Synthesis and Spectroscopic Analysis of the Nature of Coordination Modes of Ligands in Copper (II) and Cadmium (II) Complexes of Two N-Oxidobenzamide Derivatives

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Abstract:
N-Oxidobenzamide derivatives are powerful metal ion chelators. It is used as inhibitors of hypertension, tumor growth, inflammation, infectious agents, asthma, arthritis, Alzheimer’s diseases and more. In this study, Copper (II) (SRC1 and SRC3) and Cadmium (II) (SRC2 and SRC4) complexes were synthesized from potassium N-Oxidobenzamide derivative ligands and they were characterized by using various techniques such as Infra-Red spectra, electronic spectra, melting point and conductivity measurements. The electronic spectral study and the melting point analysis revealed that the ligands are coordinated to the metal centre. IR and conductivity analyses confirm the coordination of hydroxamate ions to the metal centre as O, O-bidentate mode via the hydroxyl oxygen and the carbonyl oxygen atoms of the ligands. The proposed molecular structures for the newly formed complexes are also given.

Keywords: Hydroxamic Acids, N-Oxidobenzamide, Copper(II) Complex, Cadmium (II) Complex and Analytical Techniques

1. Introduction

Hydroxamic acids are naturally occurring or synthetic weak organic acids and produce hydroxamate ion [1, 2]. They are preferably named as N-hydroxy amides*. They contain the oxime (–N–OH) and the carbonyl (C=O) groups and have the following structure as shown in Figure 1. The reasonable way of producing hydroxamic acid derivatives is the reaction of hydroxylamine with acid chlorides or esters [2].

Hydroxamic acids are hydrophilic organic compounds that can exhibit keto-iminol tautomerism, and both tautomers may exist as Z or E diastereomers [3]. The deprotonation could be either from the nitrogen or the oxygen, making them N-acids or O-acids [4]. Depending on the pH, two (O, O) binding modes of the ligands are accessible to metal ions [5]. The most important application of N-Oxidobenzamide is as good metal ion chelators [6]. This kind of compounds and their derivatives find many applications in chemistry and biology and have been the subject of many experimental investigations [7, 8].

![Figure 1. The structure of Hydroxamic acid.](image-url)
2. Main Body

2.1. Materials & Methodology.

2.1.1. Materials

Coppersulphate pentahydrate (CuSO₄·5H₂O) and Cadmium chloride (CdCl₂) (all are AR grade) were used without further purification. Methanol (GPR) was used as solvent. Ligands used are (SRL1 and SRL2) are shown in Figure 2.

![Figure 2. The structure of SRL1 and SRL2.](Image)

2.1.2. Synthesis of the Complexes

The metal salt and ligands (SRL1 and SRL2) were mixed in 1:2 ratio and the solution was refluxed to synthesized the Copper complexes (SRC1 and SRC3) and Cadmium complexes (SRC2 and SRC4) [9].

2.2. Results & Discussion

The conductivity measurements were made in DMF solution and all complexes are found to be non-electrolytes. This confirms that, there are no anions present outside the coordination sphere of the complexes. The conductivity of the complexes and the melting point of the ligands and their complexes are shown in Table 1. The different and higher values of the melting points confirm the formation of the complexes. This was further confirmed by Thin Layer Chromatography (TLC).

| Compound | V(N-H) cm⁻¹ | V(C=O) cm⁻¹ | V(C-N) cm⁻¹ | V(N-O) cm⁻¹ |
|----------|-------------|-------------|-------------|-------------|
| SRL1     | 3264        | 1653        | 1432        | 908         |
| SRC1     | 3264        | 1643        | 1438        | 903         |
| SRC2     | 3269        | 1640        | 1440        | 903         |
| SRC3     | 3240        | 1677        | 1442        | 849         |
| SRC4     | 3245        | 1643        | 1442        | 844         |

The IR spectra of the free ligands and its Cu²⁺ and Cd²⁺ complexes indicate that the strong and sharp bands from 3240 to 3269 cm⁻¹ is almost consistent with an amide type -N-H stretching mode. The carbonyl oxygen of the ligand will serve as a donor center in the metal. The conductivity measurements also show that all the complexes are non-electrolytes revealing the fact that the central ionic charge (Cu²⁺ and Cd²⁺) is neutralized by the 2 N-O ions from two ligands rather than the enolic O atom of its tautomomer, thereby the electron is donated from the carbonyl oxygen group (C=O). This was further confirmed by the shift of sharp bands to lower frequencies in SRC1 and SRC2 from the ligand SRL1 and in both complexes SRC3 and SRC4 (1643 cm⁻¹) reduced by 34 cm⁻¹ from ligand SRL2. The ν(C-N) of the metal complexes, SRC1 and SRC2 is found to be increased slightly (1438 and 1440 cm⁻¹ respectively) and in SRC3 and SRC4 is found to be consistent with that of the ligand SRL2 (1442 cm⁻¹), suggesting the coordination via π→π* and n→π* transitions. These two electronic transitions are overlapped to give a broad absorbance.
the keto oxygen atom. The reduction of ν(N-O) from the base value 908 cm⁻¹ in the ligand SRL1 to 903 cm⁻¹ in the complexes SRC1 and SRC2 and the weak intensity band at 849 cm⁻¹ in SRL2 is shifted to lower frequency 844 cm⁻¹ in both SRC3 and SRC4 indicates that the N-O bond is weakened by the coordination via the O atom of N-O moiety of the ligand.

According to the measurements and the spectroscopic assignments of these metal complexes, the possible and suggested tentative structures of the Cu (II) and Cd (II) complexes and coordination modes of the ligands are shown in Figure 3.

Figure 3. The tentative structure of Cu(II)–(a) and Cd(II)-(b) metal complexes. R: Cl, CH₃

3. Conclusion

Novel complexes with derivatives of N-Oxidobenzamide ligands and Cu²⁺ and Cd²⁺ ions were successfully synthesized and they were partially characterized. The coordination behaviour of ligands towards the metals used were analyzed by IR and electronic spectroscopic techniques and also by melting point and conductivity measurements. The increase in the melting point in complexes from the ligand is concurrent with the formation of the complexes. The significant bands and their shifts observed in IR spectra of the complexes confirmed that the coordination via O atoms of C=O and N-O moieties to the metal centre. The conductivity data show that the complexes are non-electrolytes in nature suggesting the O, O-bidentate coordination of the ligands thereby confirm the absence of any ions outside the coordination sphere. The electronic studies were also found to be supportive to the above findings. The structural analysis of crystals of the complexes revealed that the two ligands are coordinated to a metal to give neutral metal complex in which each of the ligands is coordinated via two O atoms of the carbonyl oxygen and hydroxyl oxygen. The proposed structures of the complexes are also given.

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