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# Metal Complexes of (4-Chloro) Salicylidene (3,5- Dinitro)-Benzoyl Hydrazone

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## Abstract

*This paper deals with synthesis of 4-chloro salicylidene(3,5-dinitro benzoyl hydrazone and its binuclear dimeric complexes of the type* $M_2L_2$ *.*$4H_2O$ *have been performed. The compounds were characterized through the studies of infra-red and diffuse reflectance magnetic measurements and thermogravimetry. The syntheses and characterisation of metal chelatal of several bivalent metal using (4-chloro)- salicylidene- (3,5-dinitro)- benzoyl hydrazone as ligand. After the synthesis of refluxing a mixture of metal salt and ligand solution in DMF. The compounds are coloured, powdery, insoluble in water and in organic solvent, and have the composition* $M_2(C_{14}H_{10}O_6N_4)_2$ $4H_2O$*, M stands for metal ions.; Zn(II), Cd(II) and* $UO_2(VI)$ *complexes are diamagnetic where as Mn(II), CO(II), Ni(II) and Cu(II) are paramagnetic with asubnormal magnetic moments, which indicates the binuclear, dimeric nature of this complexes a comparative study of spectra of CSDBHZ and its metal complexes suggests the enitial enolization of the legend followed by trapping of the metal thougt N and O donors, involving oxo bridging. The oxo bridge and the structure of the legand, incidentally, also point out to diametric nature of the complexes. The diffuse reflectance spectra of the complexes show an octahedral symmetry of the metal ion in the legend environment the complexes are found to presses more heat resistance then CSDBHZ. Water molecules in the complexes are present in the coordination sphere as in indicated by ir spectra and tg analysis. The order of the thermal stability of metal complexes has been found to be Zn(II) > Mn(II) > Ni(II) > Co(II) > Cu(II) >* $UO_2(VI)$*.*

## Introduction

The several reactions of metal complexes are inhibited by aromatic, hydrazones, which are catalyzed by coenzyme. The catalytic activity is enhanced in the cause of Cu (II) ions, where the aminooxidase enzyme can be taken nas a basic one.The lable of catcholamines is raised by mono amino oxidase inhibition, which affected the center nervous system regions in a few of the causes. The Many substituted hydrazones have been used in which depression is chief symptom, which can be as a result of treatment of paychotic paychoneurotic conditions. The action of acid hydrazide is certain, which can be as a result of;

(a) Pyridoxal is reacted with acid hydrazide and the related hydrazones are formed.
(b) Transition metal ions are reacted with acid hydrazide and appropriate complexes are formed.
(c) Transition metal ions and pyridoxal are associately reacted with acid hydrazides and Schiff base complexes are formed which are stable and are like the reported chelates of pyridoxal amino acid.

The coordination chemistry of solid hydrazide has attracted considerable attraction. The behavior of such type of ligands may be in different ways towards the transition metal ions. The cationic or neutral complexes are formed with ligands as their function with the nature of neutral or monobasic bidentate one, corresponding neutral complexes. The mono and dicarboxlic acidhydrazides act as neutral monodentate ligands, coordination in imidal structure through N-N nitrogen. The polymeric complexes of many bipositive metalions with N-N dibenzol hydrazine:MnL.1.5$H_2O$, CoL, NiL. $H_2O$ and ZnL have been synthesized by

Kharitonov and coworkers and these were characterized form the studies of infra-red spectra, diffuse reflectance spectra, thermogravimetry and magnetic measurements. Hydrazine of the type $MnL_3\ Cl_2.3H_2O$ and type $MnL_2.Cl_2O$—methoxybenzoyl hydrazine have been prepared and characterized.

**Experimental:**

**The Synthesis of the ligands:**

**Preparation of methyl 3,5 dintrobenzote (MDB):**

3,5-dinitrobenzoic acid hydrazine hydrate, methanol 4- chloroselicylaldehyde and the solvent used were of reagent grade. A Mixture of 18g of 3,5 – dinitro benzoic acid, 34 cm of methanol and 1 cm of concentrated sulphuric acid was refluxed for Ca=4h. The excess of the methanol was distilled off on a water bath and the mixture was allowed to cool, and neutralized by sodium carbonate till no further evolution of carbondioxide occured. The solid ester thus obtained was filtered, washed with water and dried at room temperature. The Purity of the compound was checked through determination of melting point, elemental analysis and IR spectrum studies.

**Preparation of (4-chloro) salicylidene – (3,5-dinitor) benzoyl hydrazone (CSDHZ):**

To a solution of 3,5 dinitrobenzoylhydrazide (DNBHZ) (0.01m) in acetone (50cm3), 0.01 M solution of 4- chlorosalicylaldehyde (in 20cm$^3$ acetone) was added with continuous stirring, a canary yellow precipitate of CSDBHZ was obtained, which was filtered after allowing to stand for one hour, for complete precipitation. The purity of the compound was checked by analysis and TLC. The Composition of the complexes arrived by following table.

Table-1

| Metal Complexes | Colour | M% obs (calc) | C% obs (calc) | H% obs (calc) | N% obs (calc) | CL% obs (calc) |
|---|---|---|---|---|---|---|
| $Mn_2L_2.4H_2O$ | Brown | 11.9 (12.1) | 7.5 (7.8) | 1.3 (1.5) | 12.0 (12.3) | 7.5 (7.8) |
| $Co_2L_2.4H_2O$ | Red Brown | 12.7 (12.9) | 36.3 (36.7) | 1.4 (1.5) | 12.1 (12.2) | 7.6 (7.8) |
| $Ni_2L_2.4H_2O$ | Yellow Green | 12.6 (12.8) | 36.7 (36.8) | 1.3 (1.5) | 12.0 (12.2) | 7.4 (7.8) |
| $Cu_2L_2.4H_2O$ | Light Green | 13.5 (13.8) | 36.3 (36.4) | 1.2 (1.5) | 11.9 (12.1) | 7.4 (7.7) |
| $Zn_2L_2.4H_2O$ | Yellow | 13.9 (14.0) | 35.9 (36.2) | 1.3 (1.4) | 11.9 (12.0) | 7.4 (7.7) |
| $Cd_2L_2.4H_2O$ | Dirty Green | 27.1 (27.4) | 40.9 (41.0) | 1.6 (1.7) | 12.9 (13.7) | 8.4 (8.7) |
| $(UO_2)_2L_2.4H_2O$ | Violet Brown | 39.9 (40.4) | 24.9 (25.1) | 0.9 (1.0) | 8.1 (8.4) | 5.1 (5.3) |

**Results and Discussion**

The Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd (II) and UO2(VI) acetates and solvents of reagent grade were employed .a solution CSDBHZ (0.002 mole dissolved in 75 cm$^3$ of DMF) was added slowly, with continuous stirring, to the solution of 0.0002 mole metal acetate in 50 cm$^3$ of DMF. A light green precipitate appeared immediately in the cases of Cu (II) or Ni (II), While with other metal ions no immediate precipitate was observed. In the cases of Co (II) Zn

(II), Mn (II) , and $UO_2$ (VI), The mixture was refluxed for Ca 8h. The reflexed solutions were diluted by an addition of excess of water and then on addition of 0.001M ammonia solution ( 5-12 $Cm^3$in different cases) Coloured precipitates of Mn (II) , Co (II) , Cd (II) and $UO_2$ (VI) complexes were obtained. The keto or thioketo compounds, having protons in a –Position to keto or thioketo group, in solution, undergoes tautomerization. In CSDBHZ there is one proton on nitrogen in a-position to the keto group, and hence a tautomerism of the type can be visualized. In solution [CSDBHZ (II)], the hydroxyl group (enolic) is attached to such carbon atom , which is in $sp^2$ hybridization mode, indicating that OH Group is acidic and it produces proton by ionization; also an acidic behavior is observed due phenol hydroxyl group therefore in solution, CSDBHZ ( II) may be expected to dissociated .

Thus CSDBHZ (II) acts as a bidentate acid. Firstly CSDBHZ (II)dissociates to give monobasic anion which further dissociated to produce binegative anion. The innovative anion thus formed, produces a binuclear dimeric Complex with a dispositive transition metal ion. Where M = Mn (II), Co (II), Ni (II), Cu (II), Zn (II), Cd(II) or $UO_2$(VI). A very high yield of CU (II) complex (97.8%) indicates its low solubility product, which incidentally, pointes out the possible analytical use of CSDBHZ for gravimetric estimation of Cu(II). For the Ni(II) complex only about 86% yield of the complex could be obtained. The complex of CO(II), Mn(II) Zn(II), Cd(II) and $UO_2$ (II) are precipited in ammonical media, which indicates high solubility product of the $M_2L_2.4H_2O$.

The elemental analysis is M:L as 1:1 Analysis also indicates the presence of two water molecules associated with a metal ion. The metal content was estimated by decomposing the complexes with concentrated nitric acid and concentrated sulphuric acid mixture, followed by chalometric determination of the ion.

In the Infra-Red spectra of metal complexes the disappearance of phenolic $\upsilon_o$--H and $\delta_{O-H}$ bands, shows that phenolic group is absent in these complexes. In phenolic hydroxyl group, metal replaces the proton indicating that phenolic oxygen function as a donar atom.The i.r. bands for $\upsilon_{c=o}$ and $\upsilon_{c\text{-}N}$ present in CSDBHZ are conspicuous by their absence in the complexes. A new i.r. absorption bands at 1570-1585 $cm^{-1}$ may be assigned to>C=N-N=C<group. An extra band appearing at 1225-1245 $cm^{-1}$in complexes may be assigned to $\upsilon_{c=o}$ (enolic) (. Hence the absence of bands for $\upsilon_{c\text{-}o}$ (enolic) and>c==N-N==C<show that the ligand is in keto form when it is in solution . Metal ions react with ligand only in enolic form in solution to form complexes. In the spectra of the complexes two types of C=N Stretching frequencies are observed. Azomethene C=N Strtching frequency at 1655 $cm^{-1}$ in the ligand undergoes a negative Schiff (100-90$cm^{-1}$) in the complexes, which shows participation of azomethene nitrogen. The $\upsilon_{c=N}$ in the ligand is replaced by $\upsilon_{c=o}$ (enolic), the new band in the spectra of the complexes, which can be expected to arise as a result of enolization of the ligand during complexation in solution. The enolic $\upsilon_{c=o}$ frequency being observed at 1650-1660 $cm^{-1}$ (in an appropriable arrange as is expected for free C=N group), shows that the enolic C=N nitrogen is not taking part in coordination.

The magnetic properties of complexes indicate magnetically condensed nature of the complexes, which is also confirmed by the appearance of new i.r. bands at 920-890 $cm^{-1}$ due to O – M – O – M group absorption. Hence, the complexes have either phenolic or enolic oxygen bridge . A shift of $\upsilon_{c=o}$ (Phenolic) band near 1545 $cm^{-1}$ to higher energy range by 20-10 $cm^{-1}$have been unambiguously used to indicate the formation of a phenolic oxygen bridge is magnetically condensed M(II) complexes. Since no such positive shift of $\upsilon_{c=o}$band around 15.40$cm^{-1}$was observed is the complexes, the absence of phenolic oxygen bride may be assumed. Alternatively the bridging arrangement i.e. the presence of enolic oxygen bridge is suggested.The band at 1040 $cm^{-1}$due to $\upsilon_{N\text{-}N}$ frequency in the ligand shift to a higher frequency in the complex. The magnitude of the positive shift (25-10cm$^{-1}$) indicates the monodentate linking of N-N residue, as a shift greater than 50cm$^{-1}$ is visualized for bidentate linking nature of N-N group. Mn(II), Co(II), Ni(II) and Cu(II) having 5,3,2 and 1 unpaired electrons respectively, in the d subshells, exhibit paramagnetic behaveiour. Where as Zn(II), Cd(II) and UO$_2$ (VI) do not have any unpaired electron and hence their complexes with CSDBHZ show no effective magnetic moment and$\mu_{eff}$ for these complexes have been observed negligible.

The thermograms of CSDBHZ complexes show water loss at higher temperatures (175-400$^0$) which is indicative of presence of water molecules in coordination sphere. The water in coordination sphere is lost at relatively higher tempertatre, while water of crystallization is lost at lower temperature. Some workers have been found that the coordination water loss may occur both at low and also at higher temperatures, which means that the temperature of water loss may not be a deciding factor for its presence in coordination sphere or as water of crystallization. Since the water in coordination sphere is more firmly help than when present as water of crystallization, This assumption is Confirmed, incidently, by i.r. bands of $\upsilon_{o-H}$, $\delta_{O-H}$ and $\gamma_{O-H}$ of water in complexes of CSDBHZ as discussed metal – CSDBHZ complexes are of variable thermal stabilities, because their decomposition temperature ranges from 205$^0$ to 400$^0$, as observed in thermal analysis.

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