



Synthesis and Characterisation of Phthalic Acid Complexes with Biologically Active Metal Ions

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Abstract

Animal and plants contain carboxylic acids, which are involved in their metabolic reactions. It is also well known that metal ions are involved in their metabolic reactions. So far the complexation of carboxylate ions with metal ions has been extensively studied. Since neutral or acidic medium is existing in most of the biological reactions in animals and plants it is interesting to study the complexation of organic carboxylic acids in neutral medium with biologically active metal ions such as manganese, cobalt, nickel, copper and zinc. Complexes of phthalic acid were prepared in neutral medium and were characterised. In such complexes the carboxylic acid group is not ionised and carbonyloxygen of the carboxylic acids are coordinated to the metal ions. However the microbial study is not the scope of this work.

Introduction

Biologically important metals Mn, Co, Ni, Cu and Zn were taken for this study. Manganese is an essential component of the photosynthetic mechanism of plants¹.

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Vit B₁₂ is an important complex of cobalt². Nickel is a component of the enzyme urease³. Copper is a cofactor of a number of oxidation enzymes⁴. Zinc is found in the enzyme like DNA polymerase, carbonic anhydrase and alcoholic dehydrogenates⁵. These metals and the ligand phthalic acid were taken and complexes were prepared in the methanol solvent.

Preparation and purification

Metal chloride and phthalic acid were taken in the molar ration 1:3. They were dissolved in methanol and refluxed for six hours. The complexes were purified by washing with benzene methanol mixture.

Analysis of the complexes

The percentage of metal ions in the complexes was experimentally found by volumetric methods⁶. The experimentally determined percentage of metal ions is analogous with the percentage of metal ions of the proposed geometry.

Electrical conductivity

The experimentally determined molar conductivity of complexes in acetonitrile shows that phthalic acid complexes are of 1:2 type electrolytes. Hence it is clear that chlorine is not coordinated in phthalic acid complexes.

Magnetic moments

Manganese(II) complexes are high spin complexes with spin only magnetic moment 5.9 B.M. The experimentally determined room temperature magnetic moment of phthalic acid manganese(II) chloride complex is 5.82 B.M. suggesting octahedral or tetrahedral geometry. However, the metal ion percentage calculation suggests that the complex is octahedral in geometry.

Co(II) has the spin only magnetic moment 3.89 B.M. The room temperature magnetic moments for octahedral complexes are in the range of 4.7 – 5.2 B.M. due to orbital contribution and that for tetrahedral complexes are in the range of 4.4 – 4.8 B.M. The experimentally determined magnetic moment of phthalic acid cobalt(II) chloride complex is 5.04 B.M. which suggest that the complex is octahedral in geometry.

The spin only magnetic moment of Ni(II) is 2.83 B.M. Octahedral Ni(II) complexes do not have much orbital contribution. Hence the magnetic moments are in the

range of 2.83–3.1 B.M. In tetrahedral field, due to orbital contribution the magnetic moments are in the range of 3.1–3.5 B.M.⁷. The synthesised phthalic acid nickel (II) chloride complex has the magnetic moment 2.87 B.M. which suggest octahedral geometry for the complex.

Octahedral or tetrahedral geometry is expected to have little effect on the magnetic moment of copper (II) complexes. With spin orbit coupling it has the magnetic moment about 1.9 B.M. Phthalic acid copper(II) chloride complex has the magnetic moment 1.91 B.M. suggesting octahedral geometry.

As expected, the zinc (II) chloride complex of phthalic acid is diamagnetic in nature.

Infra Red spectrum

The presence of anion and the absence of symmetric and asymmetric C = O stretching frequency in the spectra of complexes suggest that the carboxylic acid is not ionised in the complexes. That is, the complexes are not the salts of carboxylate.

The shift in C = O stretching to lower region in the spectra of complexes suggest that the carbonyl oxygen of the unionised carboxylic acid is coordinated to the metal ion.

Vandoore and Hannik reported that the unionised acetic acid is coordinated to metal atom through the carbonyl oxygen. The shift in the carbonyl stretching frequency of the carboxylic acid group to the lower frequency suggest the coordination of carbonyl oxygen to metal analogous to the complexes of unionised acetic acid⁸.

The C–O and O–H deformation at 1250–1350 cm⁻¹ is slightly shifted in the spectra of complexes in comparison with that of ligand. The other frequencies including C=C of the aromatic ring at 1500–1600 cm⁻¹ are not very much affected in the spectra of complexes.

Electronic spectrum

The S⁶ ground state of the free Mn(II) ion is not split by the ligand field. All excited states of the d⁵ system have different spin multiplicity from the ground state and transition to them are spin forbidden. Due to very weak absorption we could not

get any appreciable peak in the electronic spectra of Mn(II) complexes. However, pale pink colour and analytical data suggest octahedral geometry.

The ground state term of Co(II) ion is ${}^4T_{1g}$ which arises from the $t_{2g}^5 e_g^2$ configuration. An octahedrally coordinated cobalt (II) ion should have three spin allowed d-d transition. ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. The transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ are not observed as the first one is a weak transition and the second one is a two electron process. The band in the visible region near 20000cm^{-1} is assigned to the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. Similarly for the tetrahedral complexes, the lower energy band due to ${}^4A_2 \rightarrow {}^4T_2$ lies in the infrared region where it is frequently overlapped by vibrational levels and so this band is not often observed.

The ${}^4A_2 \rightarrow {}^4T_1(F)$ and ${}^4A_2 \rightarrow {}^4T_1(P)$ band lie in the near infra red and visible regions respectively. They differ most significantly from the octahedral absorption in their much greater intensities, thus allowing ready distinction between the two stereo chemistries. In the present study the phthalic acid cobalt (II) chloride complex shows electronic spectra of absorption at 18790cm^{-1} which is due to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ in an octahedral environment. Hence it is very clear that the synthesised complex is octahedral in geometry⁹.

For octahedral Ni(II) complexes the transitions and their bands are ${}^3A_{2g} \rightarrow {}^3T_{2g}$ $13000\text{cm}^{-1} - 7000\text{cm}^{-1}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $20000\text{cm}^{-1} - 10000\text{cm}^{-1}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ $28000\text{cm}^{-1} - 20000\text{cm}^{-1}$. For tetrahedral Ni (II) complexes the transition and bands are ${}^3T_1(F) \rightarrow {}^3T_1(P)$ 15000cm^{-1} , ${}^3T_1 \rightarrow {}^3A_2$ 7000cm^{-1} and ${}^3T_1 \rightarrow {}^3T_2$ transition is not frequently observed. In this present study the phthalic acid Nickel (II) chloride complex shows absorption at 24980cm^{-1} which suggest that the Nickel ion is in the octahedral environment .

For copper (II) complexes Jahn-Teller distortion is observed. Because of the operation of Jahn-Teller effect on the 2e_g ground state octahedral distortion is observed. In the distorted versions several absorption bands may be expected in the region 13000cm^{-1} to 18000cm^{-1} . For tetrahedral complexes of copper (II) a band around 10000cm^{-1} is expected¹⁰. The synthesised complex of phthalic acid has its absorption at 13300cm^{-1} , suggesting octahedral geometry.

Conclusion

From the investigation, it is concluded that phthalic acid acts as a bidentate ligand and forms octahedral complexes with metal chlorides.

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