IJSRM
INTERNATIONAL JOURNAL OF SCIENCE AND RESEARCH METHODOLOGY
An Official Publication of Human Journals

Human Journals
Research Article
December 2019 Vol.:14, Issue:2

Synthesis, Characterization and Activities of Anionic Transition Metal Complexes with Tetraaza Protonated 2,15-Dihydroxy-3,7,10,14-Tetraazabicyclo [14.3.1]Icosane-1(20),2,7,9,14,16,18-Heptaene

S. RAJESHWARI[1], N. LAVANYA[2], R. JAYAKUMARARAJ[3], A. SELVAN[4*]

[1]*Department of Chemistry, Prist University School of Law, Arasanoor, Sivagangai*

[2]*Department of Chemistry, Latha Mathavan Engg. College, Kidaripatty, Madurai*

[3]*Department of Botany, Government Arts College, Melur – 625 106*

[4]*Department of Chemistry, Govt. Arts College for Women, Nilakottai – 624 208, India*

Submission: 21 November 2019
Accepted: 27 November 2019
Published: 30 December 2019

www.ijsrm.humanjournals.com

Keywords: Macrocyclic Ligand; Schiff-base Macrocyclic Complexes; Metal Complexes; Protonated Polyaza Macrocycles; Biomedical Application

ABSTRACT

Research in medicinal inorganic chemistry has extended in recent times by the development of a variety of chelating ligands to modify the properties of metal ions in biological systems. Macrocyclic metal complexes offer the benefit of high stability complex formation and, through fictionalization, in the biological systems. Recent developments in coordination chemistry in particular the use of protonated polyaza macrocycles is expected to have significant impact on the design of new medicines and receptors for anion complex for its application as sensor. In the present study anionic transition metal complexes with tetraaza protonated 2,15-dihydroxy-3,7,10,14-tetraazabicyclo[14.3.1]icosane-1(20),2,7,9,14,16,18 heptaene has been analyzed for its potential as pH indicator and chemosensor.

INTRODUCTION

The era of anion coordination chemistry began with the earlier work of Shriver and Biallas, in 1968. This was followed by the work of Simmons and Park, in which the design of a suitable host system for a guest chloride anion was demonstrated[1-3]. Thereafter, the field started to bloom, in particular during the last decade, due to the inspirational work of Graf and Lehn[4], and Schmidtchen[5]. Anions in biological systems are believed to be crucial for many of the biochemical processes. For instance, more than two thirds of enzyme substrates and cofactors are anionic in nature[6]. Today, it has been well established that anions play vital role in the biological systems especially in the process of anion encapsulation and biological catalysis.

Recently, it has been shown that anion based chloride channels significantly contribute to the stabilization of the membrane potential. Thus, anion biochemistry serves as the backbone of biochemical processes associated with the regulation of pH, volume homeostasis, organic solute transport, cell migration, cell proliferation and differentiation[7] malfunction of natural Cl^- ion channels has been associated with Bartter syndrome, Dent's disease and Cystic Fibrosis (CF)[8,9]. Similarly, defects in proteins that facilitate transmembrane bicarbonate transport have been linked to diseases of the brain, heart and bones, as well as CF[10,11]. Therefore, a better understanding of the biochemical mechanisms of anion recognition is of prime importance to conceive efficient synthetic anion receptors for potential medicinal applications. However, anions such as phosphate and nitrate are largely incriminated as pollutants of drinking water[12]. Hence, anion-binding systems may be used for environmental cleanup purposes.

Anion coordination chemistry has attracted growing attention in supramolecular chemistry due to the essential roles that anions play in biology, medicine, and environmental science[13]. Much effort has been expended on the design of receptors for anion complex for its application as sensor. This has been a great challenge because anion complex with the receptor is different from that of metal cation, operates through metal coordination. Further, the characters of anions with vary size, shape and charge, and pH-dependent species[13]. Yet substantial progress has been made in the development of anion based receptors. Several excellent reviews on the recent advances in this field has been available in the literature[14–17]. Basically, anion receptors are neutral or sometimes positively charged. Further, anion–receptor interactions are favored through hydrogen bond and/or electrostatic interaction, although deprotonation of the acidic hydrogen bond donor occurs in some cases. Alternatively, neutral anion receptors are based on amide, (thio) urea and pyrrole groups that bind anions via favorable hydrogen bonds.

MATERIALS AND METHODS

Preparation of Complexes:

All the metal complexes were prepared and reported [18].

RESULTS AND DISCUSSION

Activities of Complexes

pH dependence of UV-VIS spectra

The aqueous solutions of the copper complex {(Mac.2) [$CuCl_6$]}} (20 mL (1 mM); 20 µmol) was prepared, and the electronic absorption spectra were recorded at every addition[19] of 0.66 mL of 0.03 M (20 µmol) NaOH aqueous solution until the total volume of the NaOH solution (3.96 mL; 120 µmol)) neutralized the six equivalents of macrocyclic protons. Prior to the addition of NaOH solution, pH of the complex solution is 3.70. Upon addition of 3.96 mL of 0.03 M base, the pH changed from 3.70 to 12.49. 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 2.4 mL of 0.05 M acid, the pH changed from 12.49 to 3.28.

Visible Region

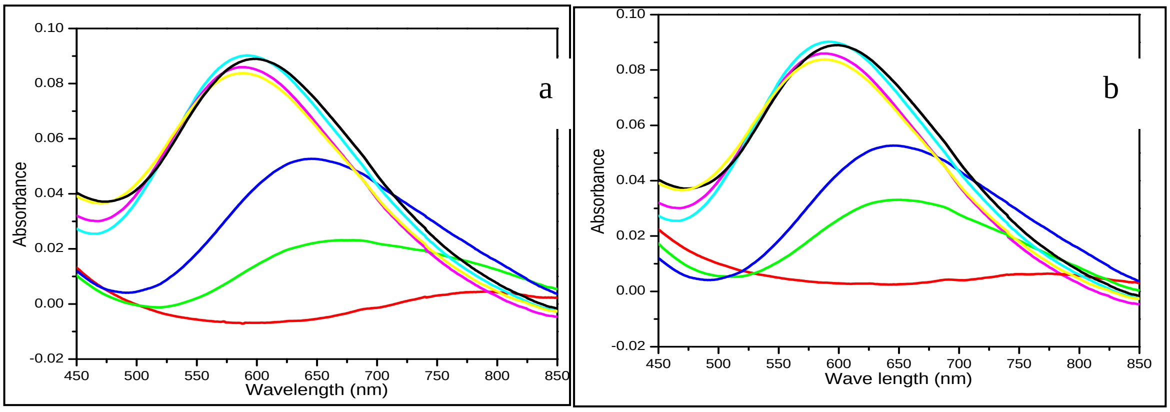
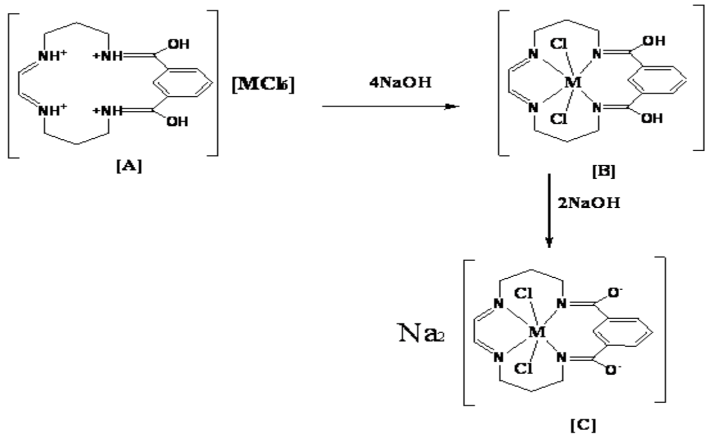


Figure No. 1: a) Absorption spectra of a 10^{-3} M solution of copper complex measured in the visible region at varying pH values (3.70(red), 5.48 (green), 6.38 (blue), 9.68 (yellow), 11.47 (pink), 12.11(cyan) and 12.49 (black)) with the addition of 0.03 M NaOH solution (deprotonation);

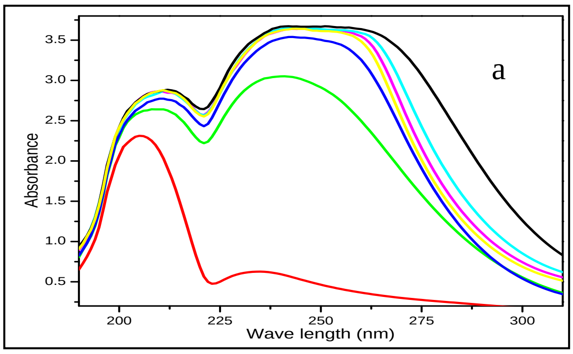
Figure No. 1: b) Absorption spectra of a 10^{-3} M solution of copper complex measured in the visible region at varying pH values (12.11 (black), 11.47 cyan), 10.01 (pink), 9.44 (yellow), 6.74 (blue), 5.83(green), and 3.28(red)) with the addition of 0.05 M HCl solution (protonation).

The electronic spectrum of yellowish green copper complex (Fig. 1 (a)) without NaOH solution exhibited a broadband at λmax = 775 nm assignable to a d-d band. On addition of 0.66 mL of 0.03 M NaOH solution, the color changed from yellowish green to green, and the d-d band shifted to lower wavelength λmax = 669 nm with an increase in intensity. On gradual addition of NaOH solution, the solution became pale green cloudy, pale blue cloudy and finally to dark blue clear solution with the d-d band shifting to lower wavelength, with an increase in intensity, from λmax = 669 nm to 587 nm.



The deprotonation involves the removal of four protons from protonated aza groups and two from iminol hydroxyl groups[20] as per the above scheme. It is envisaged that upon addition of four equivalent of base, the complex A first loses four aza protons to give a cloudy product B; subsequent addition of two more equivalents of base may lead to the formation complex C. On addition of 0.05 M HCl solution in the reverse procedure, the color changed from dark blue to yellowish green through pale blue, pale green, 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.

UV Region



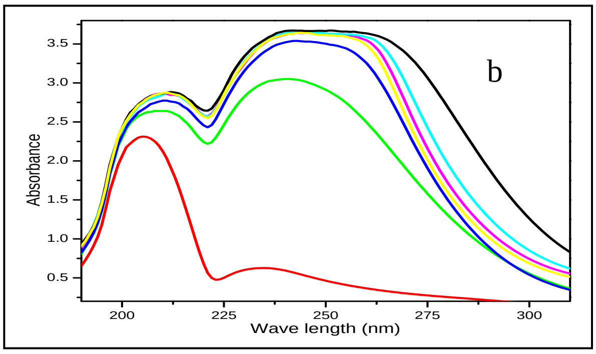


Figure No. 2: a) Absorption spectra of a 10-3 M solution of copper complex measured in the UV region at varying pH values (3.70(red), 5.48 (green), 6.38 (blue), 9.68 (yellow), 11.47 (pink), 12.11(cyan) and 12.49 (black)) with the addition of 0.03 M NaOH solution (deprotonation);

Figure No. 2: b) Absorption spectra of a 10-3 M solution of copper complex measured at varying pH values in the UV region (12.11 (black), 11.47 cyan), 10.01 (pink), 9.44 (yellow), 6.74 (blue), 5.83(green), and 3.28(red)) 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 = 205 may be assigned to π-π* transition, while lower energy band λmax = 235 is attributable to n-π* transition. The addition of base results in the increase of intensity of n-π* transition band.

On addition of 0.05 M hydrochloric acid to neutralize the added base in the reverse procedure, the 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)-]** 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. Nevertheless, in the present case, this transition seems to overlap with n-π* transition from oxygen lone pair to boost up the intensity of the transition. 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 hyper-chromism of the transition. The neutralization of the added base by the addition of HCl reverses the trend (Fig. 2 (b)) and the spectrum reaches the initial shape.

pH Indicator

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

Citation: A. SELVAN et al. Ijsrm.Human, 2019; Vol. 14 (2): 89-98.

The copper complex shows color change from pale green to blue with increase of pH (Fig. 3). This pH dependent color change (wavelength shift) divulged an idea that the complex may act as pH (acid-base) indicator[21]. 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 endpoint. 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) 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.

Figure No. 4: Variation of color with pH of Cobalt complex

The indicator behavior of the copper (II) complex solution was successful in the neutralization titration of base in the range 0.1N to 1 N. Similarly, the same indicator behavior was also performed in the cobalt complex, which shows color change from yellow to pale green with increase of pH (Fig. 4).

Chemo Sensors

Addition of various anions to the copper complex solution gives different colors (Fig. 5); 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. 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.

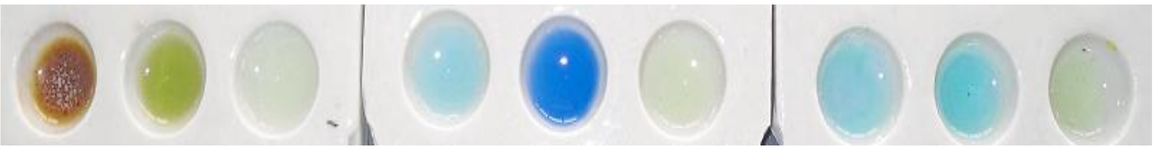


Figure No. 5: Chemosensor behavior of copper complex

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	A. SELVAN Assistant Professor Department of Chemistry, Govt. Arts College for Women, Nilakottai – 624 208, India
	S. RAJESHWARI Assistant Professor Department of Chemistry, PRIST University School of Law, Arasanoor, Sivagangai Dist. TamilNadu, India
	N. LAVANYA Assistant Professor Department of Chemistry, Latha Mathavan Engg. College, Kidaripatty, Madurai Dist. TamilNadu, India
	**R. JAYAKUMARARAJ** Associate Professor Department of Botany, Government Arts College, Melur – 625 106, Madurai Dist. TamilNadu, India

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