



Synthesis and characterization of mixed ligand Based cobalt and cadmium complexes

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Abstract

Mixed ligand complexes have a great deal of attention towards more biological macro cyclic systems. They have been synthesized and characterized by microanalyses, spectroscopic and room temperature magnetic susceptibility measurements. The microanalyses data is satisfactory with the formation of the prepared complexes. The synthesis and characterization of two new macrocyclic mononuclear transition metal complexes derived from the 1, 10 phenanthroline with benzoate. The infrared spectra of the complexes reveal the involvement of the donor groups of the selected aromatic compounds attached to the mixed ligand complexes.

Keywords: mixed ligands, aromatic ligands, ir spectra, microanalysis, 1, 10 phenanthroline

1. Introduction

The metal complexes containing synthetic macro cyclic ligands have attracted a great deal of attention because they can be used as models for more biological macrocyclic systems: metalloporphyrins (haemoglobin, myoglobin, cytochromes, chlorophylls), corrins (vitamin B12) and antibiotics (valinomycin, nonactin). These discoveries have created supramolecular chemistry and its enormous diversity [1,2]. Curtis [3] first reported the synthesis of some macrocycles, since then various macrocyclic ligands such as cyclam, cyclenaminobenzaldehyde, trimmers and tetramers have been reported [4-6]. Synthetic chemists have long been attracted to the design, synthesis of macrocyclic ligands and their metal complexes. These complexes show enhanced thermodynamic, kinetic stabilities and characteristic properties that are inaccessible for complexes of the corresponding open-chain chelate ligands [7-9]. Macrocyclic complexes have potential applications in fundamental and applied sciences [10], such as metal selective extraction [11-13], stabilization of unusual oxidation state [14], sensor technology [15-17] magnetic resonance imaging, contrast enhancing agents [18-19], catalysts [20-22] and models for biological structures and functions [23-30].

2. Materials and Methods

Cobalt

A wide variety of Co (II) complexes are known to bind dioxygen more or less reversibly and are therefore frequently studied as model compounds for natural oxygen carriers and for their use in O₂ storage, as well as in organic synthesis due to their catalytic properties under mild conditions [31].

Cadmium

Cadmium has atomic number 48. This soft, bluish-white metal is chemically similar to the two other stable metals in group 12, zinc and Pb. Cd and its congeners are not always considered transition metals.

3. Antimicrobial Activity

The antimicrobial activities were recorded for the following organisms: staphylococcus aureus, candida albicans, vibrio cholera, klebsiella pneumonia, candida tropicalis, candida parapsilosis, and micrococcus luteus. These antimicrobial activities at 10, 25, 50 and 100 µg/mL concentrations in the DMF solvent. Where a DMF poured disk was used as negative control. The bacteria were sub cultured in agar medium. The petri dishes were incubated for 24 hours at 37°C, a standard antibacterial drug (streptomycin) was also screened under similar condition for comparison. The fungi were sub cultured in potato dextrose agar medium, a standard antifungal drug (fluconazole) was used for comparison. The petri dishes were incubated for 48 hours at 37°C.

Vibrio Cholerae

Vibrio cholerae is a gram-negative, comma-shaped. The bacterium's some strains natural habitat is brackish or saltwater. Of V. cholerae cause the disease cholera. cholerae is gram-negative and comma-shaped. Initial isolates are slightly curved, whereas they can appear as straight rods upon laboratory culturing. The bacterium has a flagellum at one cell pole as well as pili. V. cholerae is a facultative anaerobe, and can undergo respiratory and fermentative metabolism.



Fig 1: Microbial Structure of Vibrio cholera

Klebsiella Pneumoniae

Klebsiella pneumonia is a gram-negative, non-motile, encapsulated, lactose fermenting, facultative anaerobic, rod shaped bacterium. These are klebsiella pneumoniae, Klebsiella ozaenae, klebsiella terrigena, klebsiella rhinoscleromatis, klebsiella oxytoca, klebsiella planticola, and (7) klebsiella ornitholytica. Of these, K oxytoca and K Rhinoscleromatics have also demonstrated in human clinical specimens. In recent years, klebsiellae have become important pathogens in nosocomial infections.



Fig 2: Microbial Structure of Klebsiella pneumonia

Candida Tropicalis

Candida tropicalis is one of the fungal species among several species in Candida family. It is considered to be second commonest yeast like fungus after Candida albicans. They serve as food for the bacteria which are useful for candidatropicalis inhabits in skin and gastrointestinal tract. However, under some circumstances when the bacterial colony becomes less, this yeast like fungus organism get an opportunity to multiply fast.



Fig 3: Microbial Structure of Candida tropicalis

Candida Parapsilosis

Candida parapsilosis is a fungal species of the yeast family that has become a significant cause of sepsis and of wound and tissue infections in immuno-compromised patients. Unlike Candida albicans and Candida tropicalis, Candida parapsilosis is not an obligate human pathogen.

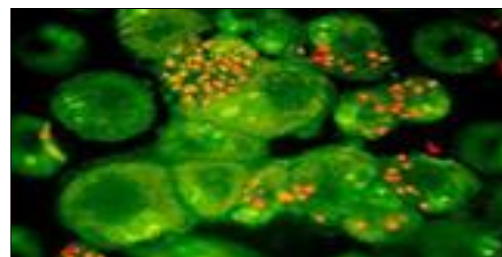


Fig 4: Microbial Structure of Candida parapsilosis

4. Aim and Scope of the Present Investigation

In this thesis, results of our studies on the synthesis and characterization of two new macrocyclic mononuclear transition metal complexes derived from the above 1,10-phenanthroline with benzoate and their applications in antimicrobial activities are presented.

Template Synthesis Data for Macrocyclic Mononuclear Cobalt (II), Cadmium (II) Complexes

Table 1

| Complex | Metal (mg) | Compounds (mg) | | Time of refluxion (hours) | Yield (mg) |
|-----------------|------------|----------------------------|-------------------------|---------------------------|------------|
| [Co(Phen)(Ben)] | 0.47g (Co) | 1,10-phenanthroline(0.36) | Sodium benzoate (0.288) | 4 | 0.372 |
| [Cd(Phen)(Ben)] | 0.45g (Cd) | 1,10-phenanthroline (0.36) | Sodium benzoate (0.288) | 4 | 0.366 |

Template Synthesis of Cobalt (Ii) Complexes

The amount of cobalt in the complex was estimated spectrophotometrically by the following method. The template condensation of 1, 10-phenanthroline ligand 0.34g dissolved in 20 ml of hot ethanolic solution in 100ml beaker and 0.288g sodium benzoate dissolved in 20 ml of ethanol added over solution slowly with constant stirring, finally add 0.47g cobalt dissolved in 20ml of ethanol in the mixture was stirrer for 4 hrs. The pink precipitate formed was filtered, washed with cold ethanol then dried in vacuum. Yield around 75%.

Template Synthesis of Cadmium (Ii) Complexes

The template condensation of 1, 10-phenanthroline ligand

0.34g dissolved in 20 ml of hot ethanolic solution in 100ml beaker and 0.288g sodium benzoate dissolved in 20 ml of ethanol added over solution slowly with constant stirring, finally add 0.45g cadmium dissolved in 20ml of ethanol in the mixture was stirrer for 4 hrs. The white precipitate formed was filtered, washed with cold ethanol then dried in vacuum. Yield around 75%.

5. Results and Discussion

Analytical Data of Macrocyclic Mononuclear Co(II) and Cd(II) Schiff base Complexes

Table 2

| S. No | Molecular formula | Colour | Elemental Analysis[Found (calcd.)] in % | | | M | Δm ($\text{ohm}^{-1} \text{Cm}^2 \text{mol}^{-1}$) |
|-------|-------------------|--------|---|------------|------------|--------------|---|
| | | | C | H | N | | |
| 1. | [Co(Phen)(Ben)] | Pink | 68.80(68.70) | 7.76(7.66) | 5.99(5.89) | 12.61(12.51) | 76.4 |
| 2. | [Cd(Phen)(Ben)] | White | 59.94(59.84) | 6.96(6.86) | 5.35(5.25) | 21.58(21.48) | 82.2 |

Cobalt Complexes

IR spectra of the samples are recorded in KBr medium in 400-4000 cm^{-1} ($\text{C}=\text{N}$) stretching vibration ^[32] band at region about 455.89 cm^{-1} is shifted to lower frequencies in most complexes as expected. The presence of sharp band corresponding to the remaining hydroxyl group at 3066 cm^{-1} but it is obscured by the presence of water molecules bands.

This was appeared for the most complexes and a very broad band at about 3385 cm^{-1} region, The other bands appeared at 982-1249 cm^{-1} region assigned to the ($\text{C}-\text{O}$), which are shifted to a higher frequency after complexation with central metal ions, compared to the free ligands in which was noted at 973-1172 cm^{-1} . In addition the two bands at 619-643 and 472 cm^{-1} is attributed to the ($\text{M}-\text{O}$) and ($\text{M}-\text{N}$) respectively ^[33]. The IR spectra of [Co(phen)(Ben)] complex exhibit a medium band at 1505 cm^{-1} which is assigned to the ($\text{C}=\text{N}$) stretching around 3444 cm^{-1} indicating the presence of coordinated or lattice water in the complex. The spectrum reversals a weak band at 1249 cm^{-1} which is attributed to ($\text{C}-\text{O}$) vibration, again this band is shifted to higher value compared to the free ligand due to formation ($\text{C}-\text{O}-\text{M}$) bond. In addition three new bands in the regions 538 and 462 cm^{-1} were emerge, which are probably due to the formation of ($\text{Co}-\text{O}$) and ($\text{Co}-\text{N}$) bond respectively ^[34].

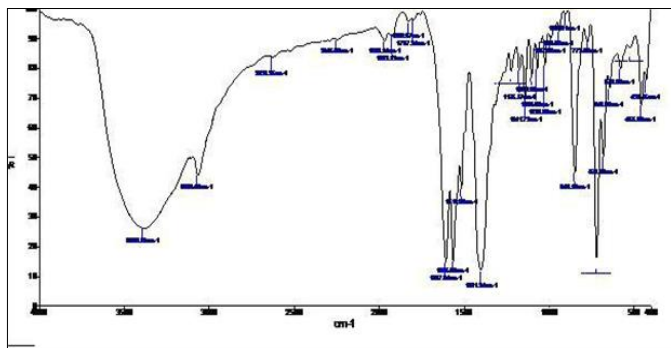


Fig 5: Infrared Spectra of Cobalt (II) Complexes

Cadmium Complexes

IR spectra of the samples are recorded in KBr medium in 400-4000 cm^{-1} range to identify coordination sites of ligands. The presence of sharp band corresponding to the remaining hydroxyl group at 3441 cm^{-1} but it is obscured by the presence of water molecules bands. This was appeared for the most complexes and a very broad band at about 3903 cm^{-1} region, which is associated with coordinated or solvent water molecules. The other bands appeared at 973-1172 cm^{-1} region assigned to the ($\text{C}-\text{O}$), which are shifted to a higher

frequency after complexation with central metal ions, compared to the free ligands in which was noted at 930-1228 cm^{-1} .

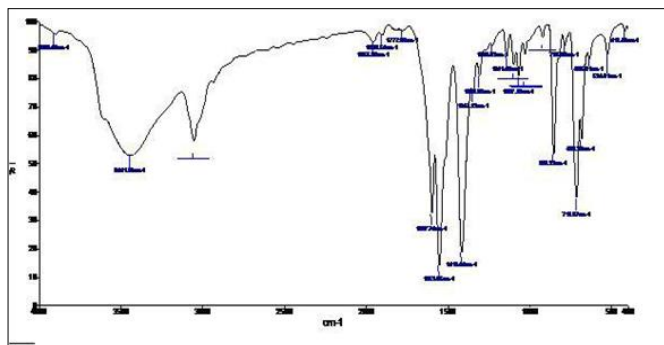


Fig 6: Infrared Spectra of Cadmium (II) Complexes

Electronic spectra

Electronic Spectra of Cobalt (II) Complexes

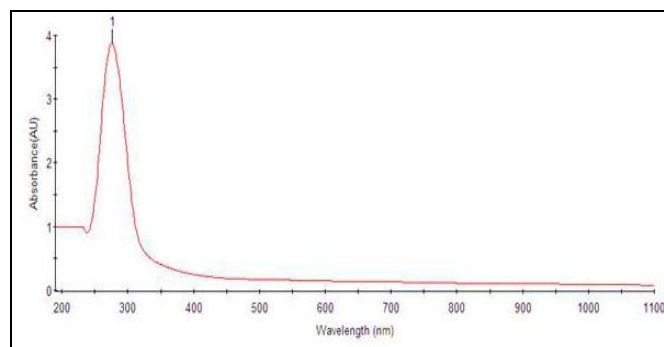


Fig 7

Electronic Spectra of Cadmium (II) Complexes

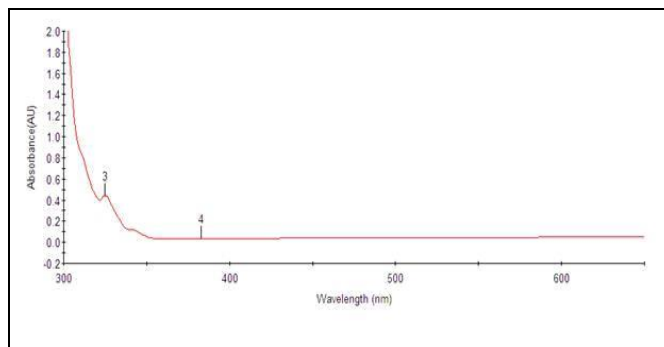


Fig 8

Table 3: Antimicrobial activity of Cobalt(II) and Cadmium(II) Complexes

| S. No | Test Bacteria | Zone of Inhibition (mm) | | | | | | | | |
|-------------|---------------|-------------------------|----------|-----------------|----------|-----------------|----------|----------|---------|---------|
| | | (Phen) | | [Co(phen)(Ben)] | | [Cd(phen)(Ben)] | | Ampho-B | A | T |
| | | 50µg/ml | 100µg/ml | 50µg/ml | 100µg/ml | 50µg/ml | 100µg/ml | 20 µg/ml | 10µg/ml | 30µg/ml |
| 1 | <i>K. p</i> | 10±1 | 13±2 | 35±1 | 37±1 | 36±1 | 38±1 | - | 16±3 | 18±2 |
| 2 | <i>V. c</i> | 9±2 | 14±1 | 29±1 | 31±1 | 29±2 | 32±1 | - | 18±4 | 16±1 |
| 3 | <i>M. l</i> | 8±1 | 10±2 | 29±1 | 31±2 | 30±2 | 33±2 | - | 20±2 | 18±2 |
| 4 | <i>S. a</i> | 9±1 | 14±1 | 22±1 | 30±1 | 22±1 | 30±1 | - | 26±3 | 21±1 |
| Test Fungal | | | | | | | | | | |
| 5 | <i>C. a</i> | 7±1 | 9±2 | 15±1 | 22±1 | 15±1 | 21±2 | 13±3 | - | - |
| 6 | <i>C. t</i> | 6±1 | 8±3 | 17±1 | 22±2 | 18±2 | 24±1 | 9±1 | - | - |
| 7 | <i>C.p</i> | 6±1 | 9±2 | 18±1 | 27±2 | 20±1 | 28±1 | 16±4 | - | - |

6. Conclusion

A series of Cobalt (II) and Cadmium (II) complexes were prepared via the template condensation of 1, 10-phenanthroline with benzoate in the presence of above metal ions to form a macrocyclic mononuclear units, were prepared and structurally characterized. The metal ion is coordinated through the azomethine nitrogen atoms. The bonding of the metal ion was confirmed by the analytical. Infrared and electronic studies. Cyclic voltammetric showed two pair of anodic and cathodic peaks, and the peak separation ΔE value indicates quasi-irreversible electrode reaction.

The synthesized macrocyclic mononuclear cobalt (II) and Cadmium (II) complexes showed good antimicrobial activities against the Gram positive (*S. aureus*), Gram negative (*P. fluorescens*) and fungi (*A. fumigatus*) strains. It has been suggested that chelation/coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor group within the whole chelate ring system. This process of chelation will enhance the activity of the complexes. Keeping in view the rising problems of antimicrobial resistance, these compounds may be used for formulating novel chemotherapeutic agents and further investigation will be necessary to identify the active principle.

7. References

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