



RESEARCH ARTICLE

Synthesis, spectral and magnetic studies of some cobalt(II), nickel(II), copper(II) and zinc(II) complexes

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Received 26 March 2015; Accepted 30 April 2015

Available online 30 April 2015

Abstract

The cobalt(II), nickel(II), copper(II) and zinc(II) complexes with 1,10-phenanthroline have been synthesized. The complexes have been characterized by elemental analyses, IR, electronic spectra, magnetic moment and molar conductance. The electronic spectra and magnetic studies confirm the octahedral geometry of the metal complexes.

Keywords

1,10-Phenanthroline

IR

Electronic spectra

Molar conductance

Introduction

Inorganic chemistry is the most widely developed field due to that of co-ordination chemistry. It applies very particularly to the co-ordination of transition metal. The Werner co-ordination theory states that a metal ion surrounds itself with the ligands and the nature of the ligands, the character of metal ligand bonds and the geometry of the ligands around the metal ion. At first an extensive theoretical treatment of co-ordination chemistry has given by valence bond theory. Later crystal field theory (CFT) was used to interpret the spectra of transition metal complexes. The metal ligand interaction can be described in terms of molecular orbital formed by metal and ligand orbital. Since the molecular orbital theory does not provide numerical results in an easy

way, a kind of modified CFT has been derived in which certain parameters are numerically adjusted to allow the effect of covalence. The modified CFT is often called as ligand field theory.

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. Any imbalance in the metal fluid ratio will lead to physiological disorder and disease [1]. 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. These include stabilization of different oxidation states and modulation of the electrophilic and nucleophilic properties of the metals. However, in spite of the influence of the ligands on the metal ions, it is striking how often certain distinctive properties of a given metallic element persists through drastic ligand changes.

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Experimental

Materials

1,10-phenanthroline (Merck), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2$ (Himedia) were used for this work. The solvents used were purified by standard methods.

Physical measurements

Conductance measurements were carried out using a Coronation digital conductivity meter. The IR spectra of the solid samples were recorded in JASCO/FT-IR 410 spectrometer in the range of 400-4000 cm^{-1} by potassium bromide disc method. 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 was estimated by EDTA complexometric titrations [2].

Preparation of metal complexes

Cobalt(II) complex

The 1,10-phenanthroline (0.36014 g, 2 mmol) was dissolved in water and magnetically stirred. The 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.

Nickel(II) complex

The 1,10-phenanthroline (0.36014 g, 2 mmol) was dissolved in water and magnetically stirred. The 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.

Copper(II) complex

The 1,10-phenanthroline (0.36014 g, 2 mmol) was dissolved in water and magnetically stirred. The 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.

Zinc(II) complex

The 1,10-phenanthroline (0.36014 g, 2 mmol) was dissolved in water and magnetically stirred. The 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.

Results and discussion

Synthesis and characterization

The metal complexes were prepared by dissolving 1,10-phenanthroline with metal salts in 2:1 molar ratio. The metal complexes are soluble in water, ethanol and methanol. The calculated analytical data indicate that the metal: ligand stoichiometry is 1:2 in the complex systems. Analytical data of the metal complex is tabulated in **Table 1**. The numbering pattern of the 1,10-phenanthroline is shown in **Fig 1**.

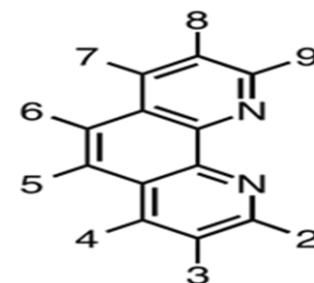


Fig 1. Numbering pattern of 1,10-phenanthroline.

Molar conductance

The metal complexes was measured in ethanol medium using 10^3 M solutions and the conductance value are determined at room temperature. The metal complex shows the molar conductance (**Fig 2**) value of $6.31 - 12.11 \text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. This data reveals that the complex is non-electrolytes [3].

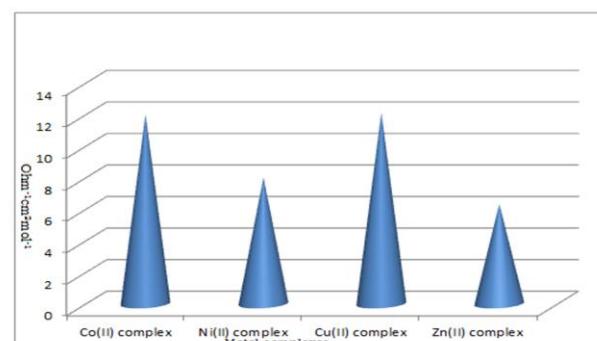


Fig 2 Conductance value of metal complexes.

Table 1 Analytical data of the metal complexes.

Complex	Empirical formula	Mol. Weight	Elemental analysis Calcd (%)					
			C	H	N	O	Cl	M
Co(II) complex	C ₂₄ H ₁₆ N ₄ Cl ₂ Co	490.25	58.80	3.29	11.43	-	14.46	12.02
Ni(II) complex	C ₂₄ H ₁₆ N ₄ Cl ₂ Ni	490.01	58.83	3.29	11.43	-	14.47	11.98
Cu(II) complex	C ₂₄ H ₁₆ N ₆ O ₆ Cu	547.97	52.61	2.94	15.34	17.52	-	11.60
Zn(II) complex	C ₂₄ H ₁₆ N ₆ O ₆ Zn	549.80	52.43	2.93	15.29	17.46	-	11.89

Infrared spectra

In the IR spectra of the metal complexes exhibit medium bands at the 1555 and 1593 cm⁻¹ are due to v(CN) absorptions, respectively. The C=C of the aromatic ring [4] in the complexes were found to be 1614 to 1612 cm⁻¹. The aromatic C-N stretching of the complexes were at 1026-1030 cm⁻¹ for the complexes. The C=N bands in the complexes are in between 1435-1437 cm⁻¹, the shifts observed in the spectra of these complexes 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. The IR spectra of the complexes, the C-H and C=C stretching bands undergo a coordination-induced lower frequency shift of 12 and 18 cm⁻¹, respectively [6]. The weak peaks in the 3075 – 2800 cm⁻¹ range are due to vCH stretching of phenanthroline 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, assigned to C-C and C-O stretching vibrations. The bands observed at 479-446 cm⁻¹ has been assigned to vM-N [7] and in the low frequency region new stretching bands occurred at 331 to 339 cm⁻¹, which are assigned to v(M-Cl) vibrations [7].

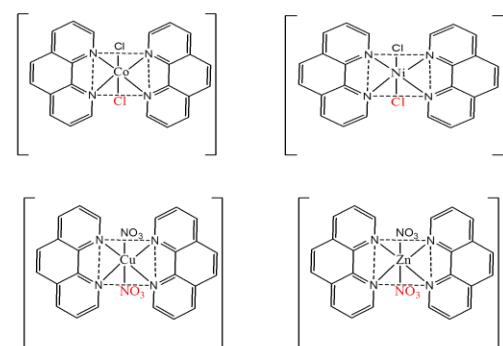
Electronic spectra

The cobalt(II) complex showed two spin-allowed transitions at 17,786 and 21,814 cm⁻¹ assignable to ⁴T_{1g}(F) → ⁴A_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{1g}(P) transitions respectively, are in conformity with an octahedral arrangement for cobalt(II) ion indicating an octahedral geometry [8-11]. The nickel(II) complex shows an intense absorption band at 18,940 cm⁻¹ due to ³A_{2g}(F) → ³T_{1g}(P) transition favours an octahedral geometry for the nickel(II) complex. Only one broad band is observed at 16,348 cm⁻¹ in the copper(II) complex assigned to ²Eg → ²T_{2g} transition

which is in conformity with an octahedral geometry. Though three transitions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope. This indicates the octahedral geometry for copper(II) complex. Zinc(II) complex due to its completely filled d¹⁰ electronic configuration, it does not exhibit any d-d electronic transition. The zinc(II) complex shows an absorption band at 22,955 cm⁻¹ attributed to the LMCT transition, which is compatible with this complex having an octahedral structure.

Magnetic moment

The magnetic susceptibilities, all of which are independent of field strength, were corrected for the diamagnetic contribution of the ligands, the anions and the metal ions using Pascal's constants. The effective magnetic moment of the cobalt(II) complex is 4.86 B.M which suggest the octahedral structure [12]. The nickel(II) chelate has a room temperature magnetic moment of 2.83 B.M as expected for octahedral geometry [12]. The copper(II) complex has effective magnetic moment of 1.92 B.M [13] indicates an octahedral geometry. The proposed structure of the metal complexes is shown in **Fig 3**. The zinc(II) complex is found to be diamagnetic as expected for d¹⁰ configuration (**Fig 4**).

**Fig 3** Structure of the metal complexes.

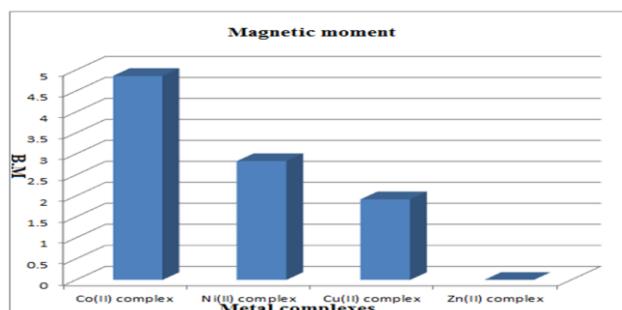


Fig 4 Magnetic moment value of metal complexes.

Conclusions

The stoichiometry confirms the metal: ligand ratio of the complexes. The low molar conductivity measurements indicate that the metal complexes behave non-electrolytes. The spectral data indicate that the complex shows $[\text{NiL}_2\text{X}_2]$ type, ($\text{L}=1,10\text{-phenanthroline}$, $\text{X}=\text{Cl}$ or NO_3). The electronic spectral measurement indicates an octahedral geometry for cobalt(II), nickel(II), copper(II) and zinc(II) complexes.

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