DIVALENT METAL ION DIRECTED SYNTHESIS AND CHARACTERIZATION OF HEXAAZAMACROCYCLIC COMPLEXES

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ABSTRACT
A new series of hexaazamacrocyclic complexes of type [M(TML)X$_2$]; where M = Co(II), Ni(II), Cu(II), Zn(II); TML is tetradeutate macrocyclic ligand and X = Cl, NO$_3$, CH$_3$COO, has been prepared from 2,6-diaminopyridine and glyoxal by template method. The complexes are formulated as: [M(TML)X$_2$] due to non-electrolytic nature of these complexes. The ligand coordinates through all four azomethine nitrogens but pyridine nitrogens do not take part in coordination as confirmed by absence of (M-Py) vibrations. These complexes have been characterized with the help of various physico-chemical techniques like IR, far-IR, NMR, elemental analyses, electronic spectra, conductance and magnetic susceptibilities. The distorted octahedral geometry has been proposed for all of these complexes.

Keywords: Macrocyclic ligand, IR, NMR, divalent metal complexes.

INTRODUCTION
The publications of several review articles and books covering various aspects of synthetic macrocyclic ligands reveal the great importance attached to them. Recent interest in the field of macrocyclic complexes have been developed by diagnostic and therapeutic medicinal application of transitional metal complexes of macrocyclic ligand. A number of nitrogen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications. Macrocyclic metal complexes are of great importance due to their resemblances with many natural systems such as porphyrins and cobalamines. Macrocyclic nickel complexes find use in DNA recognition and oxidation while macrocyclic copper complexes find use in DNA binding and cleavage. Macrocyclic metal complexes of lanthanides $\text{e.g.}$ Gd$^{3+}$ are used as MRI contrast agents. Macrocyclic metal chelating agents (DOTA) are useful for detecting tumor lesions. The chemistry of macrocyclic complexes is also important due to their use as dyes and pigments as well as NMR shift reagents. Some macrocyclic complexes have been found to exhibit potential antibacterial activities. Prompted by these, in the present paper synthesis and characterization of divalent cobalt, nickel, copper and zinc macrocyclic complexes derived from 2,6-diaminopyridine and glyoxal have been discussed.

EXPERIMENTAL

Materials:
2,6-diaminopyridine was purchased from Koch-Light, England and glyoxal was obtained from SRL Pvt. Ltd Mumbai. All other chemicals used were of AnalR grade.

Isolation of complexes:
Our several attempts to isolate the free macrocyclic ligand were unsuccessful. Hence, all the complexes were obtained by template synthesis. To a stirring methanolic solution ($\sim$50cm$^3$) of 2,6-diaminopyridine
(10 mmol) was added divalent cobalt, nickel, copper and zinc salt (5 mmol) dissolved in minimum quantity of methanol (20 cm$^3$). The resulting solution was refluxed for 0.5 h. After that glyoxal (10 mmol) dissolved in ~20cm$^3$methanol added in the refluxing mixture and again refluxed for 8-10 h. On overnight cooling dark coloured ppt. formed which was filtered, washed with methanol, acetone, dichylether and dried in vacuo. (Yield 45%) The complexes were found soluble in DMF and DMSO, but were insoluble in common organic solvents and water. They were thermally stable up to ~250oC and then decomposed. The template syntheses of the complexes may be represented by the following scheme:

$$2 \text{C}_5\text{H}_3\text{N(NH}_2\text{)}_2 + 2 \text{C}_2\text{H}_2\text{O}_2 + \text{MX}_2 \xrightarrow{\text{Methanol}} \text{[M(TML)X}_2\text{]} \quad (6-8 \text{ hours})$$

Where M = Co(II), Ni(II), Cu(II) and Zn(II)
X = Cl$^{-1}$, NO$$_3$$^{-1}$, CH$$_3$$COO$^{-1}$
TML = Tetradentate macrocyclic ligand

Analytical and physical measurements
The microanalyses of C, H, and N were carried out at Sophisticated Analytical Instrument Facility, CDRI, Lucknow. The metal contents were determined by standard EDTA methods. Electronic spectra (DMF) were recorded on Cary 14 spectrophotometer. The magnetic susceptibility measurements were carried at IIT Roorkee. The IR spectra were recorded on Infrared spectrophotometer in the range 4000-200 cm$^{-1}$ using KBr pellets. The NMR spectra were recorded on Bruker NMR spectrometer (300 MHz). The conductivity was measured on digital conductivity meter (HPG System, G-3001).

RESULTS AND DISCUSSION
The analytical data show the formula of macrocyclic complexes as: [M(C$_{14}$H$_{10}$N$_6$)X$_2$]; where M = Co(II), Ni(II), Cu(II), Zn(II) and X = Cl$^{-1}$, NO$$_3$$^{-1}$, CH$$_3$$COO$^{-1}$. The test for anions is positive only after decomposing the complexes with conc. HNO$$_3$$, indicating their presence inside the coordination sphere. All macrocyclic complexes are dark coloured solids and are freely soluble in N, N dimethylformamide or dimethylsulphoxide. Conductivity measurement in N, N dimethylformamide indicated them to be non-electrolyte (10-20 ohm$^{-1}$cm$^2$ mol$^{-1}$)$^{14}$. All compounds give satisfactory elemental analyses results as shown in the Table-1. All complexes were decomposed over 250ºC indicating their thermal stability.

IR Spectra
It was noted that a pair of bands are present in the spectrum of 2,6-diaminopyridine at 3200-3400 cm$^{-1}$ corresponding to $\nu$(NH$_2$) but are absent in the infrared spectra of all the complexes. Further, no strong absorption band was observed near 1700 cm$^{-1}$ indicating the absence of $>$$C$=O of glyoxal. This confirms the condensation of carbonyl groups of glyoxal and amino groups of 2,6-diaminopyridine$^{15,16}$. These results provide strong evidence for the formation of macrocyclic frame$^{17}$. A strong absorption band in the region $\sim$1595-1615 cm$^{-1}$ may be attributed to the C=N group$^{18,19}$. The lower values of $\nu$(C=N) may be explained on the basis of drift of lone pair density of azomethine nitrogen towards metal atom$^{16,20}$. The bands present at $\sim$3040 cm$^{-1}$ may be assigned due to $\nu$(C-H) vibrations of glyoxal moiety. The bands present in the range $\sim$300-315 cm$^{-1}$ are assigned due to $\nu$(C-N) vibration. The IR spectra of the complexes do not show any change in the pyridine ring vibrations and interestingly enough, it appears that in these complexes pyridine nitrogen does not take part in coordination$^{21,22}$. Thus in the presence of metal salts, a quadridentate macrocycle is formed which coordinates through azomethine nitrogen while pyridine nitrogen does not take part in coordination. Moreover, the coordination through pyridine nitrogen does not take place, as it will result in the formation of unstable four membered rings.

Far IR spectra
The far IR spectra show bands in the region $\sim$430-450 cm$^{-1}$ corresponding to $\nu$(M-N) vibrations$^{23-25}$. The presence of bands in all complexes in $\sim$430-450 cm$^{-1}$ region originate from (M-N) azomethine vibrational modes and gives idea about coordination of azomethine nitrogens$^{26}$. The bands present at 300 - 315 cm$^{-1}$
may be assigned as being due to $\nu$(M-Cl) vibrations\textsuperscript{23,25}. The bands present at 225 - 255 cm\textsuperscript{-1} in all nitrato complexes are assignable to $\nu$(M-O) vibrations\textsuperscript{23}. However, the absence of various (M-py) vibrations supports the non-involvement of pyridine nitrogens in coordination.

$^1$H NMR Spectra
The $^1$HNMR spectrum of zinc(II) complex show multiplets at 7.2-7.8 ppm which may be assigned due to hydrogens of aromatic rings\textsuperscript{27}. The peak (singlet) at 4.2-4.4 ppm may be assigned due to hydrogens (4H) of glyoxal moiety\textsuperscript{28}.

Magnetic measurement and electronic spectra
Co cobalt complexes: The magnetic moment was measured at room temperature and lay in the range 4.92-4.94 B.M. which corresponds to three unpaired electrons. The solution spectra of cobalt(II) complexes exhibit absorption in the regions ~8100-9100($\nu_1$), 12550-15750($\nu_2$) and 18700-20250 cm\textsuperscript{-1}($\nu_3$) respectively. The spectra resemble those reported to be octahedral\textsuperscript{29}. Thus, assuming the effective symmetry to be D$_{4h}$, the various bands can be assigned to $^4T_{1g} \rightarrow ^4T_{2g}$ ($\nu_1$), $^4T_{1g} \rightarrow ^4A_{2g}$ ($\nu_2$), $^4T_{1g} \rightarrow ^2T_{1g}$ ($\nu_3$) respectively. It appears that the symmetry of these complexes is not idealized O$_h$ but is D$_{4h}$. The assignment of the first spin-allowed band seems plausible since the first band appears approximately at half the energy of the visible band\textsuperscript{30}.

Nickel complexes: The magnetic moment of nickel complexes at room temperature lay in the range 2.96-2.98 B.M. showing octahedral environment around the Ni(II) ion in all complexes. The solution spectra of Ni(II) complexes exhibit a well discernable band with a shoulder on the low energy side. The other two bands generally observed in the region at ~16,650-17,050 cm\textsuperscript{-1}($\nu_2$), and 27,800-28,250 cm\textsuperscript{-1}($\nu_3$), are assigned to $^3A_2 \rightarrow ^3T_{1g}$($\nu_2$), and $^3A_2 \rightarrow ^3T_{1g}$($\nu_3$), respectively. The first two bands result from the splitting of one band, $\nu_1$, and are in the range at ~9700-10,300 and 11,750-12,300 cm\textsuperscript{-1}, which can be assigned to $^3B_{1g} \rightarrow ^3E_g$ and $^3B_{1g} \rightarrow ^3B_{2g}$, assuming the effective symmetry to be D$_{4h}$ (component of $^3T_{2g}$ in O$_h$ symmetry)\textsuperscript{30}. The intense higher energy band at ~34,500 cm\textsuperscript{-1} may be due to a $\pi-\pi^*$ transition of the (C=O) group. Various bands do not follow any regular pattern and seem to be anion independent. The spectra are consistent with distorted octahedral nature of these complexes.

Copper complexes: The magnetic moments of copper complexes lay in the range 1.76-1.79 B.M. The absorption spectra of the copper complexes exhibit bands in the region ~17,700-19,600 cm\textsuperscript{-1} with a shoulder on the low energy side at ~14,550-16,000 cm\textsuperscript{-1}, and show that these complexes are distorted octahedral\textsuperscript{29,30}. Assuming tetragonal distortion in the molecule, the d-orbital energy level sequence for these complexes may be: $x^2 - y^2$ > $z^2$ > xy > xz > yz and the shoulder can be assigned to: $z^2 \rightarrow x^2 - y^2$ ($^2B_{1g}$ $\rightarrow ^2B_{2g}$) and the broad band contains both the $xy \rightarrow x^2 - y^2$ ($^2B_{1g}$ $\rightarrow ^2E_g$) and $xz, yz \rightarrow x^2 - y^2$ ($^2B_{1g}$ $\rightarrow ^2A_{2g}$) transitions\textsuperscript{31}. The band separation of the spectra of the complexes is of the order 2500 cm\textsuperscript{-1}, which is consistent with proposed geometry of the complexes\textsuperscript{31}. Therefore, it may be concluded that all the complexes of Cu(II) metals of this series are distorted octahedral.

CONCLUSION
Based on various physicochemical studies like elemental analyses, conductivity measurements, magnetic measurements, electronic and IR spectral studies, a distorted octahedral geometry may be proposed for all of these complexes as shown in Fig. 1.

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Figure: 1

Where: $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and $\text{Zn(II)}$; $X = \text{Cl}^{-1}, \text{NO}_3^{-1}, \text{CH}_3$

REFERENCES

Table-1: Analytical data of divalent cobalt, nickel, copper and zinc complexes derived from 2,6-diaminopyridine and glyoxal.

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<td>(1)</td>
<td>[Co(C\textsubscript{14}H\textsubscript{10}N\textsubscript{6})Cl\textsubscript{2}]</td>
<td>14.45</td>
<td>42.08</td>
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