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SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF TRANSITION METALS WITH OXIME AND AMINO ACID

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ABSTRACT

The mixed ligand complexes of the type $[ML_1L_2]Cl_2$.Where L_1= O-hydroxyacetophenone oxime, L_2 =anthranilic acid. These complexes have been synthesized, by the reactions of metal chlorides with two different ligands O-hydroxyacetophenone oxime and anthranilic acid in 1:1:1 molar ratios. The resulting products have been characterized on the basis of elemental analysis, magnetic measurement, IR and Electronic spectra, conductivity measurement, thermal analysis, antimicrobial activities. The metal complexes show ratio 1:1:1 with metal, ligand L1 and ligand L2 .The ligands are bonded through oxygen and nitrogen to metal ion.

KEYWORDS: Mixed ligand complexes, oxime, anthranilic acid, O-hydroxyacetophenone, thermal analysis, antimicrobial analysis.

INTRODUCTION

Complexes of transition metal ions with multidentate organic ligands have been the subject of intensive research because they not only have interesting spectral and magnetic properties, but they also possess a diverse spectrum of biological activities.[1-6] These complexes often possess remarkable and unique spectroscopic, photophysical and electrochemical properties which may be exploited in sensory and diagnostic applications and there have been a number of reviews.[7-12] on the utilisation of transition metal complexes as ion and molecular sensors. Based on the widely diverse coordination environment of the transition metal complexes, and variation in the identities of the coordinating ligands, synthesis of such complexes with desired molecular geometry can be realized. It is well known that several metal chelates have been shown to inhibit tumor growth[13] and some drugs even exhibit increased activity when administered as metal complexes.[14-16] Thus, the study of the coordination of transition metal ions with different types of ligands has been amplified by the recent developments in the field of bioinorganic chemistry and medicines.[17] The rich diversity of transition metal coordination chemistry, therefore, provides exciting prospects for the design of novel coordination ligands having unique structures and valuable functional characteristics[18-24] and significant efforts directed toward the design of specific architectures formed by the self-assembly processes have been carried out in a number of fields of synthetic chemistry.[25] In many cases, transition metal ions and their complexes play a central role in controlling the reactivity and mechanism of the chemical reactions of too interest. The unique ability of transition metal ions and their complexes to control the chemistry of environmental, industrial, and biological processes has increased the importance of clarifying their mechanistic behavior in simple and complex chemical processes. While the knowledge of coordination chemistry is essential to the understanding of the structural and functional features of various biomolecules like metalloproteins, its medical application ranges from the development of MRI contrasting agents, radiopharmaceutical chemotherapeutics to the treatment of metal toxicity.[17] Studies on the complex formation of metal ions with a number of bio molecules or biologically active ligands have, in fact, attracted a lot of interest during the last few years because they act as models for the interactions of metalloenzymes[18] and other complicated proteins[19] in the biological systems.

Furthermore, development in the field of bioinorganic chemistry has also led to an increased interest in complexes of N, O-donor ligands since it has been recognized that many of these complexes may serve as models for biologically important species having N and O as bonding sites.[25]

Objectives and scope of the present work

There has been considerable interest in the studies of mixed ligand complexes due to their coordination modes when bound to metals .The wide applications and structural diversity of metal complexes of Oxime and anthranilic acid encouraged us to synthesize the tridentate ONO-donor oxime and their metal complexes. Metal complexes of O-hydroxy acetophenone oxime and anthranilic acid as ligands with transition metal as (ML_2) complexes have been already reported in early days.

Due to good chelating ability, the present work is mainly concerned on the studies of these two novel O-hydroxy acetophenone oxime [L_1] and anthranilic acid,[L_2] as a ligand. We have synthesized 3d transition metal complexes of Mn (II), Co(II) and Ni(II) with O-hydroxy acetophenone oxime [L_1] and anthranilic acid,[L_2] in the ratio 1:1:1. The compositions of these ligands were determined by the CHN and S analyses. For the characterization of these compounds we have used IR and UV spectral studies.

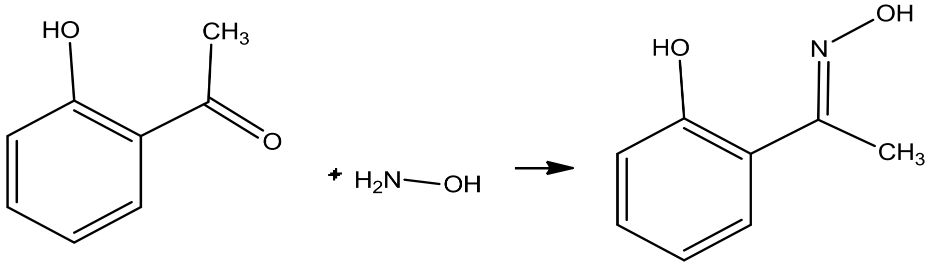
EXPERIMENTAL TECHNIQUE

The compounds O-hydroxyacetophenone and anthranilic acid and all metal chlorides used were of E MEARK, BDH analytical grade. The amount of metal is determined. Complex metrically by EDTA suitable indicator metal ions. Carbon, hydrogen and nitrogen analysis were carried from SAIF, Mumbai. Specific conductance were measured at room temperature in DMF by a Systronics direct reading 304 conductivity meter using a glass conductivity cell having a cell constant.IR spectra were taken on JASCO 6600 FTIR SPECTROPHOTOMETER and JASCO - 670 -UV SPECTROPHOTOMETER and thermo gravimetric analysis were performed on STA 6000 from from Central Research Laboratory, Pratap College, Amalner. Microbial activities were carried out from PG Department of Microbiology, Pratap College, Amalner.

Synthesis of Ligand: Ligands L_1 and L_2 were prepared. The methods of their preparation are given below.

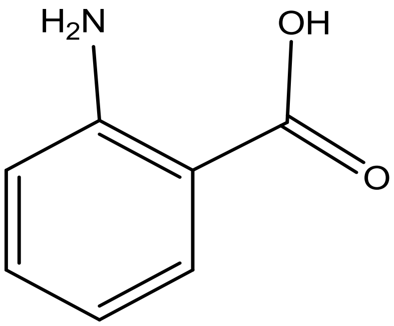
Ligand: L_1(Orthohydroxy acetophenone Oxime)

One mmole of ortho hydroxy acetophenone and one mmole of hydroxyl amine hydrochloride are dissolved in 25 ml ethyl alcohol. The resulting mixture is acidified with 3-4 drops of glacial acetic acid and refluxed for two hours in water bath. On cooling white product separates out from solution. The product obtained was filtered, wash with cold water, dried and recrystallized from aqueous ethanol.



Ligand: L_2(Anthranilic Acid)

This compound is easily available in the market. Analytical reagent compound is purchase directly from market.



Physical properties of ligands

Name of the ligand	**Nature**	**Method of purification**	**M.P C**
O-hydroxy acetophenone oxime	White shining crystals	Recrystallized from aq.ethanol	114(115)
Anthranilic acid	Faint yellow crystals	Recrystallized from aq.ethanol	147(147)

Synthesis Of complexes

1) Preparation of M $(L_1)_2$ and $M(L_2)_2$ complexes

Aquous25ml(0.01M) solution of metal chloride were mixed slowly with hot 25ml(0.02M) methanolic solution of O-hydroxy acetophenone oxime (L_1)with constant stirring. The reaction mixture is heated in water bath for two hour. Then the reaction mixture was stirred for further one hour after which colored Solid product was obtained, which was then washed with ethanol and dried in air.

Similarly, the complexes anthranilic acid was prepared by mixing of metal were prepared by mixing solution 25ml(0.01M) methanolic solution with hot 25ml(0.02M) methanolic solution anthranilic acid Then the reaction mixture was stirred for further one hour after which colored Solid product was obtained, which was then washed with ethanol and dried in air.

2) Preparation of M (L_1L_2) complexes

To a 20ml (0.01M) methanolic solution metal chloride, a mixture of 20ml (0.01M) methanolic solution of of O-hydroxy acetophenone oxime and 20ml (0.01M) methanolic solution of anthranilic acid were added slowly with constant stirring .This reaction mixture is refluxed in water bath for 3 to 4 hours on a heating mental at about 60-70^{0}C. The colored complex separates out from solution on cooling filter. Then product was filtered, wash with methanol dry and record the yield of the complex.

RESULT AND DISCUSSION

The reactions of metal chlorides with O-hydroxy acetophenone oxime and anthranilic acid in the 1:1:1 molar ratio results in the formation mixed ligand complexes. The resulting complexes were having different colors as given in the table II. They are insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF. The properties of indicated in table III. The conductance of the complexes are very low (10-100Ω^{-1}cm^{2}mol^{-1}) indicating their non-electrolyte nature.

The TLC of the mixed ligand complexes exhibit single spots with R_f values being intermediate of the two corresponding symmetrical bis-complexes indicating that these are mixed ligand complexes rather than a mixture of two corresponding bis-complexes. From the magnetic moments these complexes shows octahedral geometry.

In the IR spectra of the mixed ligand complexes the bands at 1544-1564cm^{-1}may be assigned to the symmetric and asymmetric v(C=N) vibrations. A strong band in the region 1604-1738cm^{-1} are due to v(C=O) groups. On complex formation, the position of these bands is shifted toward lower side as compared to the metal free ligand. This indicates that the coordination takes place through the nitrogen and oxygen atom of the(C=N) and (C=O) groups. A band in the region 2356-2362cm^{-1} shows presence of carboxylic group and –OH group taking in the bond formation shifting the bands towards lower side. A broad band appears in the region at 3200-3750cm^{-1} for complexes is attributed to the coordinated water molecule, supporting the octahedral nature of complexes.

The electronic ground state of Mn (II) is $^6A_{1g}$, all the transitions are spin-forbidden. The reflectance spectrum of Mn(II) complex shows four bands in the normally expected regions for octahedral stereochemistry. The three bands observed 8756, 16722 and 26315cm^{-1} shows $^6A_{1g}\rightarrow{}^4T_{1g}$ (^{4}G), $^6A_{1g}\rightarrow{}^4T_{2g}$ (^{4}G) and $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ (^{4}G) transitions respectively.

The reflectance spectrum of Co(II) complex is characteristic of Co(II) in octahedral environment, exhibiting three bands at 10460, 18125 and 28089cm^{-1} assigned for $^2B_1g\rightarrow{}^2A_1g$, $^2B_1g\rightarrow{}^2B_2g$ and $^2B_1g\rightarrow{}^2E_2g$,(Charge transfer) transitions respectively. Further support for the octahedral geometry is provided by the ratio v_2/v_1 which is 1.73 close to 2.0 as required for octahedral stereochemistry.

The reflectance spectrum of Ni(II) complex is characteristic of Ni(II) in octahedral environment, exhibiting three bands at 10417, 19207 and 24603cm^{-1} assigned for $^3A_2g(F) \rightarrow {}^3T_2g(F)$, $^3A_2g(F) \rightarrow {}^3T_1g(F)$ and $^3A_2g(F) \rightarrow {}^3T_1g(P)$ transitions.NI(II) complexes with regular octahedral structure, the ratio v_2/v_1 is expected to be in the range 1.5-1.7. The ratio is 1.55., which is the expected range.

The magnetic moments, μ_{eff} of the complexes

3d^5 Mn (II) ion has the $^6A_{1g}$ ground term, for which there is no reduction of the moment below the spin-only value of 5.92 B.M. It is also independent of the stereochemistry around it. The observed magnetic moment (4.680B.M.) of Mn(II) complex is less than that generally observed for spin-free d^5 system. Such lower magnetic moments of Mn(II) complexes have been explained with the assumption of ant ferromagnetic interaction between manganese ion in the solids.

The Co(II) complex exhibits a magnetic moment of 3.519 B.M. Electronic spectrum indicate distorted octahedral stereochemistry. Similar contradictory observations have been reported many authors.

For six coordinate Ni(II) complexes in a regular octahedral geometry consideration of spin-orbit coupling and contributions from $^3A_{2g}$ and next higher $^3T_{2g}$ state predicts the maximum value somewhat above the spin- only moment of 4.61 B.M. The magnetic moment of the complex is 3.41B.M. suggesting octahedral structure for this complex. Magnetic measurements therefore support the deductions made from spectral studies.

In Thermo gravimetric analysis the thermo grams (TG) of the complexes have been recorded in flowing nitrogen atmosphere at the heating rate of 10°C/min on approximately 10 mg samples. Thermo gravimetric analysis shows presence of two water molecules in the complexes supports the octahedral nature of complexes.

Biological Activities: The compound synthesized in the present investigation has been subjected to various antimicrobial screening programs based on their structural features so as to ascertain their activity against different microorganisms. The solvent used was DMSO.

The results of preliminary study on antimicrobial activity indicated that most of the compounds were highly and few were moderate active against these organisms.

Tables of Analytical Results

I. Characterization data of the complexes

Ligand/ Complex	Colour	Mole. wt	%YieldOf thecomp.	%of metal (Calculated)	% of C	% Of H	% Of N	% of O
Mn(ANT)$_1$ (ORTHOX)$_1$(H$_2$O)$_2$	Purple	378.93	72.31	12.41(12.72)	53.85	5.27	7.38	16.88
Co(ANT) $_1$(ORTHOX)$_1$ (H$_2$O)$_2$	Brown	382.93	69.53	13.27(13.52)	53.27	5.22	7.31	16.71
Ni(ANT)$_1$ (ORTHOX)$_1$(H$_2$O)$_2$	Green	382.69	74.28	12.99(13.46)	53.30	5.22	7.31	16.72

II. IR Spectral Analysis

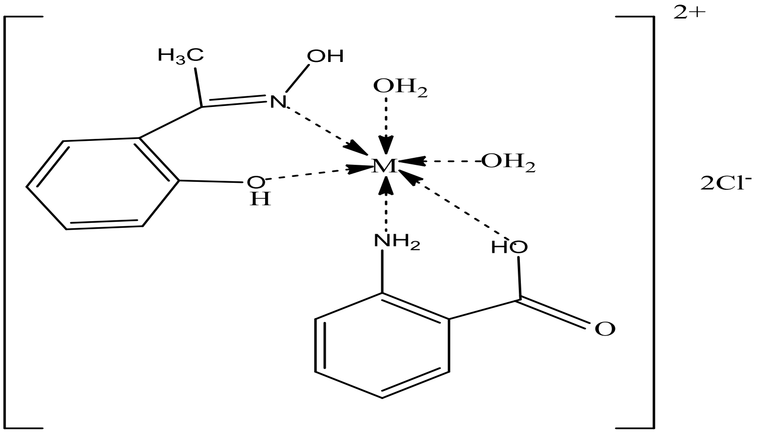
Ligand/ Complex	V-OH forH$_2$O	VN-H	VNH$_2$	VC=O	VC=N	VC-H	VM-N
ANT		3449	3263	1707	1678	1285	
ORTHOX		3440	3187	1699	1611	1268	
Mn(ANT)$_1$(ORTHOX)$_1$(H$_2$O)$_2$	3564	3432	3116	1621	1566	1269	573
Co(ANT)$_1$(ORTHOX)$_1$(H$_2$O)$_2$	3651	3428	3170	1652	1566	12770	571
Ni(ANT)$_1$(ORTHOX)$_1$(H$_2$O)$_2$	3550	3431	3174	1652	1620	1271	573

III. Conductivity and Magnetic Susceptibility Measurement

Name of complex	Molar conductivity	Magneticsusceptibility(μeff.inB.M.)
Mn(ANT)$_1$(ORTHOX)$_1$(H$_2$O)$_2$	66.62	4.680
Co(ANT)$_1$(ORTHOX)$_1$(H$_2$O)$_2$	99.93	3.519
Ni(ANT)$_1$(ORTHOX)$_1$(H$_2$O)$_2$	41.64	3.411

IV Microbioligical activities

Sr.No.	Ligand/Complex	E-coli.	Bacilli	Staphylococcus
1	ANT	10	12	13
2	ORTHOX	10	08	09
3	Mn(ANT)$_1$(ORTHOX)$_1$(H2O)$_2$	13	16	-
4	Co(ANT)$_1$(ORTHOX)$_1$(H2O)$_2$	-	-	16
5	Ni(ANT)$_1$(ORTHOX)$_1$(H2O)$_2$	14	20	



CONCLUSION

The structure of Mn(II), Co(II) and Ni(II) complexes are octahedral. The possible structure of the complexes are given in the following figures.

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