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

John S. Mendy¹, Musabbir A. Saeed¹, Frank R. Fronczek², Douglas R. Powell³, and Md. Alamgir Hossain¹

¹ Department of Chemistry, Jackson State University, Jackson, MS 39212

² Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803

³ Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019

Abstract

A macrocyclic dinuclear copper complex, $[\text{Cu}_2^{\text{II}}(\text{1})\text{Br}_3(\text{H}_2\text{O})]\text{Br}$ 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 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 which employ hydrogen bonds offered by specific binding sites as in azamacrocycles,² amides,³ thioamide,⁴ urea⁵ and pyrroles⁶ 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 aqueous medium where hydrogen bonding is weak)⁸ are known to form anion complexes in aqueous medium. An alternative approach is to use dinuclear metal complexes⁹ as shown in seminal papers by Nelson¹⁰ and Fabbrizzi¹¹ 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 correct *bite length*. For example, the dicopper(II) complex of *m*-xylyl-based cryptand (Cu(II)–Cu(II) = 6.10 Å) showed strong affinity for an anion of comparable size 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 strong selectivity for chloride.¹¹ This approach was further employed recently in the dinuclear Cu(II) complex of an expanded cryptand binding nucleotides with high selectivity for GMP,¹² and in the Co(II) complex of *m*-xylyl cryptand (Co(II)–Co(II) = 4.866(3) Å) binding chloride.¹³

Although transition metal complexes with the 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-

Correspondence to: Alamgir Hossain.

Supporting Information available: Crystallographic file in CIF format, synthetic procedures of **1** and **R**, packing diagram of **H**, UV-VIS titration spectra of **R** with various anions in acetonitrile-water mixture (3:1) and water in pdf format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

based dinuclear complexes 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 specific *bite length*. In our continuing effort in designing anion binding hosts,¹⁶ we synthesized a macrocycle-based compound **1**, whose central nitrogens are attached with methyl groups to provide an additional rigidity, and obtained the square pyramidal dinuclear copper(II) complex, $[\text{Cu}_2^{\text{II}}(\mathbf{1})\text{Br}_3(\text{H}_2\text{O})]^+$ that are suitable to recognize an anion. Herein, we report the synthesis and crystal structure of the new dinuclear complex, and its halide binding properties in acetonitrile-water mixture (3:1) and water, showing strong affinity for iodide.

The free macrocycle **1** was prepared as reported previously.¹⁷ The synthesis of macrocyclic dinuclear copper complex was accomplished from the reaction of **1** with two equivalents of anhydrous CuBr_2 in $\text{H}_2\text{O}/\text{CH}_2\text{OH}$ mixture. Crystals suitable for X-ray analysis were obtained by slow evaporation of a water solution of the complex.

The X-ray analysis¹⁸ reveals that the complex is crystallized in the space group, Pn to yield a molecular formula, $\text{C}_{26}\text{H}_{44}\text{Br}_3\text{Cu}_2\text{N}_6\text{O}\cdot\text{Br}$ (**R**) in which two Cu(II) ions reside at both N_3 sites in the macrocycle. Each Cu(II) is coordinated with three macrocyclic nitrogens and one bromide at equatorial plane, but one has an axial bromide, while the other has an axial water, thus forming a square pyramidal geometry. Such effect leads to the macrocycle adopting a bowl-shaped cavity (Figure 1) with the Cu–Cu distance of 7.101 (4) Å. The Cu–N distances are 2.025(4) to 2.056(4) Å that are comparable to the corresponding Cu–N distances (1.973(5) to 2.056(5) Å) observed in *m*-xylyl-based macrocycle.¹⁰ The Cu–Br_{axial} distance, 2.959(4) Å is significantly longer than those observed in Cu–Br_{equatorial} distances (Cu2–Br2 = 2.3890(7), and Cu1–Br1 = 2.4171(7) Å) – a phenomenon that is known as a Jahn-Teller distortion.^{15a} One bromide remains outside the cavity interacting with the secondary nitrogen (N2) through NH (N2...Br4 = 3.261 (3) Å) to satisfy the charge requirement of the complex”.

The receptor was found to be insoluble in aprotic solvents like CH_3CN or CHCl_3 , but soluble in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixture. Therefore, a solution of CH_3CN containing 25% of H_2O was used for the titration experiments of **R** (1×10^{-4} M) performed by 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 isobestic point at 277 nm (Figure 2). The similar trend was observed when Cl^- was added to **R**, whereas the addition of Br^- did not result any appreciable change in λ_{max} or 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 the rest of the halides, showing a remarkable enhancement of the absorption (Figure 3) while the 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 the interaction with iodide, displaying a new band at 360 nm. The addition of iodide to **R** (1×10^{-3} M) in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ also resulted into the visual color change (blue to green) as demonstrated in Figure 4. The blue color of the receptor solution was changed into light blue for fluoride or chloride, however, no color change was seen for bromide. The relative changes in wavelength or intensity as a function of an anion concentration, satisfied 1:1 equilibrium isotherms as calculated from the non-linear regression analysis,¹⁹ showing strong affinity for I^- (Table 1). The observed selectivity pattern of **R** for halides ($\text{I}^- > \text{Cl}^- > \text{F}^- > \text{Br}^-$) is different than dicopper(II) complex of *m*-xylyl cryptand ($\text{Cl}^- > \text{F}^- > \text{Br}^- > \text{I}^-$) reported earlier.^[11] In our study, the selectivity roughly correlates with the size of halides. The spectral changes are perhaps due to the replacement

of attached groups linked the copper ions by an added anion. We also performed UV-VIS binding studies in water under neutral condition (pH = 7.0), however, the receptor displayed negligible changes in the absorption spectra in the presence of halide, showing a weak affinity for I^- (125 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 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 complex, as an ideal receptor for iodide. The receptor binds iodide strongly, showing 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 useful for the direct identification of halides in solution. We are currently pursuing further work in this direction.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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18. Crystal data for **R**: $C_{26}H_{44}Br_3Cu_2N_6O \cdot Br$, $M = 903.39$, monoclinic, $a = 7.9327(10) \text{ \AA}$, $b = 9.1110(11) \text{ \AA}$, $c = 22.667(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 99.465(6)^\circ$, $\gamma = 90^\circ$, $V = 1616.0(3) \text{ \AA}^3$, $T = 90.0(5) \text{ K}$, space group Pn , $Z = 2$, $\mu(\text{MoK}\alpha) = 6.292 \text{ mm}^{-1}$, 30150 reflections measured, 9778 independent reflections ($R_{int} = 0.023$). The final R_I was 0.038 ($I > 2\sigma(I)$). The final R_I was 0.049 (all data). The goodness of fit on F^2 was 1.027. Flack parameter = 0.484(8). CCDC 764942.
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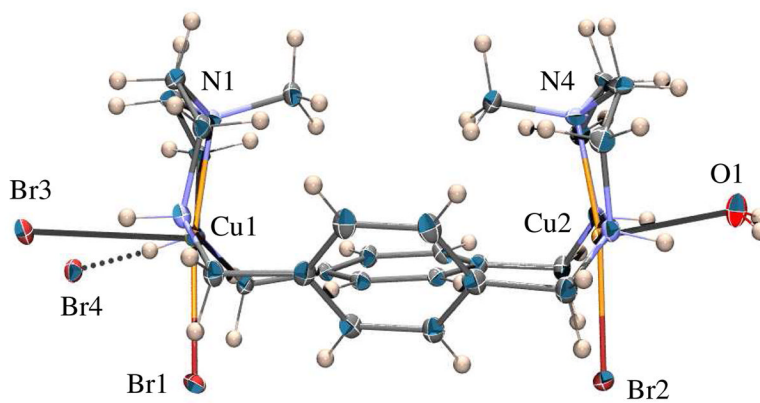


Figure 1.
Crystal structure of [Cu₂II(1)Br₃(H₂O)]Br.

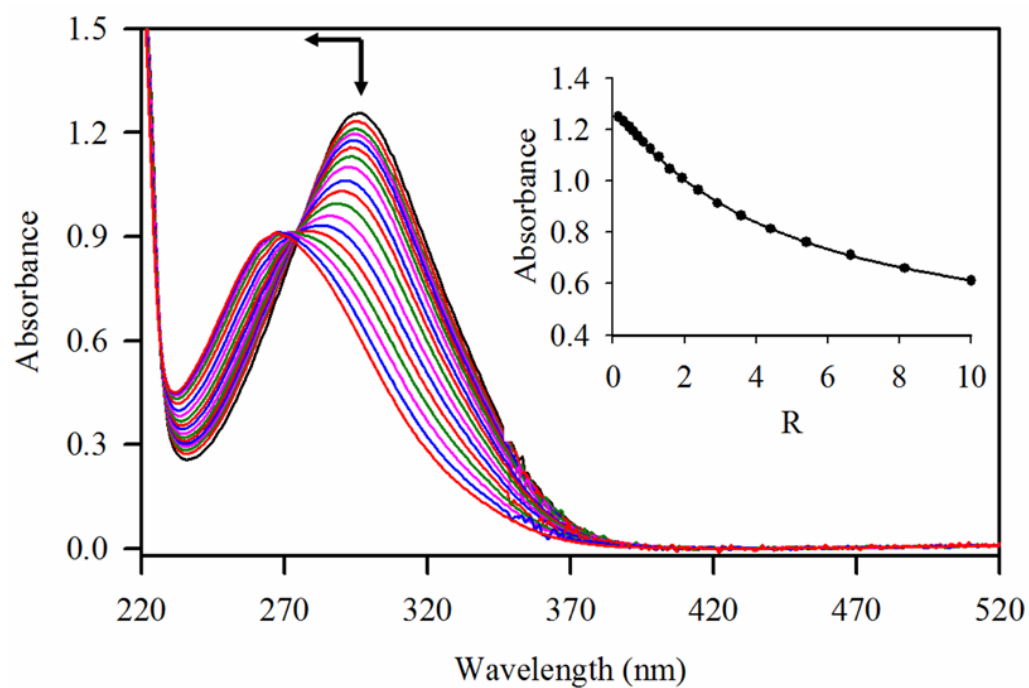


Figure 2. Changes in absorption spectra of \mathbf{R} (1×10^{-4} M) with an increasing amount of I^- ($R = [\text{I}^-]_0 / [\mathbf{R}]_0 = 0 - 10$) in $\text{CH}_3\text{CN-H}_2\text{O}$ (3:1 v/v). The titration curve is shown in the inset.

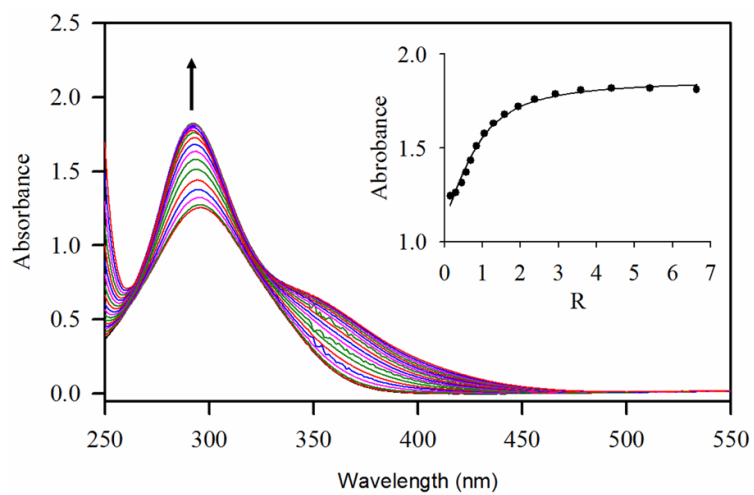


Figure 3. Changes in absorption spectra of **R** (1×10^{-4} M) with an increasing amount of F^- ($R = [F^-]_0/[R]_0 = 0 - 10$) in CH_3CN-H_2O (3:1 v/v). The titration curve is shown in the inset.

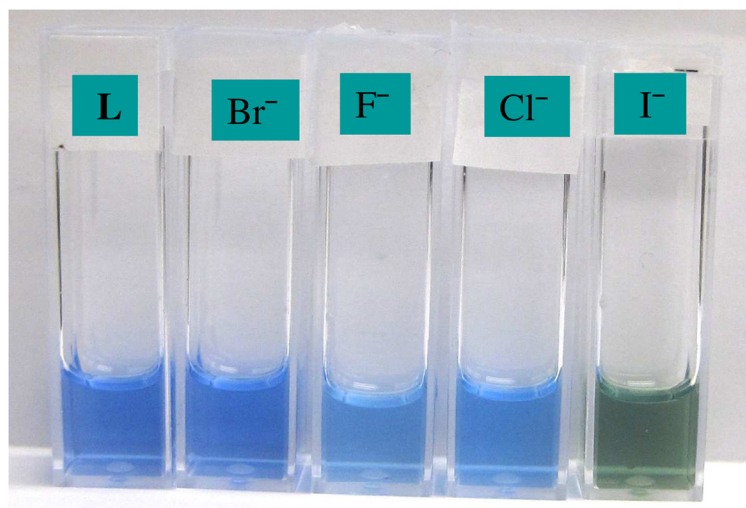


Figure 4. Color changes observed upon the addition of different halides (10 equiv.) to **R** (1×10^{-3} M) in $\text{CH}_3\text{CN-H}_2\text{O}$ (3:1 v/v).

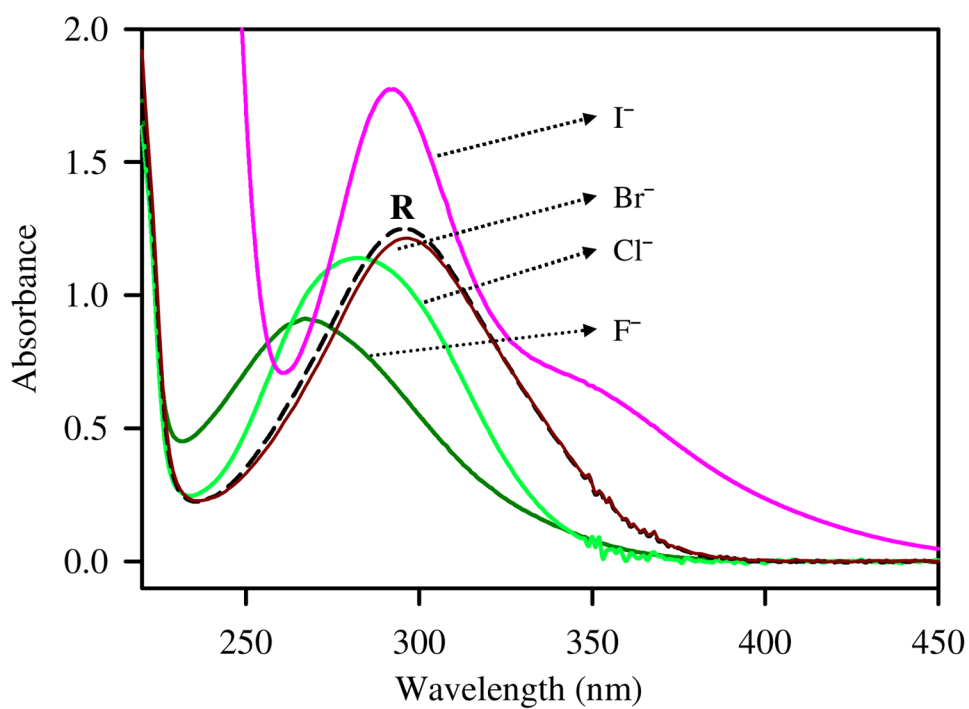
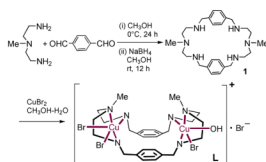


Figure 5. Changes in absorbance of **R** (1×10^{-4} M) in the presence of 10 equivalents of different anions in CH₃CN-H₂O (3:1 v/v) at room temperature. λ_{\max} : **R** = 296, I⁻ = 293, Cl⁻ = 283, F⁻ = 267 nm.



Scheme 1.
Synthesis of $[\text{Cu}_2\text{II}(\mathbf{1})\text{Br}_3(\text{H}_2\text{O})]\text{Br}$

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).

Anion	K_a (M^{-1})	
	CH_3CN-H_2O (3:1 v/v)	H_2O
	No binding	No binding
Fluoride	2270	20
Chloride	3200	25
Iodide	23900	125