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Studies of Some New Macrocyclic Metal Cr (Iii), Mn (Ii) and Fe (Ii) Complexes with Bidentate Schiff Base Ligand

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ABSTRACT

The complexes o a new hydrogen bonded macro cyclic ligand derived from metal ion catalyzed template synthesis of dinitro-orthophenylenediamine and diacetylmonoxime with Cr(III), Mn(II) and Fe(II) have been synthesized. Characterizations have been done on the basis of their elemental analyses, conductivity, magnetic moment in addition to spectral data of I.R and UV-visible. Metal to ligand ratio in all complexes has been found to be 1:1. The Schiff base behaves as neutral tetra dentate ligand utilizing all its azomethine nitrogen for coordination. Metal complexes have been assigned octahedral stereochemistry.

The metal complexes were prepared by refluxing hot ethanolic solutions of metal salts (0.01 mole) [except in case of Fe(II)] with the components of the ligand namely dinitro ortho phenylene di a mine (0.01 mole) and diacetylmonoxime (0.02 mole) for 4 hrs. on a water bath. The obtained products were filtered, washed with cyclohexanol followed by petroleum ether (60-80°c) and dried in air. For preparation of Fe(II) complexes, ethonolic solution of ferric chloride was kept in bright sunlight for six hours (10 A.M to 4 PM) when intense yellow colour of ferric chloride changed to faint green, almost colourless due to reduction of Fe(III) to Fe(II). The components of the ligand were added to it in inert atmosphere.]

KEYWORDS

- diacetylmonoxime
- tetradentate ligand
- ethanolic
- cyclohexanol
- dinitroorthophenylenediamine

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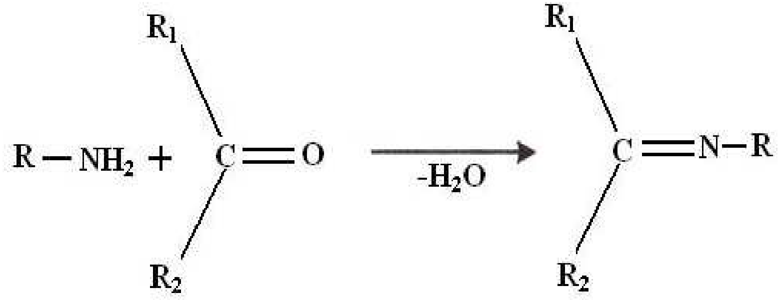
INTRODUCTION

Coordination compounds have received great attention in the field of inorganic chemistry during recent years. The renaissance is due to the important roles they play in a large number of widely differing processes of technological and biological importance. A central metal ion bonded to other atoms, ions or molecules constitutes a coordination compound. The surrounding atoms, molecules or ions are called ligands. The metal ion is usually an electron pair acceptor and ligands are electron pair donors. The nature of bonding in coordination compounds can be predominantly electrostatic or predominantly covalent or intermediate between the two extremes depending on the mode of sharing of electron pairs between the metal ion and the ligands. The number of electron pairs involved in bonding is called the coordination number which is known to have the values from 1 to 16 but 4 and 6 mostly predominate. Ligands are called monodentate, bidentate or polydentate depending on numbers of coordination sites satisfied by them about the metal ion. Ligands, capable of forming a ring structure after coordinating with the metal ion, are called chelating agents and the resulting agglomeration is termed a metal chelate. The phenomenon is called chelation. The tendency for coordination with ligands has been observed with all metal ions but transition metal ions have proved to be most versatile in this respect. On the other hand, the tendency to donate electron pairs is limited to the more electronegative elements such as, carbon, nitrogen, Phosphorus, arsenic, oxygen, sulfur, fluorine, chlorine, bromine and iodine of groups 14, 15, 16 and 17 of the periodic system. The ability of a ligand to coordinate depends mainly on the nature of atoms or groups present in it *i.e.* theirElectronegativity and stereochemistry. It also depends on 4 numbers of lone pairs present. The historical development of the chemistry of coordination compounds may be dated back to the end of the eighteenth century. Several compounds of this kind were reported in the following century. However, theories prevailing in those days were inadequate to explain the structure of the complexes and much success was not achieved. It was Werner who had the genius to correlate the experimental facts on many different systems and proposed his coordination 5 theory in 1891 introducing the concept of primary and secondary valences and suggested that the primary valences were those which satisfied the charge of the metal ion and the secondary valences were those used in attaching coordination groups. According to the theory, the hexamine cobaltic chloride is formulated as: The nature of bonding in coordination compounds has been undeniably a challenging and exciting problem since the early days of coordination chemistry. Amongst the earlier workers, G.N. Lewis was the first who laid down the foundation of electronic theory of valence recognizing that stable shells of electrons could be created by the transfer of electrons from one atom to another forming a covalent bond. The theory has been successful in explaining the nature of bonding in most of the compounds and predicting their structures but was unable to explain the bonding in electron 6 deficient compounds like boron hydrides and certain other facts such as absorption spectra. In order to remove the inadequacy of the valence bond theory.

MATERIALS AND METHOD

Coordination chemistry, widely developed in the last few decades, is highly considered in inorganic, organic and biological field. Coordination chemistry has always been a challenge to the chemists has always been a challenge to the chemists as it has more branches now-a-days



Formation of Schiff base by condensation reaction
(R group may be various substitute)
Fig-2.1

In coordination chemistry, Schiff base ligands, which can be synthesized from the condensation of primary amines with carbonyl. Compounds play an important role. Schiff base ligands regarded as “privileged ligands” received a great attention because they are able to coordinate metals through imine nitrogen and another group usually linked to aldehyde or ketone. Not only they have played a role in the development of coordination chemistry, but they can also be found at key points in the development of inorganic biochemistry. These ligands containing donor atoms like N.O.S show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities. Schiff bases and their metal complexes have wide application in food industry, dye industry, analytical chemistry, catalysis, agrochemical, and biological fields. A stable open and macrocyclic Schiff base ligands and their metal complexes have become the most well-known of all metal based drugs. More than thousands of articles have been published on the synthesis and biological activities of Schiff base metal complexes, such as chromium, manganes, cobalt, iron, calcium, lanthanum, nickel, and coper. More recently, these ligands and their metal complexes have been found to possess antiviral, antitumor, antioxidant, DNA binding and DNA cleavage, antibacterial and antifungal activities. This review highlights extensive studies on syntheses, and the antibacterial and antifungal activities of open chain and macrocyclic

Schiff-base ligands (mono and polydentate) and their metal complexes. The present review updated these results.

Physical measurement and analysis:-

Melting points were recorded on Gallen Kamp melting point apparatus and were uncorrected. FTIR spectra were recorded using FTIR-8300 Shimadzu in the range (4000-2000) cm^{-1}. Samples were measured as CsI-disc. The U.V.-visible spectra of compounds were recorded on UV-1650 PC shimdzu spectrophotometer. Magnetic susceptibility measurements were done at room temperature by Gouy method using mercury tetrathiocyanato cobalt (II) as calibrant. Metal estimations were carried out spectro photo metrically using atomic absorption Shimadzu AA670spectrophotometer.Conductivity measurements were obtained using Corning conductivity meter 220. The elemental analysis data of the ligand and complexes were obtained on a Carlo Erba Model EA 1108 (C.H.N.) elemental analyzer.

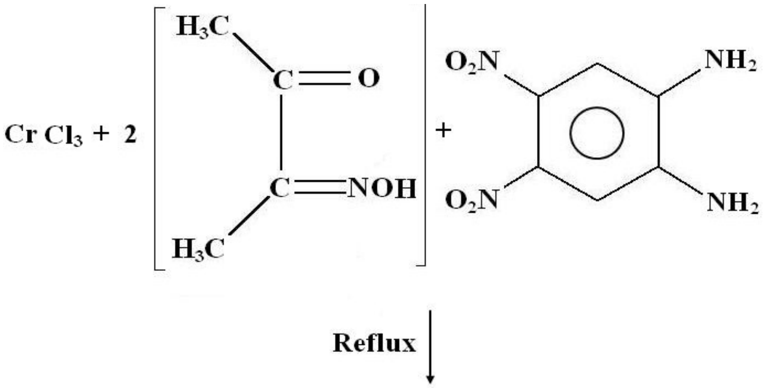
Study of complex formation in solution: -

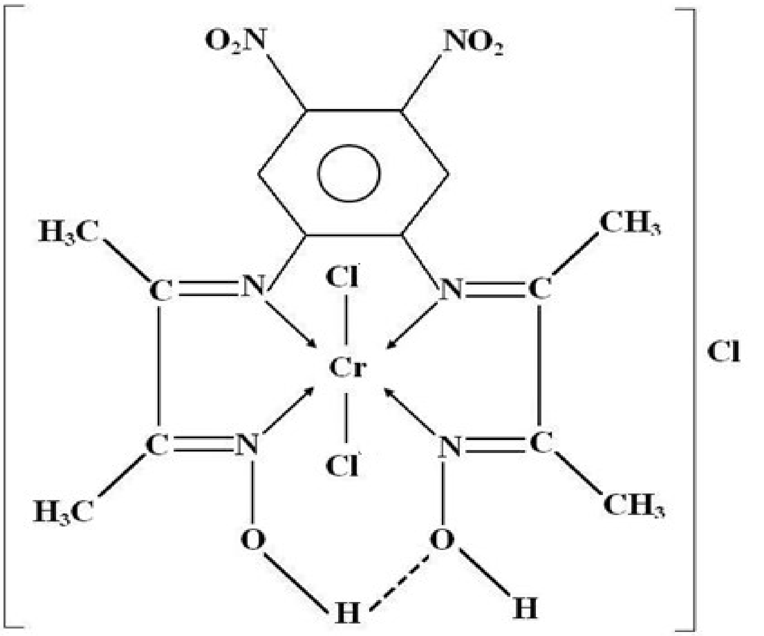
The complexes of the ligand (H_2L) with the selected metal ions [Cr (III), Mn (II) and Fe (II)], were studied in solution using ethanol as solvent, in order to determine (M: L) ratio in the prepared complexes, following molar ratio method. A series of solutions were prepared having a constant concentration (C) 10^{-3} M of the hydrate metal chlorides or vandyl sulfate $VOSO_4.5H_2O$, and the ligand (L). The [M: L] ratio was determined form the relationship between the absorption of the absorbed light and the mole ratio of [M: L].

Preparation of complexes:-

$$[Cr(H_2L)Cl_2]Cl$$

The synthetic reaction taking place during the synthesis can be shown in following manner.





RESULT

0.01mole of ethanolic solution of chromic chloride, 0.02 mole of diacetylmonoxime and 0.1 mole of dinitroorthophenylenediamine were refluxed for 4 hrs. On a water bath. A green coloured solid separated out. It was filtered, washed, dried and analysed. Analytical results were as follows,

Elements	Found%	Calculated %
Chromium	11.75	11.76
Nitrogen	18.27	18.28
Chlorine	36.56	36.57
Hydrogen	3.48	3.49

RESULT AND CONCLUSION

In general, coordination compounds are prepared by combination of ligands with metal captions. Recently under the principle of green chemistry, numbers of steps are being reduced. In this process components of ligands are allowed to combine in the presence of metal ion. The complexes of a new hydrogen bonded macro cyclic ligand derived from metal ion catalyzed template synthesis of dinitro-orthophenylenediamine and diacetylmonoxime with Cr (III), Mn (II) and Fe (II) have been synthesized. Characterizations have been done on the basis of their elemental analyses, conductivity, magnetic moment in addition to spectral data of I.R and UV- visible. Metal to ligand ratio in all complexes has been found to be 1:1. The Schiff base behaves as neutral tetradentate ligand utilizing all its azomethine nitrogen for coordination. Metal complexes have been assigned octahedral stereochemistry. The metal complexes were prepared by refluxing hot ethanolic solutions of metal salts (0.01 mole) [except in case of Fe(II)] with the components of the ligand namely dinitroorthophenylenediamine (0.01 mole) and diacetylmonoxime (0.02 mole) for 4 hrs. On a water bath. The obtained products were filtered, washed with cyclohexanol followed by petroleum ether (60-80°c) and dried in air. For preparation of Fe(II) complexes, ethonolic solution of ferric chloride was kept in bright sunlight for six hours (10 A.M to 4 PM) when intense yellow colour of ferric chloride changed to faint green, almost colorless due to reduction of Fe(III) to Fe(II). The components of the ligand were added to it in inert atmosphere.

Elemental analysis:-

The physical and analytical data of the complexes are given in Table which is in satisfactory agreement with the calculated values. The suggested molecular formals are supported by the subsequent spectral as well as magnetic moment, molar conductivity in 10^{-3} M solution of DMSO, the value of Λ_m show that Mn(II) and Fe(II) complexes are non-electrolytic in nature whereas Cr(III), complexes are 1:1 electrolyte.

Physical and analytical datas for the complexes

Complexes	Color	Yield (%)	Elemental analysis Calc. (Found)			
			M%	N%	C%	H%
[Cr (H$_2$L) Cl$_2$] Cl	Green	79	11.76(11.75)	18.28(18.27)	36.57(36.56)	3.49(3.48)
[Cr (H$_2$L) Br$_2$] Br	Green	77	9.09(9.08)	14.14(14.13)	28.28(28.27)	2.70(2.69)
[Cr (H$_2$L) (NO$_3$)$_2$] NO3	Green	72	9.82(9.81)	22.91(22.90)	30.54(30.53)	2.91(2.90)
[Cr (H$_2$L) (ClO$_4$)$_2$] ClO$_4$	Green	78	8.28(8.27)	12.87(12.86)	25.75(25.74)	2.45(2.44)
[Mn (H$_2$L) Cl$_2$]	Brown	65	12.91(12.90)	19.72(19.71)	39.44(39.43)	3.76(3.75)
[Mn (H$_2$L) Br$_2$]	Brown	60	10.68(10.67)	16.31(16.30)	32.62(32.61)	3.11(3.10)
[Mn(H$_2$L) (NO$_3$)$_2$]	Brown	62	11.48(11.47)	23.38(23.37)	35.07(35.06)	3.34(3.33)
[Mn (H$_2$L) (ClO$_4$)$_2$]	Brown	68	9.93(9.92)	15.16(15.15)	30.32(30.31)	2.89(2.88)
[Fe (H$_2$L) Cl$_2$]	Red	95	13.11(13.10)	19.67(19.66)	39.34(39.33)	3.75(3.74)
[Fe (H$_2$L) Br$_2$]	Red	90	10.85(10.84)	16.28(16.27)	32.56(32.55)	31.10(31.0
[Fe (H$_2$L) (NO$_3$)$_2$]	Red	93	11.67(11.66)	23.33(23.32)	35 (34)	3.33(3.32)
[Fe (H$_2$L) (ClO$_4$)$_2$]	Red	91	10.09(10.08)	15.14(15.13)	30.27(30.26)	2.88(2.87)

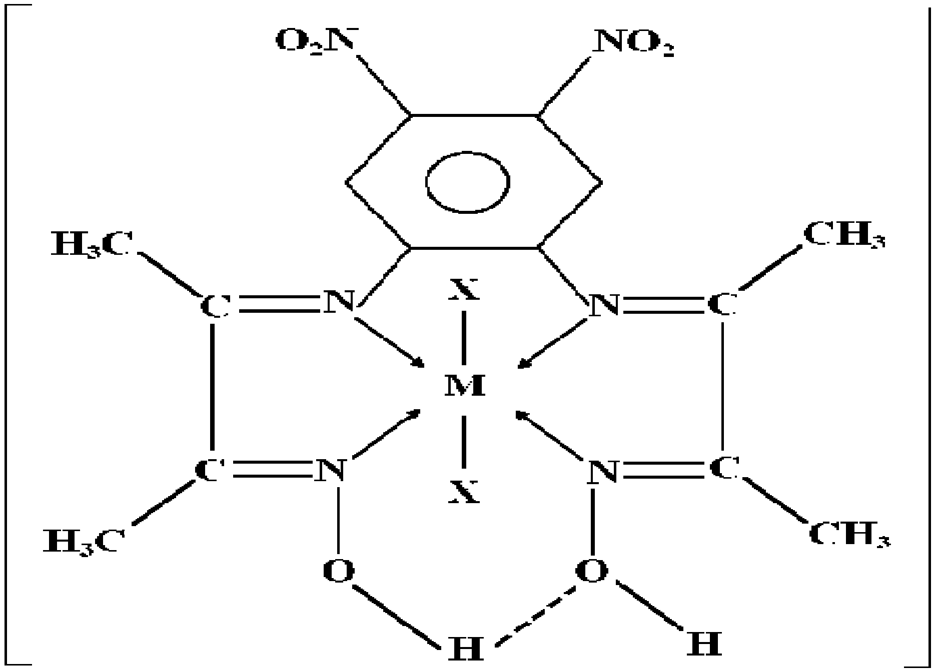
Infrared Spectra:-

Table lists the most useful infrared assignments for those bands most diagnostic of the mode of coordination of ligand. The most important band in the i.r spectra of dinitroorthophenylenediamine is due to υ_s and υ_{as} of NH_2 groups. The I.R. spectra of diacetylmonoxime exhibits $\upsilon_{C=O}$ and $\upsilon_{C=N}$. In the Spectra of the complexes υ_{NH2} of dinitro-orthophenylenediamine and $\upsilon_{C=O}$ of diacetylmonoxime is significantly absent indicating Schiff base condensation during macrocyclization. The $\upsilon_{C=N}$ oxime shows a down ward shift indicating its involvement in coordination. In the i.r. spectra of nitrato complexes two additional bands have been observed, one in the region 1035-970 cm^{-1} and other in the region 1290-1200 cm^{-1} which can be attributed to the υ_{N-O} of the NO^-_3 group. The third band which is expected to appear for the υ_{N-O} in the region 1530-1480 cm^{-1} appears to have been overlapped with the deformation vibration of $C\text{-}CH_3$ group. By comparing the spectra with known unidentate and bidenatenitrato complexes, it is concluded that the nitrate group is coordinated in aunidentate manner in the metal complexes. Same is the case with perchlorato complexes.In the far I.R region two bands one in the region 440-610 cm^{-1} and another in the region 395-415 cm^{-1} may be assigned to υ_{M-N} and υ_{M-O} respectively. In the halo complexes, a band in region 295-350 cm-1 may be attributed to υ_{M-X} (X=Cl, Br).

I.R Spectrea datas for the complexes

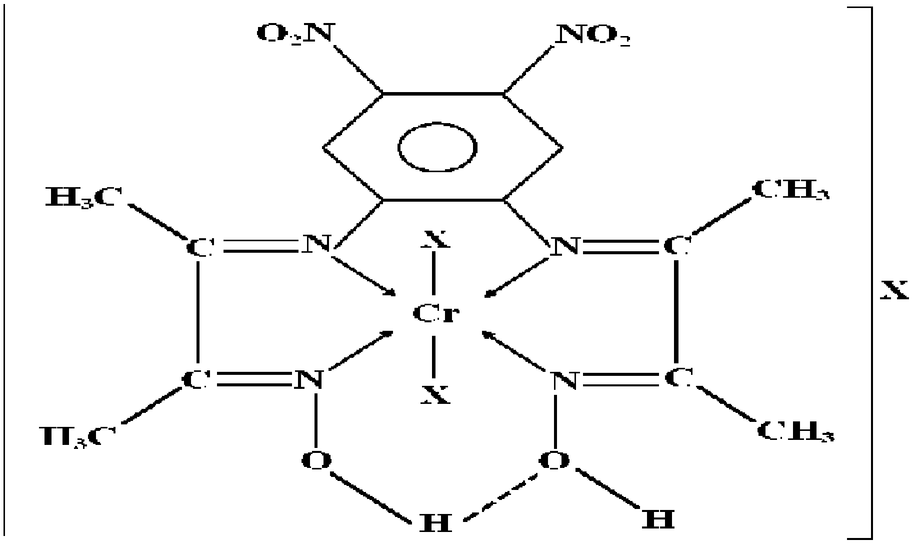
Complexes	$\upsilon_{C=N}$ (Oxime)	$\upsilon_{C=N}$ ( )	$\upsilon_{M=N}$	$\upsilon_{M=O}$
[Cr (H_2L) Cl_2] Cl	1490	1590	440	395
[Cr (H_2L) Br_2] Br	1495	1595	460	400
[Cr (H_2L) $(NO_3)_2$] NO3	1500	1600	465	405
[Cr (H_2L) $(ClO_4)_2$] ClO_4	1505	1605	470	400
[Mn (H_2L) Cl_2]	1505	1590	590	410
[Mn (H_2L) Br_2]	1500	1600	595	415
[Mn(H_2L) $(NO_3)_2$]	1495	1600	605	400
[Mn (H_2L) $(ClO_4)_2$]	1480	1605	610	395
[Fe (H_2L) Cl_2]	1490	1610	480	405
[Fe (H_2L) Br_2]	1505	1595	490	410
[Fe (H_2L) $(NO_3)_2$]	1500	1590	475	405
[Fe (H_2L) $(ClO_4)_2$]	1495	1610	490	395

On the bases of above discussion complexes can be proposed to have the following structures.



M = Mn(II), Fe(II)

X = Cl^-, Br^-, NO_3^-, ClO_4^-



X = Cl^-, Br^-, NO_3^-, ClO_4^-

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