

Synthesis, spectral and antimicrobial studies of mixed ligand complexes with transition metal ions [Mn (II), Cu (II), Co (II) and Ni (II)]

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ABSTRACT

The synthesis of metal complexes of mixed ligand nitrosalicylaldehyde & b- diketones with transition metal ions such as Mn(II), Cu(II), Co(II) and Ni(II). The complexes have been characterized by elemental analysis, molar conductance, TLC, IR. The molecular formula of mixed ligand complexes corresponds to $[ML_1L_2(NO_3)_2]$ where M = [Mn(II), Cu(II), Co(II) and Ni(II)], L_1 = 2- Hydroxy-5-nitrobenzaldehyde & L_2 = b- Diketones. All the mixed ligand complexes have been screened for their antimicrobial activity against fungi viz. *A. niger*, *A. flavous*, *P. triticena*, *F. species* and bacteria viz. *E. coli*, *B. subtilis*, *S. typhi*, *S. aureus*. The results of antimicrobial activity show that mixed ligand complex of Cu (II) have more potency towards experimental fungi and bacteria. It also shows that mixed ligand complex of Cu (II) is more toxic against bacteria *S. aureus*. The complexes were found to be nonelectrolyte in nature on the basis of low value molar conductance.

Key words: Antimicrobial activities, mixed ligand complexes, transition metal ions.

INTRODUCTION

In recent years there has been a growing interest in the synthesis of coordination compounds starting directly from metals¹⁻⁶. Mixed ligand complexes play an important role in biological processes, as exemplified by many instances in which enzymes are known to be activated by metal ions⁵⁻⁶. Such complexes have been implicated in the storage & transport of active substances through membrane⁹. Many mixed ligand complexes are finding applications in the microelectronic industry, chemical vapour deposition of metals and as drugs^{8,9}. ESR studies of some Cu (II) b- diketone chelate complexes in heterocyclic basic solvent by H. Yokoi *et al.*,¹⁰. The synthesis and characterization of vinyl substituted b- diketones for polymerizable metal complexes by Glen E. Southard *et al.*¹¹. Synthesis, crystal and molecular structure of 5-bromosalicylaldehyde-2- methylthiosemicarbazonato Cu (II) monohydrate by Douglas *et al.*,¹². A few

complexes of Co (II) with 14- and 16-membered tetraazamacrocycles derived from b-diketones have been synthesized. Fenton *et al.*¹⁵⁻¹⁶ prepared complexes of the type ML_2L' by the reactions of acetylacetonates and fluorinated acetylacetonates with various ligands. Crystal and molecular structures of $M(dpm)_2(phen)_2$ type complexes of Ca(II), Sr(II) and Ba(II) have been reported recently by Sobotera *et al.*¹⁵ However, such mixed ligand complexes with substituted salicylaldehydes have not been studied so far. In the present paper mixed ligand complexes, $[ML_1L_2(NO_3)_2]$ where M = [Mn(II), Cu(II), Co(II) and Ni(II)], L_1 = 2- Hydroxy-5-nitrobenzaldehyde and L_2 = b- Diketones, pentane-2,4-dione, 1-phenylbutane-1,3-dione or 1,3-diphenylpropane-1,3-dione] are reported.

EXPERIMENTAL

All the chemicals used were of A.R grade. Pentane-2,4-dione (IDPL, India) was purified by

distillation and 1-phenylbutane-1,3-dione (Fluka), 1,3-diphenylpropane-1,3-dione (S. Ds, India) and 5-nitrosalicylaldehyde (Aldrich) were purified by recrystallization from ethanol. The complexes were prepared by mixing the molar solutions of respective metal nitrates and ligands with molar ratio 1: 1: 1 at pH 6 to 7. The product were crystallized from ethanol and their purity checked by TLC. The metal nitrates were dissolved in double distilled water and standardized ¹⁶. The stiochiometric ratio was confirmed by Fengers method ¹⁷. The molar conductivities in DMF (10^{-3} M) at room temperature were measured using an Equiptronics digital conductivity meter.

Synthesis of Mixed Ligand Complexes of Mn(II), Cu(II), Co(II) and Ni(II)

Metal complexes were prepared by the mixing of equimolar solutions of ligands 5-nitrosalicylaldehyde and b- diketones and metal nitrate solutions. A clear solution was obtained and the temperature was maintained at 50-60°C. The stoichiometry of the complexes of the both ligands (0.025 M) with Mn (II), Cu(II), Ni(II) and Co (II) (0.025 M) metal ions was found by carrying out potentiometric titration against standard (0.1 M) NaOH solution in ethanol – water mixture. The pH of the reaction mixture was adjusted between 6.5 to 7.5. The 1:1 stiochiometric ratio was confirmed by Fengers mass estimation method¹⁷. The coloured precipitates were filtered washed several times with hot water folled by ethanol to free it form the soluble impurities. The resulting coloured solids were dried in an oven at 100°C of Stored in a desiccators over anhydrous CaCl₂. The complexes were purified by recrystallization & TLC in silica Gel – G.

Biological Experimental

The biological experiments for determining antimicrobial activity of mixed ligand metal complexes have been done by serial dilution method²⁰. In this technique the solutions of different concentrations (viz. 250 ppm, 500 ppm, 750 ppm and 1000 ppm) were prepared in dimethyl formamide. The graded dilution of the test compounds in a suitable nutrient (agar) and PDA medium were inoculated with the organisms under examination using aseptic techniques in an incubator at 37 °C . The antibacterial and antifungal activity of carboxylic acids and their metallic soaps

have been screened in vitro, against bacteria (*Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Salmonella typhi*) and fungi (*Aspergillus flavous*, *Aspergillus niger*, *Penicillium triticena* and *Fusarium species*).

The percentage of growth inhibition was calculated by measuring the diameter of the microbial colony in the control and test plates by the following expression-

$$\% \text{ inhibition} = \frac{C-T}{C} \times 100$$

Where

C = diameter of microbial colony in millimeter in control plate.

T = diameter of microbial colony in treated (test) plate.

Analytical and Physical Measurement

The purity of metallic soaps were confirmed by running their T.L.C. on silica gel- G. The IR spectra in KBr matrix were recorded on Perkin- Elmer 842- spectro photometer at CDRI, Lucknow and elemental analysis of C, H, N, were carried out at NCL Pune.

RESULTS AND DISCUSSION

The complexes are microcrystalline colored powder, stable at room temperature, and are not sensitive to exposure to atmosphere. However, on heating they decompose. The complexes are soluble in methanol and DMSO but insoluble in water, carbon tetrachloride and chloroform. The elemental analyses were satisfactory, show that the complexes have a ligands to metal ratio of 1 : 1 : 1, and have the general formula $[ML_1L_2(NO_3)_2]$ where M = [Mn(II), Cu(II), Co(II) and Ni(II)], L₁ = 2- Hydroxy-5-nitrobenzaldehyde and L₂ = b-Diketones (pentane-2,4-dione, 1-phenylbutane-1,3-dione and 1,3-diphenylpropane-1,3-dione). The molar conductance value (11.30–21.6 mhos cm² mol⁻¹) indicates the nonelectrolytic nature of the complexes. These complexes are quite stable and are not sensitive to exposure to atmosphere. Their characteristics, yields, analyses and temperatures of decomposition are recorded in Table -I. The conductances of the complexes are very low, indicating their non-electrolytic nature.

Infrared Spectra

The IR spectra of complexes are compared with that of free ligands to determine the changes that might have taken place during complexation. The bands in the region 1600-1680 cm^{-1} may be assigned to coordinated $\nu\text{C=O}$ groups and those in the region 1500-1580 cm^{-1} to $\nu\text{C=C}$ stretching modes. The $\nu\text{C=O}$ frequencies of the complexes are in the lower region as compared to those of the free ligands. The IR spectra of β -diketones and their metal complexes have been reported by Bellamy and Beecher²¹. For 2,4-pentanedione bands at $\nu 1724 \text{ cm}^{-1}$ and 1608 cm^{-1} have been assigned to $\nu\text{C=O}$ and $\nu\text{C-O}$ respectively. In 1-phenyl-1,3-butanedione bands due to $\nu\text{C=O}$ and $\nu\text{C-O}$ have been reported at 1724 cm^{-1} and 1600 cm^{-1} respectively and in case of 1,3-diphenylpropane-1,3-dione $\nu\text{C-O}$ band appears at 1600 cm^{-1} . In case of Cu(II) complexes, bands at

1580 cm^{-1} , 1550 cm^{-1} and 1524 cm^{-1} have been assigned to $\nu\text{C=O}$ frequencies and those at 1389 cm^{-1} , 1389 cm^{-1} and 1391 cm^{-1} have been assigned to $\nu\text{C-O}$ frequencies of pentane-2,4-dione, 1-phenylbutane-1,3-dione and 1,3-diphenylpropane-1,3-dione ligand moieties respectively. However, Bellamy and Branch²⁰ observed $\nu\text{C=O}$ absorption bands at 1524 cm^{-1} and 1552 cm^{-1} in Cu(II) complexes of 1-phenylbutane-1,3-dione and 1,3-diphenylpropane-1,3-dione respectively. The substitution of methyl group by a phenyl group affects the perturbed $\nu\text{C=O}$ bands. Holtzclaw and Collman²³ suggested that a phenyl group attached to a carbonyl group in the ligand might set up an interfering conjugation through a quinoid like structure decreasing the double bond character of the adjacent carbonyl group. In some cases nitrate ions existed simply as counter-anions of the supramolecular network but in others as coordinated

Table 1: Analytical and physical data of Mixed Ligand Complexes

S. No	Mixed ligand Complexes	Mol. wt.	Yield %	Molar Conductivity $\text{mhos cm}^2 \text{ mol}^{-1}$	Elemental analysis / Found % (Cal.)			
					C	H	N	M
1.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Co}[\text{C}_5\text{H}_8\text{O}_2](\text{NO}_3)_2$	455	82	9.3	31.64 (29.89)	2.85 (1.59)	9.23 (7.98)	12.96 (10.89)
2.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Co}[\text{C}_{10}\text{H}_{10}\text{O}_2](\text{NO}_3)_2$	512	79	9.9	39.84 (38.32)	2.92 (1.64)	8.20 (7.20)	11.52 (9.82)
3.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Co}[\text{C}_{15}\text{H}_{12}\text{O}_2](\text{NO}_3)_2$	574	81	10.7	45.99 (43.04)	2.96 (1.20)	7.31 (5.89)	10.27 (8.98)
4.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Mn}[\text{C}_5\text{H}_8\text{O}_2](\text{NO}_3)_2$	451	80	13.3	31.92 (29.67)	2.88 (1.09)	9.31 (7.98)	12.17 (10.03)
5.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Mn}[\text{C}_{10}\text{H}_{10}\text{O}_2](\text{NO}_3)_2$	508	76	15.62	40.15 (38.64)	2.95 (1.09)	8.26 (6.98)	10.80 (8.75)
6.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Mn}[\text{C}_{15}\text{H}_{12}\text{O}_2](\text{NO}_3)_2$	569	89	19.7	46.39 (44.09)	2.98 (1.07)	7.38 (6.05)	9.64 (7.09)
7.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Cu}[\text{C}_5\text{H}_8\text{O}_2](\text{NO}_3)_2$	454.5	82	23.3	31.68 (28.98)	2.86 (1.81)	9.24 (7.81)	13.97 (11.87)
8.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Cu}[\text{C}_{10}\text{H}_{10}\text{O}_2](\text{NO}_3)_2$	516.5	82	20.7	39.49 (37.85)	2.90 (1.67)	8.13 (6.96)	12.29 (10.92)
9.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Cu}[\text{C}_{15}\text{H}_{12}\text{O}_2](\text{NO}_3)_2$	578.5	78	22.4	45.63 (44.81)	2.93 (1.09)	7.26 (5.98)	10.97 (9.07)
10.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Ni}[\text{C}_5\text{H}_8\text{O}_2](\text{NO}_3)_2$	449.7	79	23.6	32.02 (30.91)	2.89 (1.35)	9.33 (7.89)	13.05 (11.09)
11.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Ni}[\text{C}_{10}\text{H}_{10}\text{O}_2](\text{NO}_3)_2$	511.7	72	15.3	39.86	2.93	8.20	11.47
12.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Ni}[\text{C}_{15}\text{H}_{12}\text{O}_2](\text{NO}_3)_2$	573.5	76	12.7	46.03	2.96	7.32	10.23

Table 2: Percentage of zone of inhibition of Mixed Ligands Metal Complexes against Fungi

Compounds	A. flavous					A. niger					P. triticena					F. species				
	% Conc. In ppm					% Conc. In ppm					% Conc. In ppm					% Conc. In ppm				
	250	500	750	1000	250	500	750	1000	250	500	750	1000	250	500	750	1000	250	500	750	1000
[C ₇ H ₅ O ₄ N]Co[C ₅ H ₈ O ₂](NO ₃) ₂	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00
[C ₇ H ₅ O ₄ N]CO[C ₁₀ H ₁₀ O ₂](NO ₃) ₂	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00
[C ₇ H ₅ O ₄ N]CO[C ₁₅ H ₁₂ O ₂](NO ₃) ₂	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	64.00	69.13
[C ₇ H ₅ O ₄ N]Mn[C ₅ H ₈ O ₂](NO ₃) ₂	39.50	62.66	64.00	69.13	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	64.00	69.13	71.55
[C ₇ H ₅ O ₄ N]Mn[C ₁₀ H ₁₀ O ₂](NO ₃) ₂	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00
[C ₇ H ₅ O ₄ N]Mn[C ₁₅ H ₁₂ O ₂](NO ₃) ₂	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75	39.50	69.13	71.55	75	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00
[C ₇ H ₅ O ₄ N]Cu[C ₅ H ₈ O ₂](NO ₃) ₂	47.84	71.55	71.55	47.84	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55
[C ₇ H ₅ O ₄ N]Cu[C ₁₀ H ₁₀ O ₂](NO ₃) ₂	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00
[C ₇ H ₅ O ₄ N]Cu[C ₁₅ H ₁₂ O ₂](NO ₃) ₂	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55
[C ₇ H ₅ O ₄ N]Ni[C ₅ H ₈ O ₂](NO ₃) ₂	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55
[C ₇ H ₅ O ₄ N]Ni[C ₁₀ H ₁₀ O ₂](NO ₃) ₂	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00
[C ₇ H ₅ O ₄ N]Ni[C ₁₅ H ₁₂ O ₂](NO ₃) ₂	47.84	71.55	71.55	47.84	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55

Table 3: Percentage of zone of inhibition of Mixed Ligands Metal Complexes against Bacteria

Compounds	E. coli					S. typhi					S. aureus					B. subtilis				
	% Conc. In ppm					% Conc. In ppm					% Conc. In ppm					% Conc. In ppm				
	250	500	750	1000	250	500	750	1000	250	500	750	1000	250	500	750	1000	250	500	750	1000
[C ₇ H ₅ O ₄ N]Co[C ₅ H ₈ O ₂](NO ₃) ₂	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00
[C ₇ H ₅ O ₄ N]CO[C ₁₀ H ₁₀ O ₂](NO ₃) ₂	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00	39.50	54.00	62.66	64.00
[C ₇ H ₅ O ₄ N]CO[C ₁₀ H ₁₀ O ₂](NO ₃) ₂	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55
[C ₇ H ₅ O ₄ N]Mn[C ₅ H ₈ O ₂](NO ₃) ₂	39.50	62.66	64.00	69.13	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	64.00	69.13	71.55	39.50	64.00	69.13	71.55
[C ₇ H ₅ O ₄ N]Mn[C ₁₀ H ₁₀ O ₂](NO ₃) ₂	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00
[C ₇ H ₅ O ₄ N]Mn[C ₁₅ H ₁₂ O ₂](NO ₃) ₂	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00
[C ₇ H ₅ O ₄ N]Cu[C ₅ H ₈ O ₂](NO ₃) ₂	47.84	75.00	75.00	75.00	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55
[C ₇ H ₅ O ₄ N]Cu[C ₁₀ H ₁₀ O ₂](NO ₃) ₂	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00
[C ₇ H ₅ O ₄ N]Cu[C ₁₅ H ₁₂ O ₂](NO ₃) ₂	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55
[C ₇ H ₅ O ₄ N]Ni[C ₅ H ₈ O ₂](NO ₃) ₂	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55	39.50	62.66	69.13	71.55
[C ₇ H ₅ O ₄ N]Ni[C ₁₀ H ₁₀ O ₂](NO ₃) ₂	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00	39.50	69.13	71.55	75.00
[C ₇ H ₅ O ₄ N]Ni[C ₁₅ H ₁₂ O ₂](NO ₃) ₂	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00	47.84	71.55	71.55	75.00

ligands. Nitrate ions as ligands show three coordination modes. Mode I (monodentate coordination) and II (bidentate coordination) are the most commonly observed coordination mode in which nitrate ions as blocking ligands that make appropriate coordination sites available for other ligands²⁴⁻²⁶. The presence of new bands in the region 568 cm^{-1} & 497 cm^{-1} in all the complexes is attributed to $\nu(\text{M-O})$ linkage²⁷⁻²⁸. Other strong bands around 1360 cm^{-1} & 860 cm^{-1} in all complexes, suggest monodentate coordination of $-\text{NO}_3$ group in the complexes²⁹.

Antimicrobial studies

The antibacterial and antifungal activity of mixed ligands metal complexes were screening *in vitro*, against bacteria (*Bacillus subtilis*, *Staphylococcus aureus*, *E. coli* and *Salmonella typhi*) and fungi (*Aspergillus flavous*, *Aspergillus niger*, *Penicillium triticena* and *Fusarium* species). The results are recorded in Table 2 and 3. The results of biocidal activities show that the percentage of zone of inhibition of 500 ppm concentration is the best. The percentage of growth inhibition capacities of

metal complexes follows the following order against different bacteria and fungi-

Bactericidal activities of metal

E. coli: Cu (II) > Co (II) > Mn (II) > Ni (II)
S. typhi: Cu (II) \approx Mn(II) > Co (II) > Ni (II)
S. aureus: Cu (II) > Mn (II) \approx Co (II) > Ni (II)
B. subtilis: Mn (II) \approx Cu (II) > Co (II) \approx Ni (II)

Fungicidal activities of metal complexes

A. flavous: Cu (II) > Mn (II) \approx Co (II) > Ni (II)
A. niger: Cu (II) > Mn (II) \approx Co(II) > Ni (II)
P. triticena: Cu (II) \approx Mn (II) > Co (II) \approx Ni (II)
Fusarium
 species: Cu (II) > Mn (II) \approx Co (II) > Ni (II)

The results indicate that the Cu (II) complexes are more toxic compared to other complexes, as well as Cu (II) complex is more effective towards bacteria *S. aureus* compared to other microbes. The overall results obtained from the above studies confirm that with increase in the concentration of the complexes the activity almost remains unchanged or is slightly increase.

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