

Template Synthesis, Characterization and Reactivities of Anionic Transition Metal Complexes with Tetraaza Protonated 11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-4,6,10,13-tetraene-5,6-Diol as Cation

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Received: 2 July 2019;

Accepted: 22 August 2019;

Published online: 16 November 2019;

AJC-19642

Template synthesis, characterization and reactivities of anionic transition metal complexes with tetraazaprotonated 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-4,6,10,13-tetraene-5,6-diol as cation has been achieved. By magnetic and spectral studies, hexachlorometallate(II) anionic complexes have been found to be octahedral. It is envisioned that the cationic macrocycle may be associating with both the complex and chloride anions through hydrogen bonding thereby rendering the molecule as a whole neutral. Deprotonation, protonation analysis and chemosensor behaviour have been showed by pH variation studies and relevant anionic additions, respectively. All of these data supports the newly synthesized anionic complexes in a strange manner.

Keywords: Anionic coordination complexes, Schiff-base macrocyclic complexes, Protonated polyazamacrocycles.

INTRODUCTION

An important aspect of modern coordination chemistry mainly focus the mimic form and biological structure. It has been developed by a principle which governed from biological, spontaneous self-assembly of well-defined and complex structural groups. In coordination chemistry, self-assembly has been formed by the coordination bonds rather than weak inter- or intramolecular interactions. For molecular recognition, it is to be needed the metal complexes with open coordination sites. They perform as binding sites in the development of chemosensors [1,2] for studying metalloenzyme activity in bioinorganic chemistry [3-5] and for the direction of supramolecular self-assembly [6-8]. Lewis basic functional groups has been targeted by Lewis-acidic metal complexes, which develops suitability for the depiction of synthetic receptors. Metal ion coordination happens generally with huge enthalpies compared to those for hydrogen bond formation, salt-bridges and dipole-dipole interactions. Multidentate and macro-monocyclic ligands with metal template syntheses have been extensively reviewed [9-15] and different types of template effects towards transition metal ions have been recognized. The stereochemistry, imposed

by metal ion coordination brings a template effect and kinetic template effect and characteristically display the routes to products which does not formed in the absence of metal ions [16]. Amino acid Schiff base complexes have gathered the importance not only from the inorganic point of view and also because of their pharmacological and physiological activities [17,18]. A variety of huge number of synthetic bifunctional macrocyclic complexes have been prepared and examined, because there are vast examples of naturally occurring metal complexes with macrocyclic ligands *e.g.* porphyrin, corrin ring derivatives. Macrocyclic polyamines induces continuous interest by their biological properties and their significance in coordination chemistry [19]. New properties has been exhibited by macrocyclic polyamines and also they have anticipated from mere assemblies of amines and linear polyamines [20]. They revealed a pronounced capability to connect a vast variety of metals and in many cases to undergo specified conformational changes during the course of binding. Synthesis of nitrogen-based receptors has been designed by the selective binding of anions generally consist of either positively charged ammonium salts *i.e.* polyamines which are protonated, amines which are quaternized or neutral species such as amides, ureas, thioureas,

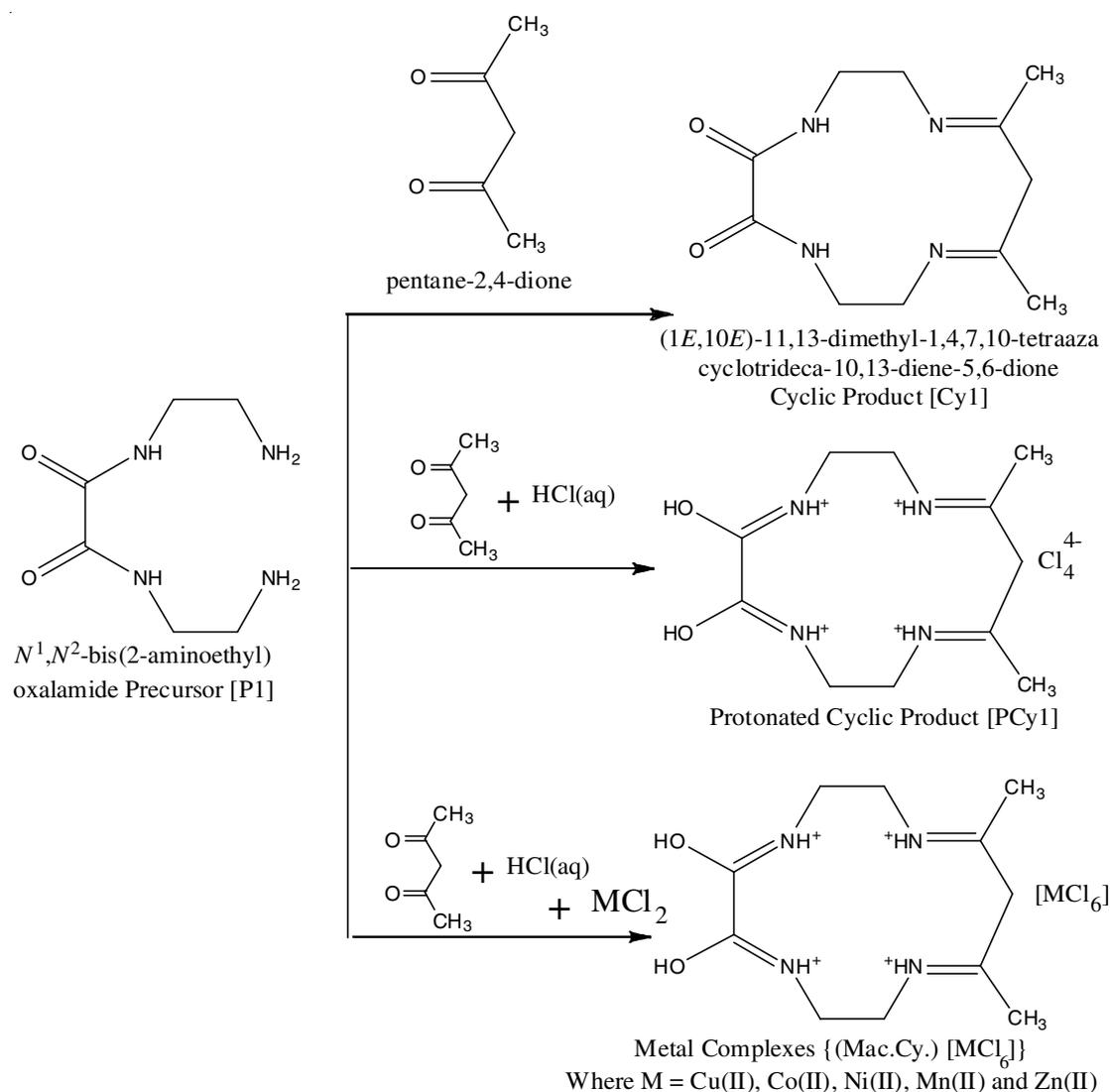
sulfonamide and pyrroles [21-23]. The robust amides usually have been closed in nature for its anion receptors which has led to significant focus on those systems [24-32] of selective binding of a large number of anions. The past decades of anion coordination chemistry started with the help of previous works of Shriver and Biellas and also by Simmons and Park for a host system for a guest chloride anion [33-35]. Several years later, Lehn *et al.* [36] investigated a same types of bicyclic azacryptand *i.e.* [bis-tren](ClO₄)₆ which is able to bind a linear azide anion by its six protonated amine function. This innovative area is initiated blossoming especially in the last ten years. Because of the inspired work of Graf and Lehn and also by Schmidtchen *et al.* [37]. In addition to that they focused on anion encapsulation and catalysis which on coupled with the recognition of the fact that anions play important role in biological systems. Anions are omnipresent in biosystems and are critical to several processes for many instance, more than two thirds of enzyme substrates and cofactors are anionic [38]. In present investigation, the synthesis of macrocyclic ligand in protonated form has been achieved not only for their anion coordination behaviour but also for the efficacies of the anionic complexes in diverse applications.

EXPERIMENTAL

Synthesis of precursor [P1]: In minimum amount of ethanol in a beaker, about 60 mmol of ethane-1,2-diamine is dissolved. To this solution, 7.4 mmol of diethyl oxalate is added drop wise. A white precipitate is obtained. It is identified as the precursor [P1] *N*¹,*N*²-bis(2-aminoethyl)oxalamide by TLC technique. To ensure the completion of the reaction, the solution is further stirred for about 0.5 h and the precursor formed is filtered, washed with warm water and then subsequently dried in vacuum over anhydrous CaCl₂.

Synthesis of cyclic product [Cy1]: In ethanol, about 2.87 mmol of precursor [P1] is dissolved in a beaker. To this solution, 2.92 mmol of acetyl acetone is added and stirred for 45 min and obtained a white precipitate, which is identified as a cyclic product [Cy1] by the TLC technique. Then it is filtered and dried in vacuum over anhydrous CaCl₂.

Protonated cyclic product [PCy1]: In a minimum amount of ethanol in a beaker, about 2.87 mmol of precursor [P1] is dissolved. Acetyl acetone of 2.92 mmol is added to the solution. In order to get a protonated cyclic product, an excess of (10 N, 2.9 mL) HCl is added to the above mixture and stirred for 30



Scheme-I

min, and then the solution is evaporated completely over water bath. The protonated cyclic product was washed with ether, filtered and dried in vacuum over anhydrous CaCl_2 .

Metal complexes $\{(\text{Mac.Cy.})[\text{MCl}_6]\}$: The precursor (2.87 mmol) is dispersed in hot ethanol. To this about 2.93 mmol of copper(II) chloride dihydrate in hot ethanol is added. To the above mixture, 2.92 mmol of acetyl acetone is added followed by HCl (10 N, 2.9 mL) and stirred for 1 h. Then solution is evaporated completely over water-bath to obtain a yellow coloured precipitate (**Scheme-I**). The precipitate formed is washed with ether, filtered and dried in vacuum over anhydrous CaCl_2 and the precipitate formed is identified as $\{(\text{Mac.Cy.})[\text{CuCl}_6]\}$. Similarly cobalt(II), nickel(II), manganese(II) and zinc(II) complexes are synthesized using corresponding metal salts, respectively.

RESULTS AND DISCUSSION

Tables 1 and 2 show the results of various physico-chemical studies. By X-ray microanalysis technique, copper (Fig. 1) and cobalt complexes have been analyzed and by mass spectrometry, manganese (Fig. 2a) and cobalt complexes (Fig. 2b) have been analyzed.

From the X-ray microanalysis, the elements identified in copper complex are carbon, nitrogen, oxygen and chlorine.

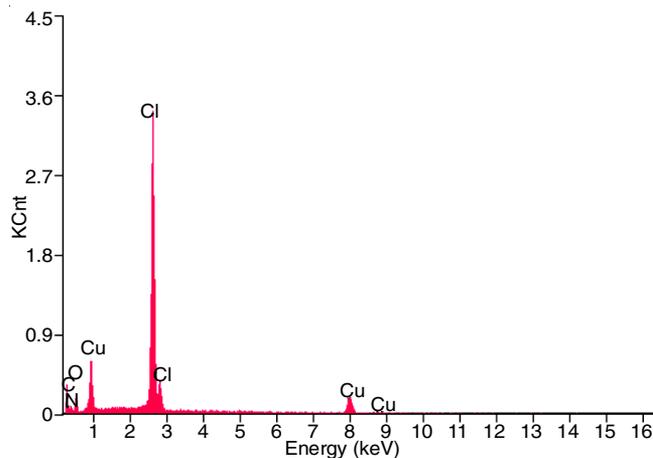


Fig. 1. X-ray microanalysis of copper complex

The proposed formula for the complex is ascertained by the % weight obtained, with the individual atoms. The same experimental analysis with results and spectral details obtained for cobalt complex. By the weight loss method, thermal studies of copper, cobalt, manganese, nickel and zinc complexes are analyzed at 120°C for 2 h and found to be no water molecules present in any of the so-called metal complexes.

TABLE-1
ANALYTICAL DATA OF SYNTHESIZED COMPLEXES (m.f.: $\text{C}_{11}\text{H}_{22}\text{N}_4\text{O}_2\text{Cl}_6\text{M}$, M = Cu, Co, Ni, Mn AND Zn)

Complexes	Colour	Yield (%)	Elemental analysis (%): Obsd. (Calcd.)				
			Metal	C	H	N	Chloride
$\{(\text{Mac.cy.})[\text{CuCl}_6]\}$	Yellow	89	12.39 (12.25)	25.63 (25.46)	4.19 (4.24)	10.84 (10.80)	40.96 (41.08)
$\{(\text{Mac.cy.})[\text{CoCl}_6]\}$	Blue	88	11.58 (11.46)	25.78 (25.69)	4.22 (4.28)	10.87 (10.89)	41.31 (41.45)
$\{(\text{Mac.cy.})[\text{NiCl}_6]\}$	Pale green	89	11.54 (11.41)	25.86 (25.70)	4.23 (4.28)	10.93 (10.90)	41.34 (41.47)
$\{(\text{Mac.cy.})[\text{MnCl}_6]\}$	Pale brown	87	10.90 (10.77)	26.04 (25.89)	4.26 (4.31)	10.94 (10.98)	41.62 (41.77)
$\{(\text{Mac.cy.})[\text{ZnCl}_6]\}$	Colourless	82	11.06 (10.92)	26.01 (25.84)	4.25 (4.31)	10.88 (10.96)	41.57 (41.70)

TABLE-2
SPECTRAL AND MAGNETIC MOMENT DATA OF THE COMPLEXES

Complex	Vibrational frequency (cm^{-1})			Electronic spectral data		Magnetic moment, μ_{eff} (B.M.)
	$\nu(\text{C}=\text{N})$	$\delta(\text{NH})$	$\nu(\text{OH})$	λ_{max} (cm^{-1})	ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	
$[\text{PP}_{\text{cy}}]$	1656	2010	3395	—	—	—
$\{(\text{Mac.Cy.})[\text{CuCl}_6]\}$	1680	2039	3401	15773	94	2.01
$\{(\text{Mac.Cy.})[\text{CoCl}_6]\}$	1653	2040	3419	13550 & 20703	19 & 3	4.85
$\{(\text{Mac.Cy.})[\text{NiCl}_6]\}$	1653	2032	3417	—	—	2.95
$\{(\text{Mac.Cy.})[\text{MnCl}_6]\}$	1652	2036	3298	—	—	5.98
$\{(\text{Mac.Cy.})[\text{ZnCl}_6]\}$	1663	2003	3457	—	—	—

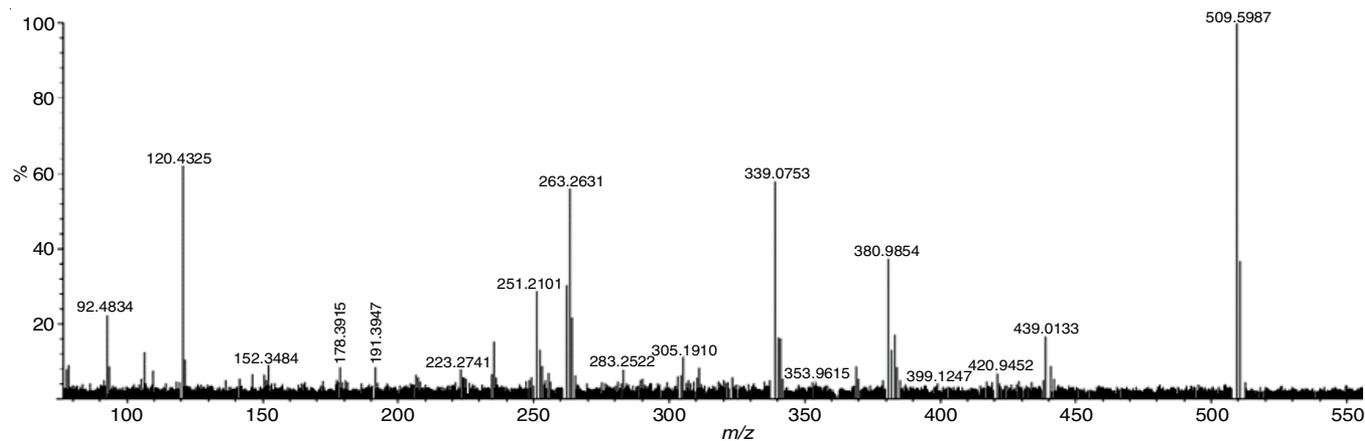


Fig. 2a. Mass spectrum of manganese complex

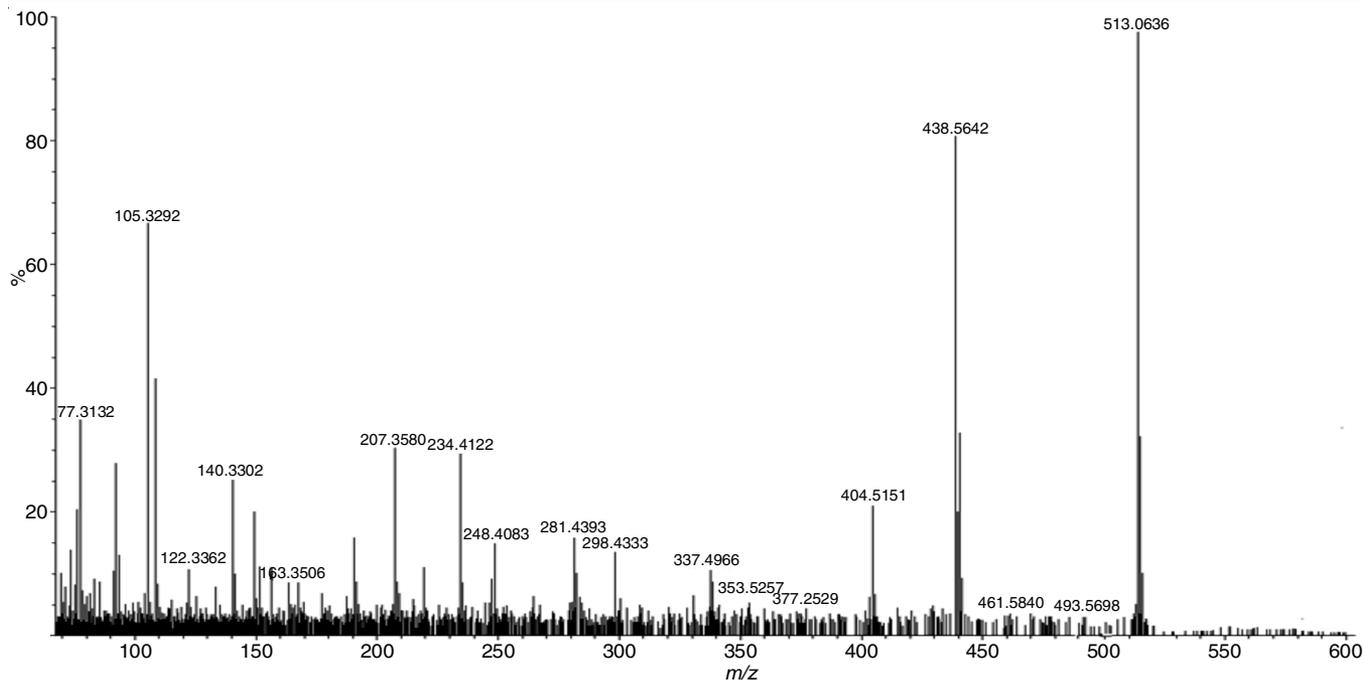


Fig. 2b. Mass spectrum of cobalt complex

From the mass spectroscopic analysis, the base peak observed at $m/z = 509.5$ (Fig. 2a) and corresponding to M^+ shows that the whole molecule is neutral. The above observation towards the formation of anionic coordination complexes are compared with previous reported anionic complexes [21,39,40], in which same types of complexes such as $(H_{10}[30]aneN_{10})[Pt(CN)_4] \cdot 5.2H_2O$ and $(H_{10}[30]aneN_{10})[Pt(CN)_4]_2Cl \cdot 6.2H_2O$ where $(H_{10}[30]aneN_{10}) =$ decaazaprotonated-1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane and was examined through the crystal structures of the complexes. From the reported crystal data, as well as the observation of base peak at $m/z = 509.5$ brings a clear idea about that in the present investigation, the observed M^+ ion value indicates that the cationic macrocycle may be associating with both the complex and chloride anions, through hydrogen bonding thereby describing the molecule as a whole neutral. Further it has been predicted that these H-bonding leads to the same three dimensional network as reported in the literature [39,40]. Thus, the general formula for complexes may be proposed as $\{(Mac.Cy.)[MCl_6]\}$. Similarly, a set of mass spectra values have been observed for cobalt complexes with the corresponding m/z value.

By IR analysis, the presence of amide moiety in the precursor is confirmed by the appearance of the bands at 1658 cm^{-1} [amide I (C=O stretching)] and 1528 cm^{-1} [amide II (NH deformation)]. Consequently, the absence of band at 1751 cm^{-1} in the IR spectra shows that there is no unreacted carbonyl group of ester during the formation of precursor from condensation reaction of ester with amine.

In order to identify the mode of coordination of amide in complexes, a cyclic polyamide [Cy1] is synthesized by the reaction between the precursor [P1] with pentane-2,4-dione in the absence of metal. By FTIR analysis, the formation of imine-based protonated cyclic product and anionic metal complexes are investigated. A new peak has been found [41] at about 2010 cm^{-1} in the protonated cyclic product and also

in the metal complexes (Fig. 3), but which are not observed in the spectra of precursor and cyclic product. The deformation of NH^+ group in protonated cyclic product and metal complexes are known by the sharp peaks observed in the region of 2010 cm^{-1} .

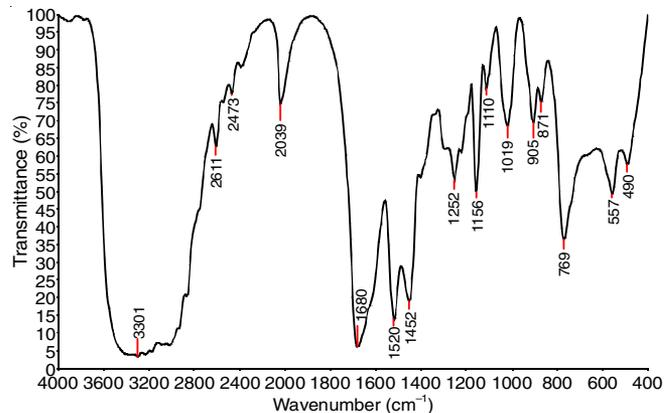


Fig. 3. IR spectrum of copper complex

The macrocyclic cation exists as protonated iminol form and is evident from the IR spectrum of the copper complex, in which expected strong peak for $>C=O$ stretching is absent around 1751 cm^{-1} . The peak observed at 1680 cm^{-1} indicates the presence of $>C=N$ stretching, while NH stretching of $>C=N^+HR$ groups are assigning by the series of bands observed in the region of $2700\text{--}2250\text{ cm}^{-1}$. The NH deformation of $>C=N^+HR$ groups are observed by the peak appearing at 2039 cm^{-1} . These observations together with the appearance of a new peak at 3301 cm^{-1} due to OH stretching which is responsible for the existence of the complex as the iminol form predominantly. This observation has also been evident from reported [41] that OH deformation by the appearance of peak at 1452 cm^{-1} in the complex and also supports that macrocycle is present as in

iminol form. Similar IR analysis of the protonated cyclic product and other complexes indicates that all the complexes exist in iminol form.

The magnetic moment for $\{(\text{Mac.Cy.})[\text{CuCl}_6]\}$ is found as 2.01 B.M, which indicates one unpaired electron present in the system. The electronic spectrum of copper(II) complex shows a band at 15773 cm^{-1} which is associated with the reported studies in which the electronic spectra of Cu(II) complexes felt the band in the region 11500 to 17430 cm^{-1} . It has attributed to the transition ${}^2B_{1g} \rightarrow {}^2E_g$ which implies that the geometry of Cu(II) complex is tetragonally distorted octahedral.

It might be expected that cobalt(II) forms tetrahedral halide complexes. The ground state for tetrahedral cobalt(II) complex is 4A_2 and a low magnetic moment of 3.87 B.M. However, in the present investigation, cobalt(II) complex shows magnetic moment of 4.86 B.M. (higher than spin only value). In addition to that electronic spectrum of the complex displays bands with lower ϵ values. This observed higher magnetic moment than spin only value and the electronic bands with lower ϵ values proposed that formed cobalt(II) halide complex in the present study has octahedral geometry. This proposed geometry has been further ascertained by the reported literature studies [42], in which cobalt (II) halide possesses an octahedral geometry with corresponding crystallographic data. Thus the present observed bands at 13550 cm^{-1} and 20703 cm^{-1} may be corresponds to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ of an octahedral Co(II) halide complex. The existence of octahedral geometry of manganese(II) and cobalt(II) halide complexes also compared by their corresponding m/z value with the reported crystal studies [43]. The magnetic moment value for Mn (II) and Ni(II) complexes are found to be 5.98 and 2.95 B.M., which supports the same structural geometry.

At room temperature, EPR spectrum of Cu(II) complex (Fig. 4) is recorded in solid state. Analysis of the spectrum shows that $\mu = 1.82$ and is in good agreement with the usual observed value for Cu(II) system corresponding to one unpaired electron.

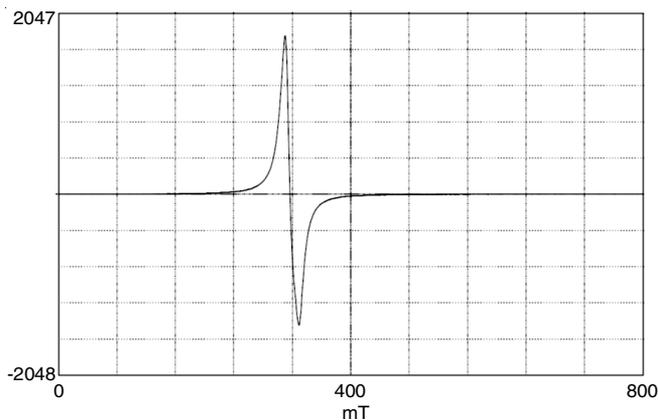


Fig. 4. ESR spectrum of copper complex

The copper complex $\{(\text{Mac.Cy.})[\text{CuCl}_6]\}$ (20 mL, 1 mM); 20 μmol) is prepared as an aqueous solutions and the electronic absorption spectra are recorded at every addition of 0.66 mL of 0.03 M (20 μmol) with NaOH aqueous solution until the total volume of NaOH solution (3.96 mL; 120 μmol) neutralized the six equivalents of macrocyclic protons [44]. Before the addition of NaOH solution, pH of the complex solution is 4.71 and then the pH changed from 6.19 to 11.40 upon addition of 3.96 mL of 0.03 M base. In order to know the reverse procedure of protonation, the above neutralized solution is added with 0.05 M HCl solutions in 0.4 mL (20 μmol) increments and the electronic spectra are recorded. The pH changed from 11.40 to 4.69 during the addition of 2.4 mL of 0.05 M acid.

The electronic spectrum of yellowish green copper complex (Fig. 5a) without NaOH solution shows a broad band at $\lambda_{\text{max}} = 672 \text{ nm}$, which relates to a $d-d$ band. The colour changed from yellowish green to green, by the addition of 0.66 mL of 0.03 M NaOH solution, and the $d-d$ band moved to lower $\lambda_{\text{max}} = 655 \text{ nm}$ 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 $d-d$

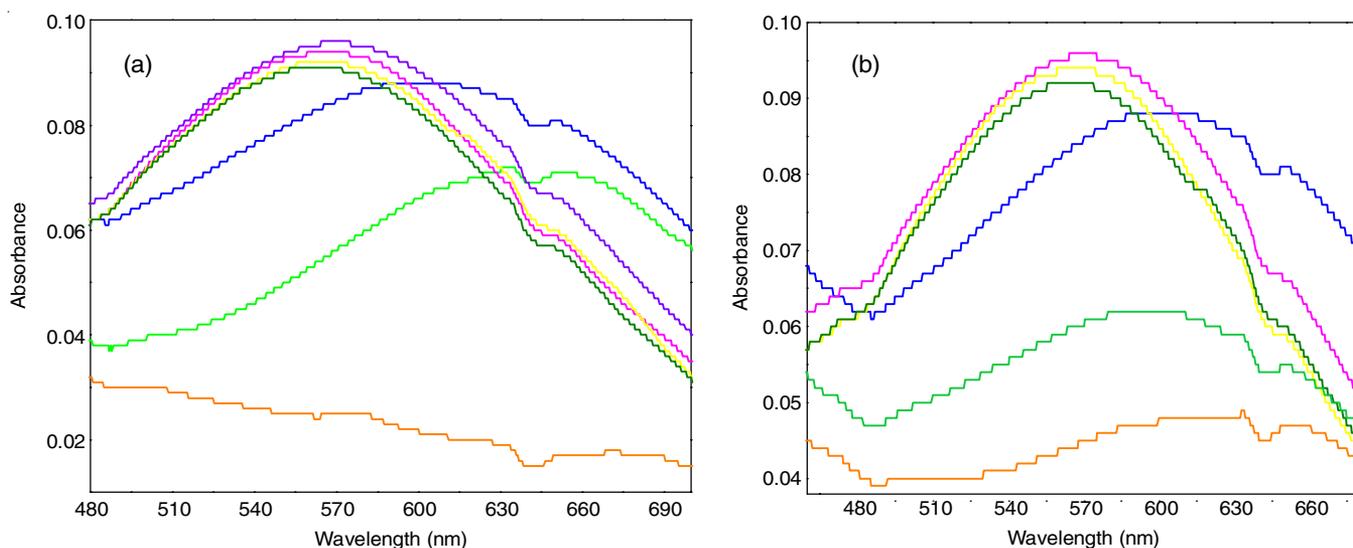


Fig. 5. (a) Absorption spectra of a 10^{-3} M solution of copper complex measured in the visible region at varying pH values [4.71 (orange), 6.19 (green), 7.29 (blue), 8.69 (olive), 9.83 (yellow), 10.99 (magenta) and 11.40 (violet)] with the addition of 0.03 M NaOH solution (deprotonation). (b) Absorption spectra of a 10^{-3} M solution of copper complex measured in the visible region at varying pH values [10.64 (magenta), 10.02 (yellow), 8.57 (olive), 7.36 (blue), 6.28 (green)] and 4.69 (orange) with the addition of 0.05 M HCl solution (protonation)

band shifting to lower wavelength, with an increase in intensity, from $\lambda_{\text{max}} = 655 \text{ nm}$ to 567 nm .

The deprotonation involves the removal of four protons from protonated aza groups and two from iminol hydroxyl groups [45]. In the reverse procedure, by addition of 0.05 M HCl solution, 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. 5b) finally reached its original value.

This pH dependent colour change studies (wavelength shift) imparts an idea about the complex may act as pH (acid-base) indicator [46]. The idea is further verified by analyzing neutralization titrations. The concurrence 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.

Copper complex solution gives different colours by the addition of various anions; drastic colour change is observed for iodide, thiocyanate and carbonate anions but for other anions such as acetate, oxalate there is little or no colour 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 colour change will depend on the strength of the field imposed by substituting ligands around metal.

It is clearly known that three dimensional network of H-bonding exists between cationic macrocycle and anionic complexes. Ligands such as acetate, oxalate, having strong tendency for making hydrogen bonding, which will associate with cationic macrocycle rather than substitution of chloride of anionic complex; subsequently colour 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 a noticeable colour change. These observations support that the inference that the anions and anionic complexes are present outside the macrocyclic cavity.

Conclusion

A set of new hexachlorometallate(II) anionic complexes are synthesized by a template fashion. All the new anionic transition metal complexes are characterized by X-ray microanalysis, elemental analysis, mass, IR, UV and ESR techniques. All the complexes possess octahedral geometry. The copper complex shows chemosensor behaviour, acts as pH indicator and shows deprotonation and protonation when the addition of base and acid reversibly as well. Thus an interesting nitrogen based receptors have been designed for the selective binding of anions.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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