



RESEARCH ARTICLE

Structural characterization studies of some cobalt(II), nickel(II), copper(II) and zinc(II) complexes

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Abstract

The metal complexes play an important role in many biological processes. The ligand 1,10-phenanthroline is condensed with metal chlorides to form cobalt(II), nickel(II), copper(II) and zinc(II) complexes. The structural characterization was carried out using, elemental analysis, molar conductance, magnetic studies, infrared and ultraviolet spectra. The geometry of the metal complexes was confirmed by spectral data.

Introduction

Transition metals are essential for the normal functioning of living organisms. Therefore, it is not surprising that transition metal compounds are of great interest as potential drugs. Transition metal complexes have largely been exploited for these purposes not only because of their unique spectral and electrochemical signatures but also due to the fact that by changing the ligand environment one can tune the DNA binding and cleaving ability of a metal complex. Certain metals like iron, cobalt, nickel, copper, zinc and magnesium are present in human physiological systems in trace quantities. The biological fluids in the body are held by these essential metal ions in fine balance

as coordination compound. The studies on the complexation of these metal ions with the model ligand, which can duplicate the body fluids *in vitro* condition, can be of great help to have a correct understanding of physiological systems. Hence the stabilities and structure of such complexes has been studied by a host of research workers in the past five decades.

Coordination complexes with different donor atoms of the same ligand bonded to the central metal ion are known as mixed donor complexes. The simplest case of a mixed ligand complexes arises when two different ligands are simultaneously bonded to the same metal ion and is known as ternary complexes [1]. Such complexes are important as models for metalloenzyme-substrate complexes and components of the multi-metal-multi-ligand system in biological fluids.

Experimental

Conductance measurements were carried out using a

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Coronation digital conductivity meter. The infrared spectra of the solid samples were recorded in JASCO/FT-IR 410 spectrometer in the range of 400-4000 cm^{-1} . Potassium bromide disc method was employed for sample preparation. Electronic spectra were recorded using Thermo Evolution 201 UV/VIS Spectrophotometer using ethanol as solvent in the range of 190-1100 nm. Magnetic susceptibility measurements of the complexes in the solid state were determined by Gouy balance using CuSO_4 as the calibrant. The metal content in the complex derived from the ligand was estimated by EDTA complexometric titrations.

Preparation of metal complexes

Cobalt(II) complex

The 1,10-phenanthroline (0.18007 g, 1 mmol) was dissolved in water and magnetically stirred for half an hour. To the above solution cobalt(II) chloride (0.23793 g, 1 mmol) dissolved in water was added dropwise with constant stirring for about 3 h, when light violet colour crystals were separated out. It was recrystallized and dried in vacuum desiccator over fused anhydrous calcium chloride.

Nickel(II) complex

The 1,10-phenanthroline (0.18007 g, 1 mmol) was dissolved in water and magnetically stirred for half an hour. To the above solution nickel(II) chloride (0.23769 g, 1 mmol) dissolved in water was added dropwise with constant stirring for about 3 h, when blue colour crystals were separated out. It was recrystallized and dried in vacuum desiccator over fused anhydrous calcium chloride.

Copper(II) complex

The ligand, 1,10-phenanthroline (0.18007 g, 1 mmol) was dissolved in water and magnetically stirred for half an hour. To the above solution copper(II) chloride (0.2416 g, 1 mmol) dissolved in water was added dropwise with constant stirring for about 3 h, when dark orange colour crystals were separated out. It was recrystallized and dried in vacuum desiccator over fused anhydrous calcium chloride.

Zinc(II) complex

The 1,10-phenanthroline (0.18007 g, 1 mmol) was dissolved in water and magnetically stirred for half an hour. To the above solution zinc(II) chloride (0.29747 g, 1 mmol) dissolved in water was added dropwise with constant stirring for about 3 h, when colourless crystals were separated out. It was recrystallized and dried in vacuum desiccator over fused anhydrous calcium chloride.

and dried in vacuum desiccator.

Results and discussion

The metal complexes were prepared by dissolving 1,10-phenanthroline with metal salts in 1:1 molar ratio in water medium. The calculated analytical data indicate that the metal: ligand stoichiometry is 1:1 in the complex system. The metal content in the complex was determined by complexometric titration with EDTA [2].

Molar conductance

The molar conductance of the complex was measured in distilled water medium using 10^{-3} M solutions determined at room temperature. The metal complex (Fig 1) shows the molar conductance value of 15.26 to 6.00 $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. This data reveals that the complex is non-electrolytes [3].

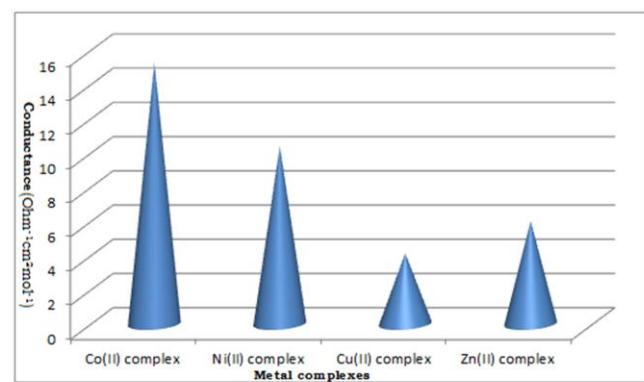


Fig 1 Conductance value of metal complexes.

Infrared spectra

In the metal complexes, the medium bands observed at 1555 and 1593 cm^{-1} are due to $\nu(\text{CN})$ stretching absorptions, respectively. The C=C of the aromatic ring in both the zinc and nickel complexes were found at 1614 cm^{-1} while in the cobalt and copper complex is seems lower value [4] of 1612 cm^{-1} . The aromatic C-N stretching of the complexes were at 1026 cm^{-1} for only the nickel complex while it was at 1030 cm^{-1} for the remaining three complexes. The C=N bands in the complexes are found between 1435-1437 cm^{-1} , the shifts observed in the spectra of these complexes, compared with the literature value of 1600 cm^{-1} indicate the use of the nitrogen atom of the ring to form the complexes [5]. The observed shifts in band positions are a clear indication that the ligands are coordinated to the respective metal centers. Similarly, in the IR spectra of the complexes, the C-H and C=C stretching bands undergo a coordinationinduced lower

frequency shift of 12 and 18 cm^{-1} , respectively [6]. The weak peaks in the $3075 - 2800 \text{ cm}^{-1}$ range are due to vCH stretching of phen ligand. The IR vibration modes of the anion, which are broad and very strong, were observed at 1520 and 1527 cm^{-1} for the complexes, respectively, and assigned to a mixture of C–C and C–O stretching vibrations. The bands observed at $479-446 \text{ cm}^{-1}$ has been assigned to vM-N [7] and in the low frequency region new stretching bands occurred at $331-339 \text{ cm}^{-1}$, which are assigned to v (M-Cl) vibrations.

Electronic spectra

The electronic spectral data of the metal complex is recorded in ethanol solution. In the tetrahedral environment, cobalt(II) complex shows only one absorption band in the UV/Vis range due to the transition, ${}^4\text{A}_2 (\text{F}) \rightarrow {}^4\text{T}_1 (\text{p})$ (600-700 nm). The cobalt(II) complex shows a broad band centered at 522 nm, which is the characteristic of tetrahedral geometry for cobalt(II) complex [8-11]. The electronic spectrum of the nickel(II) complex shows an intense absorption band at 563 nm is due to the transition [11], ${}^3\text{T}_1 (\text{F}) \rightarrow {}^3\text{T}_1 (\text{P})$ (550-700 nm). Which is the characteristic of four coordinate tetrahedral geometry for nickel(II) complex. Normally square planar geometry occurs at 600-700 nm respectively. This corresponds to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transitions, respectively. The copper(II) complex shows an energy band at 679 nm, which is the characteristic for square planar geometry for copper(II) complex. Zinc(II) complex due to its completely filled d^{10} electronic configuration, it does not exhibit any d-d electronic transition, since it is diamagnetic. Therefore it would have been predicted the tetrahedral geometry for this complex.

Magnetic moment measurements

The effective magnetic moment of the cobalt(II) Complex is 4.22 B.M., suggesting its tetrahedral structure [12]. The nickel(II) chelate has a room temperature magnetic moment of 2.76 B.M as expected for tetrahedral geometry [12]. The copper(II) complex

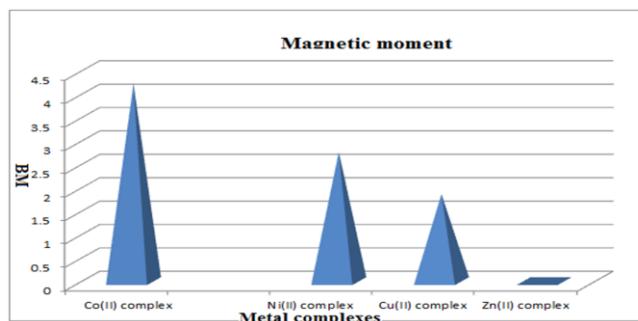


Fig 2 Magnetic moment value of metal complexes.

has effective magnetic moment of 1.86 B.M [13] indicates the square planar geometry. The zinc(II) complex is found to be diamagnetic. The room temperature magnetic moment of the complexes is shown in **Fig 2**.

Conclusions

The conductivity measurements indicate that the metal complex was found to be non-electrolytes. The spectrum of the complex clearly indicates the coordination. The spectral results indicate that the complex shows $[\text{NiLX}_2]$ type, ($\text{L}=1,10\text{-phenanthroline}$, $\text{X}=\text{Cl}$ or NO_3). The electronic spectral data indicates the tetrahedral geometry for cobalt(II), nickel(II) and zinc(II) complexes, whereas copper(II) complex has square planar geometry.

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