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RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION AND ANTIFUNGAL STUDIES ON CHROMIUM(III), MANGANESE(III), IRON(III) AND COBALT(III) COMPLEXES WITH THIOHYDANTOINS.

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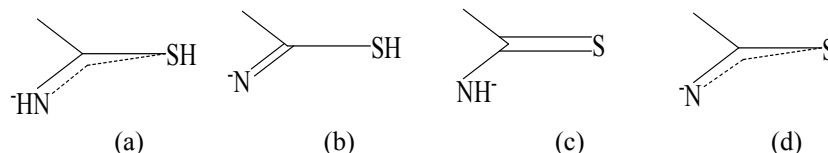
Abstract

A series of metal complexes of Cr(III), Mn(III), Fe(III) and Co(III) with 1-aryl-2-thiohydantoin having composition $[M(L)_3]$ ($M=Cr(III)$, $Mn(III)$, $Fe(III)$ and $Co(III)$); $LH=$ 1-phenyl/o-methylphenyl/o-chlorophenyl/o-bromophenyl-2-thiohydantoin) are prepared and characterized on the basis of elemental analyses, electrical conductance, magnetic moment, spectral (electronic, IR, PMR) data. The magnetic moment and electronic spectral data suggest an octahedral geometry around the central metal ion. The molar conductance of complexes is an indicative of their non-electrolytic nature. IR and PMR data indicate that the ligands act as bidentate chelating agents, coordinating through thiolsulphur and azomethine nitrogen. The antifungal activity screening against *Colletotrichum falcatum*, *Fusarium oxysporum* and *Curvularia pallescens* show that the complexes are more potent in comparison with free ligands

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Introduction:-

In, recent years, there has been considerable interest in the chemistry of transition metals with heterocyclic thione donor¹⁻²⁰. The combination of an exocyclic thione (thio keto) group and heterocyclic molecule, which may contain nitrogen, oxygen, sulphur or a combination of these, generates a group of molecules with considerable coordination potential. A common feature of all nitrogen containing heterocyclic thione is 'thione' (c) 'thiol' (b) tautomerism (I). Structural evidences, particularly from X-ray crystallographic studies indicate a tendency for the thione form to dominate.

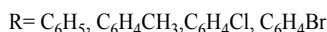
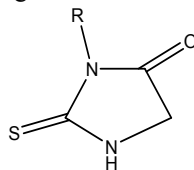


Tautomeric equilibria may be further modified in solution by changes in pH. In highly acidic media, fully protonated species (a) are likely and may appear to have all coordination sites blocked. Alternatively, because imido (NH) protons are labile species such as (a) are also potentially ambidentate with p^{ka} values varying from 5 to 11, deprotonation is possible over a wide pH range. The resultant thiolate anion (d) is capable of monodentate, bidentate or bridging coordination behaviour and of involving either or both, sulphur and nitrogen in these processes. Thus, the coordination behaviour of heterocyclic thione molecule depends upon reaction conditions, nature of metal ion and pH of the medium. Extensive use has been made of spectroscopic methods in determining the coordination character of heterocyclic thione molecules.

The stimulus for much of the research into the coordination chemistry of hetrocyclic thione donors stems from their wide ranging applications^{21,22} in analytical chemistry, in polymers and plastics, in biological systems, in metal finishing and electroplating industries etc.

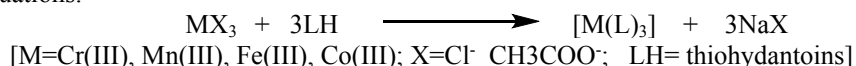
Structure of Ligands:-

The structures of various 1-aryl-2-thiohydantoin are given below-



Preparation of Complexes:-

The reactions of chromium(III) chloride, manganese(III) acetate, iron(III) chloride and cobalt(III) acetate with 1-aryl-2-thiohydantoin (LH) in 1:3 molar ratios in methanol yielded complexes of type $[\text{M}(\text{L})_3]$ according to the following equations.



All these complexes are coloured. They are thermally stable but decompose in the temperature range 120-275°C. They are quite stable in air. Conductance measurements in dimethylformamide reveal that they are essentially non-electrolytes.

Magnetic Moments:-

The chromium complexes show the magnetic moments in the range 3.80-3.90 at room temperature which is in accord with the observed spin-only value having no TIP contribution, suggesting octahedral environment around chromium ion. The complexes of manganese(III) have magnetic moments in the range 4.80-4.90 B.M. at room temperature. These values are in the range expected for spin-only value for four unpaired electrons. The iron(III) complexes show magnetic moment between 4.98-5.20 B.M. The cobalt(III) complexes ($d^6, t^4_{2g}e_g^2$) are spin paired complexes (diamagnetic).

Electronic Spectra:-

UV-vis spectra have been recorded for 1.5×10^{-3} solution of complexes $[\text{M}(\text{L})_3]$ in DMSO or CHCl_3 . The electronic spectra of chromium(III) complexes show bands at 16400-17000, 21000-22030 and 29400-30000 cm^{-1} . The positions of these bands are consistent with the six-coordinate stereochemistry. The electronic spectra of manganese(III) complexes show bands in the regions 15200-15620, 18890-19600 and 21600-22820 cm^{-1} . The values of these parameters indicate six-coordinate geometry for the complexes²⁷⁻²⁹. The electronic spectra of iron(III) complexes show three bands in the 14230-15200, 20300-21275 and 25190-25550 cm^{-1} regions. The spectra of these complexes resemble those of octahedral, high-spin iron(III) complexes containing N,S donors^{30,31}. The electronic spectra of cobalt(III) complexes show bands in the regions 15790-16600, 21450-22900 and 23630-24740 cm^{-1} . The positions of these bands indicate the octahedral geometry for these complexes.

Infrared Spectra:-

Thiohydantoin contains a thioamide group. Organic compounds having a thioamide group ($\text{HNC}=\text{S}$) give rise to four thioamide bands in the I.R. spectra. These are thioamide-I at about 1560-1550 cm^{-1} , band-II at about 1400-1300 cm^{-1} , band-III at about 1090-1080 cm^{-1} and band-IV at about 850-700 cm^{-1} . These bands have contributions from $\nu(\text{C-H}) + \delta(\text{N-H})$, $\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \delta(\text{C-H})$, $\nu(\text{C-N}) + \nu(\text{C}=\text{S})$ and $\nu(\text{C}=\text{S})$ modes of vibrations, respectively. In the present ligands, these bands appear at ca. 1500, 1400-1350, 1050 and 880-840 cm^{-1} respectively. These bands are expected to be affected differently by different modes of coordination after complexation with the metal ions^{1,18}. The appearance of these bands indicate the existence of ligands in the thione form in the solid state. In the solution (basic) infrared spectra of the ligands, all these bands were absent but one weak band at ca. 2480 cm^{-1} appears,

assignable to ν (S-H). These facts indicate the possibility of thione thiol tautomerism in the solution. In the spectra of the complexes all thioamide bands as well as (S-H) disappear, suggesting coordination of the sulphur atom to the metal ion in the thiol form. The ν (M-S) vibration appears at 400-370 cm^{-1} . The infrared spectra of 1-aryl-2-thiohydantoin ligands show bands at ca. 3300 cm^{-1} , which may be assigned to ν (N-H). In the complexes, this band disappears. In the solution I.R. spectra of ligands, one band appears at ca. 1600-1580 cm^{-1} , assignable to ν (C=N), formed as a result of thione \rightleftharpoons thiol tautomerism. In the complexes, this band shifts to lower frequency which may be taken as an evidence for the coordination of azomethine nitrogen³¹⁻³⁵. This is further confirmed by the appearance of new bands around 450-420 cm^{-1} assignable to ν (M-N). A sharp band appearing at 1720-1700 cm^{-1} , due to ν (C=O) in the spectra of ligands, appears at the same place in the spectra of the complexes, ruling out the possibility of coordination through the carbonyl group.

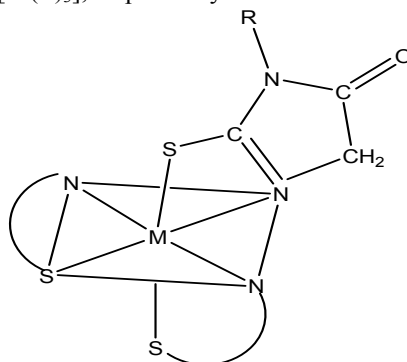
Thus, it becomes evident that the ligands act as bidentate chelating agents, coordinating through thiol sulphur and azomethine nitrogen.

Proton Magnetic Resonance Spectra:-

The proton NMR spectra of cobalt(III) complexes were recorded in deuterated chloroform and dimethylsulphoxide; the intensities of all the resonance lines were determined by planimetric integration. In general, a slight low field shift of the resonance signals of various protons (R) in these complexes, in comparison with the respective proton signals in free ligands, may be attributed to deshielding upon coordination. The spectra of 1-aryl-2-thiohydantoin show one sharp signal at δ 4.8-4.92 due to NH proton which disappears in the corresponding complexes. The signals due to aromatic ring appear in the range δ 7.25-7.48.

Structure of Complexes:-

On the basis of elemental analysis, electrical conductance measurements and spectral features, the following structures are tentatively proposed for $[M(L)_3]$, respectively.



(M= Cr(III), Mn(III), Fe(III) and Co(III))

Fungicidal Activity:-

The newly synthesized complexes of chromium(III), manganese(III), iron(III) and cobalt(III) derivatives containing thiohydantoin were screened for their fungitoxic properties against *Colletotrichum falcatum*, *Fusarium oxysporum* and *Curvularia pallescens* (all parasitic on sugarcane). Most of the complexes displayed significant fungitoxicity. The metal complexes containing thiohydantoin show promising results in inhibiting the mycelial growth of all the test fungi. In this series, the best activity was recorded with manganese(III) complex containing 1-o-chlorophenyl-2-thiohydantoin. This compound showed activity up to 78.5% against *C. falcatum*, 75.2% against *F. oxysporum* and 76.4% against *C. pallescens* at 1000 ppm concentration. Other derivatives showed inhibition from 22.9% to 75% against all test fungi at 1000 ppm concentration.

Screening data conclusions:-

1. There is significant alteration in the antifungal activity with the change in the nature of organic group attached to metal ion.
2. Metal complexes are found to be more active than their corresponding ligands. In other words, chelation increases the fungicidal activity.
3. For any particular species of fungus, manganese(III) derivatives show better activity than iron(III) derivatives which in turn show better activity than cobalt(III) derivatives. Chromium(III) complexes show least activity as compared to manganese(III), iron(III) and cobalt(III) derivatives.
4. The activity decreases on dilution.

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