Evaluation of Anionic Transition Metal Complexes with Octaaza Protonated 2,3,10,11,18,19,26,27-Octahydroxy-1,4,9,12,17,20,25,28-Octa Azacyclodotriacontane-1,3,9,11,17,19,25,27 -Octaene as Cation

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ABSTRACT

In the present study, evaluation of anionic transition metal complexes with octaaza protonated 2,3,10,11,18,19,26,27-octahydroxy-1,4,9,12,17,20,25,28-octa-azacyclodotriacontane-1,3,9,11, 17,19,25,27-octaene as cation has been undertaken. Data indicates that this macrocyclic molecule can potentially be used as pH indicator and chemosensors for varied biological and non biological applications.

INTRODUCTION

The supramolecular chemistry of anions is one of the most promising vistas within the field of supramolecular chemistry. Anion supramolecular chemistry involves the development and use of selective anion receptors[1-3]. In fact, today a large number of coordination studies in literature describe a wide range of ligands for anion coordination involving hydrogen bonds[4,5], electrostatic interactions[6,7] or coordination with suitable metal cation[8,9]. The nature of the binding sites and their specific spatial arrangement determine the binding constant with a certain anion. Usually, a selective coordination is established when a large host-guest complementarily is attained. An issue related with anion binding is the development of anion chemosensors or reagents. These are molecular entities or ensembles that are capable of signaling the presence of a certain anion[10,11]. Whereas chemical sensors or chemosensors usually refer to systems that typically employ coordinative forces for anion binding, the term reagents or chemodosimeter is related with the use of specific irreversible reactions involving anions. Additionally, a chemosensors contains a ''signaling subunit'' capable of giving information about the binding event; i.e. electrochemical shifts of the redox potentials in redox-active molecules through color changes or modification of the fluorescence emission. This property has been exploited in the development of chemical sensors and reagents[12].

Anions play a major role in regulating crucial physiological function and industrial processes. Consequently, in the environment, anionic species can be either essential to sustain growth or act as harmful pollutants. It is therefore not surprising that in the last decade the development of colorimetric and luminescent sensors for anions, where the function, concentration and location of the negatively charged species can be monitored, has become an active area of research in supramolecular chemistry[13]. While earlier examples of anion sensors focused on the proof of various principles, often using structurally simple hydrocarbon-based chromophores/ fluorophores, furnished with one or more charged or charge-neutral recognition moieties, recent anion sensing research has become more focused[14]. Such target based investigations include the development of more specific sensors (e.g. recognition of a particular anion, or family of anions); more potent sensors (e.g. that can target a particular anion within a given concentration range); sensors that function in more competitive media (e.g. aqueous media, for use in environmental, biological or biomedical applications); and

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more economical sensors (e.g. that can be formed in few synthetic steps using inexpensive starting materials)[15,16].

For practical applications, these sensors are need to satisfy strict photo-physical criteria, such as being able to absorb and emit at long wavelengths to facilitate the use of naked eye detection or the use of inexpensive optics, posses relatively long lived excited states[17], and have high quantum yields. Due to its unique photophysical properties, the naphthalimide structure has found application in many areas of chemistry[18]. Its absorption and fluorescence emission spectra lie within the UV –VIS regions and the various photophysical properties can be easily fine tuned through judicious structural design. Synthetic modifications are readily accommodated on either the aromatic 'naphthalene' moiety itself or at the 'N-imide site', allowing for varieties of functional groups and structural motifs to be incorporated.

MATERIALS AND METHODS

Preparation of complexes:

All the metal complexes were prepared and reported[19].

RESULTS AND DISCUSSION

Activity of Complexes

pH –Dependence of UV-visible spectra

The aqueous solutions of the copper complex {(Mac.1) [$CuCl_6$] Cl_4. 1.5 H_2O} (20 mL (1 mM); 20 μmol) was prepared, and the electronic absorption spectra were recorded at every addition[20] of 0.66 mL of 0.03 M (20 μmol) NaOH aqueous solution until the total volume of the NaOH solution (2.66 mL; 80 μmol)) neutralized the four equivalents of macrocyclic protons. Prior to the addition of NaOH solution, pH of the complex solution is 3.74. Upon addition of 2.66 mL of 0.03 M base, the pH changed from 3.74 to 10.05. Then, to the above neutralized solution was added 0.05 M HCl solutions in 0.4 mL (20 μmol) increments for the reverse procedure of protonation, and the electronic spectra were recorded. During addition of 1.6 mL of 0.05 M acid, the pH changed from 10.05 to 3.74.

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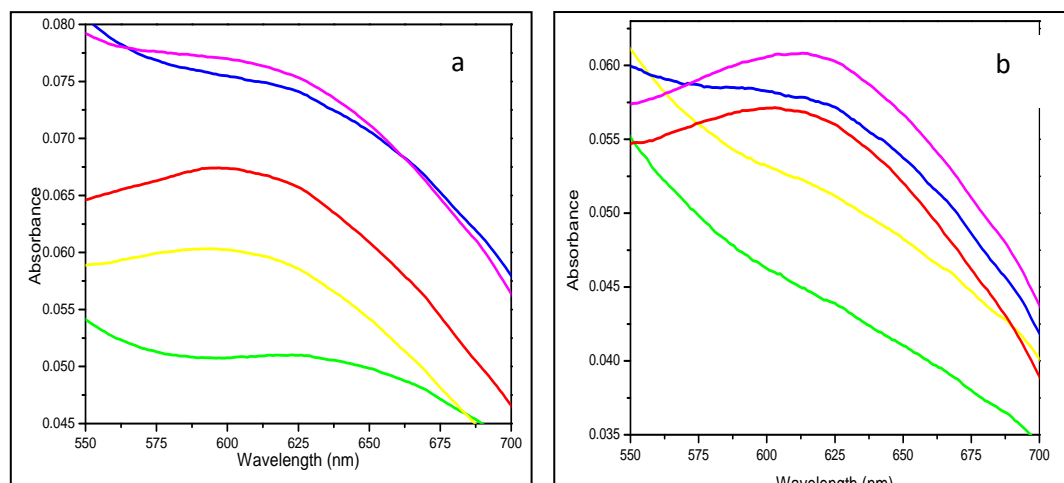
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Visible region

Figure No. 1: a) Absorption spectra of a 10^{-3} M solution of copper complex measured in the visible region at varying pH values (3.74 (green), 5.20 (yellow), 6.57 (red), 8.61 (blue) and 10.05 (pink)) with the addition of 0.03 M NaOH solution (deprotonation);

Figure No. 1: b) Absorption spectra of a 10^{-3} M solution of copper complex measured in the visible region at varying pH values (9.57(pink), 8.61(blue), 6.57(red), 5.20(yellow) and 3.74(green)) with the addition of 0.05 M HCl solution (protonation).

The electronic spectrum of copper complex (Fig.1 (a)) without NaOH solution exhibited a broad band at λmax = 625 nm assignable to a d-d band. On addition of every 0.66 mL of 0.03 M NaOH solution, the color changed gradually from light green to dark blue and the d-d band shifted to a lower wavelength with an increase in intensity (λmax = 603, 602, 600 and 598 nm). On addition of 0.05 M HCl solution to neutralize the added base in the reverse procedure, the color changed from dark blue to light green and the d-d band shifted to a higher wavelength with decrease in intensity and the spectrum (Fig.1 (b)) finally reached its original value.

The neutralization of four macrocycle protons may be attributable to either

i)   {(Mac.1) [CuCl$_6$] Cl$_4$. 1.5 H$_2$O} to {(Mac.1-4H$^+$) [CuCl$_4$] Cl$_2$. 1.5 H$_2$O} or

ii) {(Mac.1) [CuCl$_6$] Cl$_4$. 1.5 H$_2$O} to {(Mac.1-4H$^+$) [CuCl$_6$] 1.5 H$_2$O} conversion.

Had the conversion is taking place by (ii), there could not be any color change (wavelength shift) as neither geometry nor the ligand field of the anionic complex is changed; Contrary to

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this the expected color change (wavelength shift), due to the change in geometry[21] of the anionic complex in the conversion route (i), is experimentally observed. This leads to the inference that upon deprotonation/protonation the interconversion of geometries for anionic metal complex is taking place as given in conversion (i) thereby excluding the route (ii).
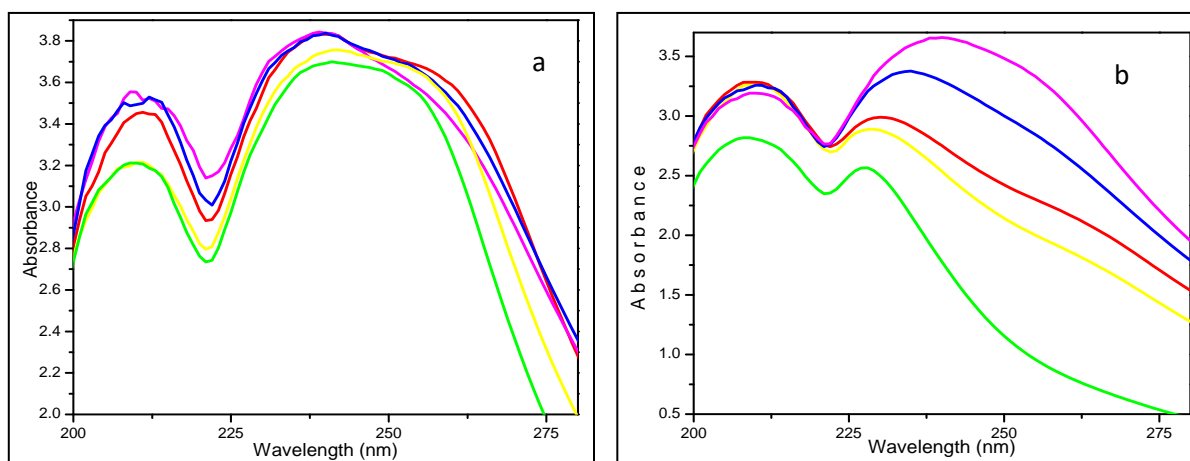
UV region

Figure No. 2: a) Absorption spectra of a 10^{-3} M solution of copper complex measured in the UV region at varying pH values (3.74(green), 5.20(yellow), 6.57(red), 8.61(blue) and 10.05(pink)) with the addition of 0.03 M NaOH solution (deprotonation);

Figure No. 2: b) Absorption spectra of a 10^{-3} M solution of copper complex measured at varying pH values in the UV region (9.57(pink), 8.61(blue), 6.57(red), 5.20(yellow) and 3.74(green)) with the addition of 0.05 M HCl solution (protonation).

The electronic spectrum of copper complex (Fig. 2 (a)) without NaOH solution exhibited two bands in the UV region. The higher energy band λmax = 209 may be assigned to π-π* transition, while lower energy band λmax = 240 is attributable to n-π* transition. The addition of base results in the increase of intensity of n-π* transition band; simultaneously a new band begins to appear at higher wavelength. On addition of 0.05 M hydrochloric acid to neutralize the added base in the reverse procedure, the new band begins to disappear and intensity of n-π* transition band decreases. These observations can be explained as follows. As no lone pair of electrons is available on nitrogen atom in the protonated iminol system **[-NH+=C(OH)-],** it is expected that n-π* transition is due to the excitation of non-bonding electrons localized on oxygen atom. Upon addition of one equivalent of base one equivalent of protonated aza groups lose their protons to create free iminol group **[-NH=C(OH)-]**

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wherein nitrogen contains lone pair of electrons. Now additionally n-π* transition is expected from the excitation of non-bonding electrons localized on nitrogen atom.

Due to the lower electronegativity of nitrogen relative to oxygen, the nonbonding electrons of nitrogen will have higher energy relative to that of oxygen. Therefore n-π* transition will have lower energy (higher wavelength) if transition takes place from nitrogen lone pair and lead to the observation of a new band at higher wavelength. Progressively more free iminol groups are formed by addition of further equivalents of base thereby increasing the transition probability of n-π* transition. This culminates in the hyperchromism of the transition. The neutralization of the added base by the addition of HCl reverses the trend and the spectrum (Fig. 2 (b)) reaches the initial shape.

pH Indicator

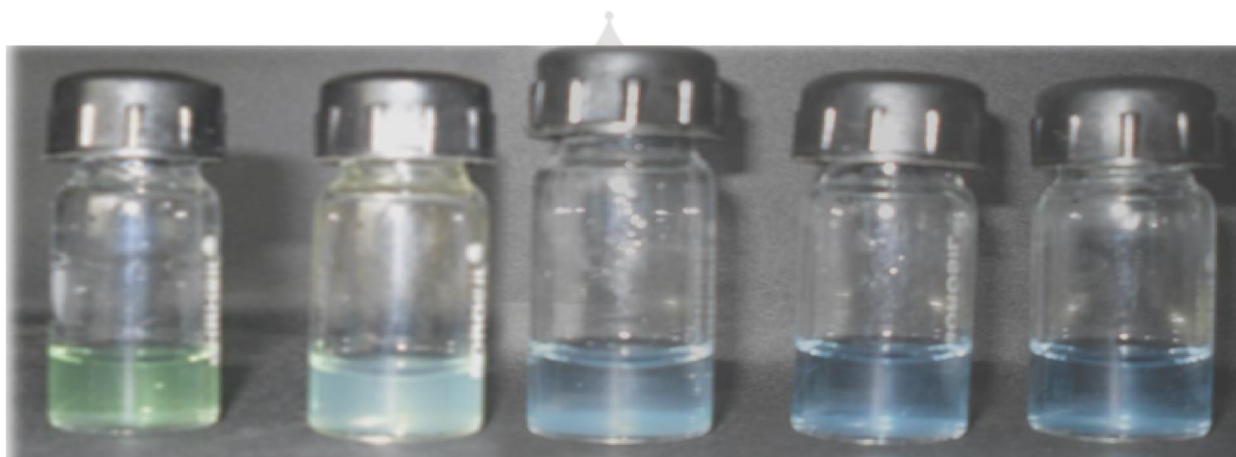The copper complex shows color change from yellowish green to blue with increase of pH (Fig. 3).

Figure No. 3: Variation of color with pH of copper complex

This pH dependent color change (wavelength shift) divulged an idea that the complex may act as pH (acid-base) indicator[22]. The idea was subsequently verified by performing neutralization titration as discussed below. The NaOH (0.8140 N, 10 ml) solution, when the saturated aqueous copper(II) complex solution was added as indicator, becomes dark blue colored. This blue colored solution was titrated with HCl (1.031 N) solution till it becomes yellowish green at end point. The endpoint was observed at 7.9 ml of HCl and just before the endpoint pale green color was noticed. The same titration was repeated using phenolphthalein indicator and the endpoint occurred exactly at 7.9 ml of HCl. The color change (transitions)

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of the complex was found to be 4.5 to 6.5 pH range. The exactness of the volume of acid consumed for the neutralization of base regardless of using either phenolphthalein/metal complex indicator ascertains the validity of the metal complex as indicator. The indicator behavior of the copper(II) complex solution was successful in the neutralization titration of strong base and weak base in the range 0.1N to 1 N.

Chemosensors

Addition of various anions to the copper complex solution gives different colors (Fig. 4); drastic color change is observed for iodide, thiocyanate and carbonate anions while for other anions such as sulphate, nitrate, acetate, oxalate little or no color change is seen. The color change is expected when the chloride ligand (weak field) of anionic metal complex is substituted by other anionic ligands; the color change will depend on the strength of the field imposed by substituting ligands around metal.
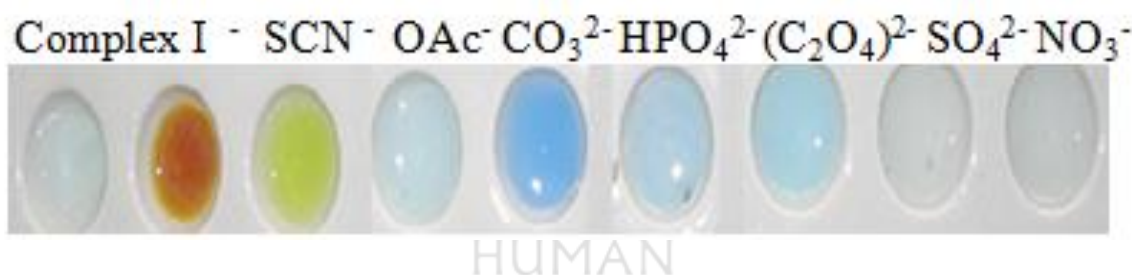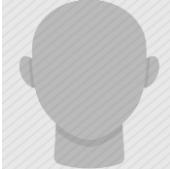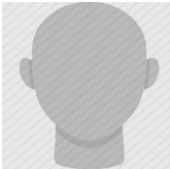

Figure No. 4: Chemosensor behavior of Copper complex

It is envisioned that three dimensional network of hydrogen bonding exists between cationic macrocycle and anionic complexes. Ligands such as sulphate, nitrate, having strong tendency for making hydrogen bonding, will associate with cationic macrocycle rather than substitution of chloride of anionic complex; consequently, color change is not observed. On the other hand ligands such as iodide, thiocyanate having weak tendency for hydrogen bonding could diffuse through the network and substitute chlorides of anionic metal complex to effect an observable color change. These observations augment the inference that the anions and anionic complexes are present outside the macrocyclic cavity.

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