crystallographic file in CIF format, synthetic procedures of **1** and **L**, packing diagram of $[Cu_2^{II}(\mathbf{1})Br_3(H_2O)]Br$, and UV−vis titration spectra of **L** with various anions in an CH_3CN-H_2O mixture (3:1) and water. This material is available free of charge via the Internet at http://pubs.acs.org.