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SYNTHESIS AND CHARACTERISATION OF SOME MIXED LIGANDS ADDUCTS OF BENZOYLACETONE AND SALICYLALDEHYDE

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ABSTRACT
A series of four mixed ligand complexes were synthesized by reacting benzoylacetone and salicylaldehyde with different metal chlorides in ethanolic medium. The complexes have been characterized by molar conductance measurements and spectral techniques such as IR and Uv-visible electronic spectra. Decomposition temperature was also determined. The results indicated that the compounds have bands at 400-500cm^{-1}, with very sharp melting points. This proved the formation of metal-oxygen bond, purity and high thermal stability of the compounds that could lead to a high antimicrobial activity.
Keywords: Adduct Synthesis, Ligands, and Complexes

INTRODUCTION

The chemistry of mixed ligand complexes has received interest in recent decades due to the wide applications of coordination compounds in various fields. Mixed ligand complexes appeared to be relevant in biological fluids, create specific structures and manifest themselves as enzyme-metal ion-substrate complexes (Reddy *et al* 2005).

N-Anilinoacetohydrazobenzoylacetone (H_2L) and their manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes have been synthesized and characterized by IR, electronic spectra, molar conductivities, thermal analyses and magnetic susceptibilities. Binuclear complexes with molar ratios of (M:L) = 2:1 are formed. The IR spectra of these compounds showed that the ligand (H_2L) coordinates to the metal ions in a tetradentate manner with O_2N_2 as donor sites in Mn(II), Co(II), Ni(II) and Zn(II) complexes while in the Cu(II) complexes the ligand coordinated as bidentate via N and O donor atoms. The copper(II) complexes, also, shows higher antibacterial activity towards gram positive (G+) bacteria *Bacillus subtilis* than the ligand and other complexes while Mn(II) complex shows higher antifungal activity than the free ligand (Kashar, 2014).

Aliyu and Mustapha (2009) reported the synthesis of some oxovanadium (IV) complexes of acetylacetone, dibenzoylmethane, 2-thionyltrifluoroacetone, Triflouroacetylacetone and benzoylacetone. The complexes were characterized by elemental analysis, molar conductance, decomposition temperature, solubility and infrared spectral studies with 1:2 M:L ratio.

Dinuclear complexes from salicylaldehyde and 2-aminophenol with Cu(II), Ni(II) and Co(II) and Fe(III) were synthesized and characterized by IR, UV-visible and elemental analysis. The mass spectral data obtained was in good agreement with the result obtained from the thermogravimetric analysis (TGA) in accordance with its fragmentation pattern (Bhatt, 2008). The magnetic properties of these complexes were studied and the probable mechanism for the formation of the complexes was proposed.

MATERIALS AND METHODS

Materials: Benzoylacetone (Aldrich), Salicylaldehyde (Aldrich), Manganese (II) Chloride, Iron (III)Chloride (lobachem), Nickel (II) chloride, copper(II) chloride, ethanol (Glanson chemicals ltd), chloroform (cartvalues ltd), solvents were AnalaR and were used as supplied.

Analytical methods and Physical measurements:
The compounds were analyzed for IR using CARY 630 FT-IR, thermo Nicolet instrument in the range of 400-4000. The UV spectral measurements was carried out using T60 spectrophotometer The solubility of each metal complex was tasted using various non-polar solvents like hexane and distilled water. While the polar solvents includes chloroform, acetic acid, acetone etc. Molar conductances were measured at room temperature in DMSO using digital conductivity meter-T60. The melting points of the complexes were also carried out using Barnstead electronic thermal -IA9110.

Synthesis of Copper (II) complex with mixed ligand

To an ethanolic solution (10 ml) of $CuCl_2.2H_2O$ (5.24 mmol, 0.893g), an ethanolic solutions (10 ml) of benzoylacetone (5.24 mmol, 0.85g) and salicyaldehyde (5.24 mmol, 0.64g) were added with constant stirring. The reaction mixture was stirred for about 40 minutes. The precipitate formed was filtered, washed with ethanol and dried under reduced pressure. (Agrawal, *et-al* 2003)

Synthesis of Manganese (II) complex with mixed ligand

To an ethanolic solution (10 ml) of $MnCl_2.4H_2O$ (5.24 mmol, 1.03g), an ethanolic solution (10 ml) of benzoylacetone (5.24 mmol, 0.85g) and salicyaldehyde (5.24 mmol, 0.64g) were added with constant stirring. The reaction mixture was stirred for about 40 minutes. No precipitate was obtained. Then, few drops of Triethylamine solution (4 ml) was added drop wise to the above reaction mixture to raise the pH to 6.0. The solution was stirred and refluxed for 3-4 hrs and the reaction mixture was kept at room temperature. The solution, was filtered, washed with ethanol and dried properly under reduced pressure. (Agrawal, *et-al* 2003)

Synthesis of Nickel (II) complex with mixed ligand

To an ethanolic solution (10 ml) of $NiCl_2$ (5.24 mmol, 0.68g), an ethanolic solution (10 ml) of benzoylacetone (5.24 mmol, 0.85g) and salicyaldehyde (5.24 mmol, 0.64g) were added with constant stirring. The reaction mixture was stirred for about 40 minutes. No precipitate was obtained. Then, few drops of Triethylamine solution (4 ml) was added drop wise to the above reaction mixture to raise the pH to 6.0. The solution was stirred and refluxed for 3-4 hrs and the reaction mixture was kept on room temperature. The precipitate was settled down. The solution, was filtered, washed with ethanol and dried properly under reduced pressure. (Agrawal, *et-al* 2003)

Synthesis of Iron (III) complex with mixed ligand

To an ethanolic solution (10 ml) of $FeCl_3.6H_2O$ (5.24 mmol, 0.85g), an ethanolic solution (10 ml) of benzoylacetone (5.24 mmol, 0.85g) and salicyaldehyde (5.24 mmol, 0.64g) were added with constant stirring. The reaction mixture was stirred for about 40 minutes. No precipitate was obtained. Then, few drops of Triethylamine solution (4 ml) was added drop wise to the above reaction mixture to raise the pH to 6.0. The solution was stirred and refluxed for 3-4 hrs and the reaction mixture was kept on room temperature. The resulting solution, was filtered, washed wit ethanol and dried properly under reduced pressure (Agrawal *et al.,* 2003).

RESULTS AND DISCUSSION

Table 1 provides some of the physical parameters that serves as supporting evidence for the proposed complexes.

Mixed ligand complexes of Cu (II), Fe (III), Mn (II), and Ni (II) have been prepared by the reaction of manganese (II) chloride tetrahydrate , ferric (III) chloride hexahydrate, nickel(II) chloride, zinc(II) chloride with the ligands Salicylaldehyde and Benzoylacetone in 1:1:1 ratio. The resulting synthesized complexes were coloured solids and have a relatively high decomposition point.

The complexes of copper (II), Iron (III), Manganese (II) and Nickel (II) gave decomposition temperatures of 235^{o}C, 220^{o}C, 239^{o}C and 239^{o}C respectively. These high decomposition temperatures revealed that the complexes are thermally stable. However, the complexes appeared to have dark brown, reddish, light orange and pale green colours respectively.

The complexes showed variable solubilities in different solvents with very few showing slight solubility in the same solvent used. However, all the complexes were soluble in DMSO (Table 2) being it a polar aprotic solvent, it has the ability to dissolve a wide range of solutes and also has a high di-electric constant.

Being DMSO the only solvent that can dissolve the compounds, it was used to measure the molar conductivities of the compounds at 10^{-3} M solutions (Table 4). The results of conductivity measurements showed that the Mn(II), Fe(III), Ni(II) and Cu(II) complexes, have values in the range 49–90.6 Ω^{-1} mol^{-1} cm^2. This indicates that they are non-electrolytes, the slight increase in the conductance values observed, may be due to some solvolysis or dissociation (El-Qisairi *et al*., 2007). Moreover, it is reported that, in a complex, the positive charge of the metal is partially shared with the donor atoms present in the ligand, and there may be π-electron delocalization over the whole complex (Sanap *et al.,* 2013).

The UV-visible spectra of the mixed ligand complexes were also recorded in DMSO in the region 300 to 600nm. All the complexes showed peaks in the UV region with wavelengths in the range 300-400nm this may be assigned to the π-π* transition of the chromophores, while bands above 400nm may be assigned to charge transfer transition (Table 4). The above Uv-visible results of the complexes conformed to the literature report by (Mustapha *et al*., 2014).

In addition, the IR spectra of all the complexes have been studied and assignments were given to the manifested bands regions. The complexes of Fe(III), Mn(II) and Cu(II) showed absorption at the bands regions of 2080cm^{-1} , 2143cm^{-1} and 2119cm^{-1} respectively, this can presumably be attributed to the aromatic ν(C-H) stretching (Malathy, 2004). The strong intensity bands that appeared at 1624cm^{-1} for Mn(II), 1617cm^{-1} for Fe(III), 1624cm^{-1} for Ni(II) and Cu(II) $cm^{-1}$are assigned to ν(C=O) stretching vibration (Halli *et al*., 2012). A band in the region 1419-1522cm^{-1} can be ascribed to ν(C=C) bond. This can be presumed that the anionic ligand is coordinated to metal in the tautomeric form (Ahmadzadeh *et al*., 2014) as shown in Table 3 Bands for ν(M-O) were observed in the spectra of Cu(II) complex at 419cm^{-1} , Fe(III) at 472cm^{-1} region, Ni(II) complex at 419cm^{-1} and Mn(II) at 419cm^{-1}. This complied with the reported literature (Dnyaneshwar *et al*., 2014). Therefore, from the IR spectra it is concluded that the ligands behaved as monobasic or neutral ligands coordinated to the metal ion via carbonyl oxygen of benzoylacetone and enolic oxygen of the salicylaldehyde as shown in the diagram below.

Table 1: Physical measurements

S/N	Compound	Empirical Formula	Mwt.	M.P (^{O}C)	Cond. Λ, Ω-1 mol-1 cm^{2}	%C found	%H found	%Cl found	%O found	% M. found	Color
1	Mn(II) complex	$[MnC_{17}H_{15}ClO_4]$	373.00	239	52.9	54.64	4.05	9.49	17.13	14.74	Light Orange
2	Fe(III) Complex	$[FeC_{22}H_{15}Cl_3O_5]$	408.97	220	90.6	49.79	3.69	17.29	15.61	13.62	Reddish Brown
3	Ni(II) complex	$[NiC_{17}H_{15}ClO_4]$	377.44	239	51.2	54.10	4.01	9.39	16.96	15.55	Pale green
4	Cu(II) complex	$[CuC_{17}H_{15}ClO_4]$	382.30	235	49.6	53.42	3.95	9.27	16.74	16.62	Dark brown

Key; Mwt**:** Molecular weight, Cond: Conductivity

Table 2: Solubility of the complexes.

Solvents	Cu(II) complex	Fe(III) complex	Mn (II)complex	Ni (II)complex
Distilled water	S	IS	S	SS
Ethanol	IS	SS	S	S
Methanol	S	SS	S	S
Acetone	S	S	S	SS
Chloroform	S	SS	S	SS
N-hexane	S	SS	S	S
Dimethylsulfoxide	S	S	S	S

S= Soluble, SS= slightly soluble, IS=Insoluble

Table 3: Infrared spectra data of the complexes

Compounds	ν(C=O)cm^{-1}	ν(C=C)cm^{-1}	ν(C-H)cm^{-1}	ν (M-O)cm^{-1}
$[MnL_1]$ ($C_{17}H_{15}ClO_4$)	$1624_{(s)}$	$1419_{(s)}$	$2143_{(m)}$	$419_{(w)}$
$[FeL_2]$ ($C_{22}H_{15}Cl_3O_5$)	$1617_{(s)}$	$1522_{(s)}$	$2080_{(m)}$	$472_{(w)}$
$[NiL_3]$ ($C_{17}H_{15}ClO_4$)	$1624_{(s)}$	$1457_{(W)}$	-	$419_{(w)}$
$[CuL_4]$ ($C_{17}H_{15}ClO_4$)	$1624_{(s)}$	$1510_{(m)}$	$2119_{(b)}$	$456_{(m)}$

Key; S=strong, m=medium, b=broad

Table 4: Uv-visible spectral data of the complexes

S/N	Wave length (nm)	Cu(II) complex Absorbance	Fe(III) complex Absorbance	Mn(II) complex Absorbance	Ni(II) complex Absorbance
1	300	0.255	0.235	0.442	0.222
2	320	0.232	0.212	0.345	0.232
3	340	0.212	0.215	0.331	0.205
4	360	0.225	0.477	0.206	0.324
5	380	0.354	0.244	0.285	0.424
6	400	0.476	0.213	0.124	0.357
7	420	0.205	0.173	0.164	0.259
8	440	0.234	0.127	0.163	0.171
9	460	0.324	0.124	0.122	0.288
10	480	0.166	0.164	0.145	0.211
11	500	0.134	0.163	0.155	0.123
12	520	0.114	0.146	0.255	0.135
13	540	0.222	0.155	0.145	0.112
14	560	0.184	0.224	0.112	0.132
15	580	0.127	0.174	0.178	0.112
16	600	0.139	0.167	0.224	0.121

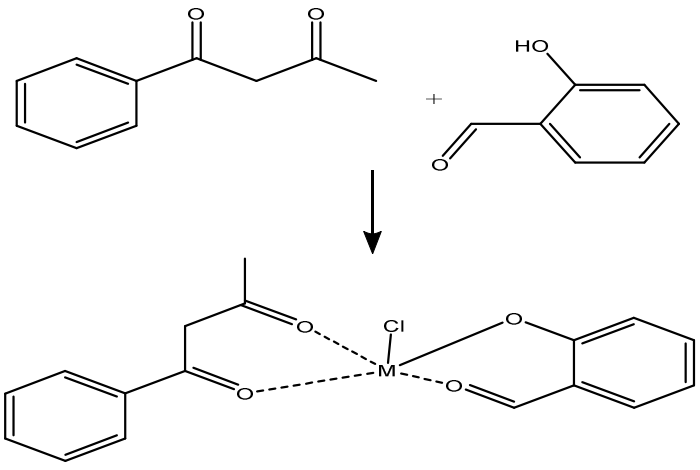

Figure 1: proposed structure of the complexes where 'M' represents the divalent transition metals (Cu, Mn, and Ni)

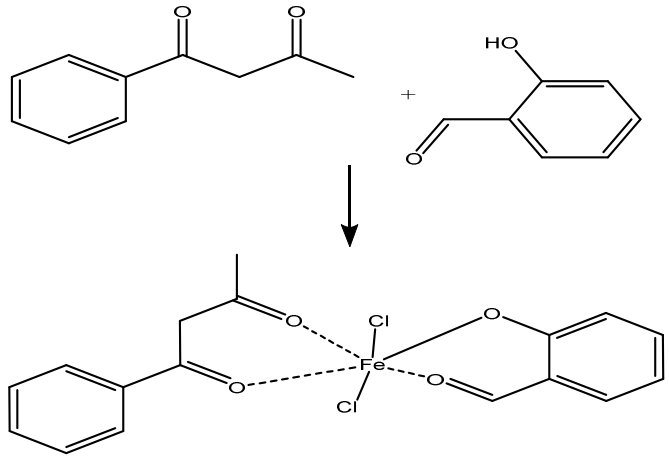

Figure 2: proposed structure of the complex with Fe (III) as the central metal

CONCLUSION

This paper has reported a series of four mixed ligand complexes synthesized by the reaction of benzoylacetone and salicylaldehyde with suitable metal chlorides in ethanolic medium. The synthesized complexes have been characterized by molar conductance measurements, thermal stabilities and spectral techniques such as IR and Uv-vis electronic spectra. On this basis and the literature obtained, it can be suggested that, three (3) five coordinated trigonal bipyramidal complexes and one (1) six coordinated octahedral complexes were formed. The complexes showed high thermal stability.

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