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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF SOME TARTARATES AND TRANSITION METAL COMPLEXES

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3-{[(*E*)-(4-fluorophenyl) methylidene] amino} benzoic acid, Metal ion complexes, Biological activities

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ABSTRACT: Metal complexes having two or more different metal ions not only possess excellent catalytic applications but also have many biological activities. In the present work, some ligand tartarate based mixed transition metal complexes of type $[M_xM^I_{1-x}(C_4H_4O_6)]$. XH_2O [Where M and M^I are Cu and Ni, and x= 0.2, 0.4, 0.6 and 0.8] have been successfully synthesized and were characterized by different sophisticated analytical techniques such as elemental analysis, FT-IR, TGA and XRD. From the analytical data; it was observed that all the complexes exhibited 1:1 (methyl: ligand) ratio. IR data shows that the ligand co-ordinates with metal ions in a bidentate manner through the two oxygen atoms. Thermal analysis shows the degradation pattern of the complexes. The synthesized metal complexes were then tested *in vitro* for biological activities against *Bacillus subtilis, Staphylococcus Aureus, and Escherichia coli* to assess their antibacterial and antifungal effect. Some of them showed promising antimicrobial activity.

INTRODUCTION: Metal complexes containing two or more different metal ions are always of interest in different field like multimetallic enzymes [1] and catalysis [2, 3]. A large number of Schiff bases and their complexes have been studied for its interesting and important properties such as catalytic activity [4] and transfer of the amino group, photochromic properties and complexing ability towards some toxic metals [5]. A number of hydrazone derivatives possess interesting bioactivity towards anti-bacterial, antifungal [6] anti-convulsant [7], anti-inflammatory [8], anti-malerial [9, 10], analgesic [10], anti-platelets [11] anti-tuberculosis [12] and anticancer activities [13].

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Although, much attention has been directed on the study of Schiff base complexes with 'N' and 'O' donor atoms; none of the investigation has appeared in literature which describing the metal complexes of ligand containing 'O' donor atoms.

In continuation of our work in synthesis and characterization of mixed metal oxalate complexes [14], the present investigation deals with the synthesis of different composition of copper nickel tartarates of the type $[Cu_xNi_{1-x}(C_4H_4O_6)]$ H_2O using co-precipitation technique.

Tartarate act as donor site of carboxyl oxygen atoms. The complexes were screened for their biological and catalytic activity.

EXPERIMENTAL:

Synthesis of Precursor: All the chemicals used were of the analytical grade (A.R.) and of high purity.

The copper-Nickel taratrates with different composition (X=0.2 to 1.0) were prepared by the co-precipitation method by taking high purity $CuSO_4.5H_2O$ and $NiSO_4.6H_2O$ in distilled water. The mixture of metal sulphate solution was prepared with respect to molar ratio of Cu and Ni and placed in a beaker. p^H of the medium was adjusted to a low enough value (pH<6), so that hydroxide does not precipitate. The solution was stirred vigorously and sodium tartarate (10%) solution was added slowly with stirring till a permanent precipitate occurred. Further an acetone was added in equal amounts to metal salts to ensure a high yield of product. The resultant precipitate was light bluish-green. The solution was filtered after stirring it for 30 minutes. The filtrate was checked for Cu^{+2} and Ni^{+2} whose absence ensured complete coprecipitation. The residue was washed with cold distilled water and then with acetone to speed up drying. The solid was dried at ambient temperature.

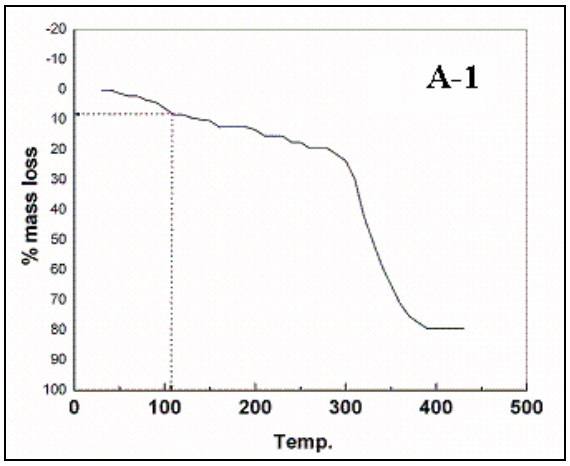
Antimicrobial Activity: Mixed metal complexes are well known for their biological activity [15-16]. All the synthesized mixed metal complexes were screened for antibacterial as well as antifungal activity.

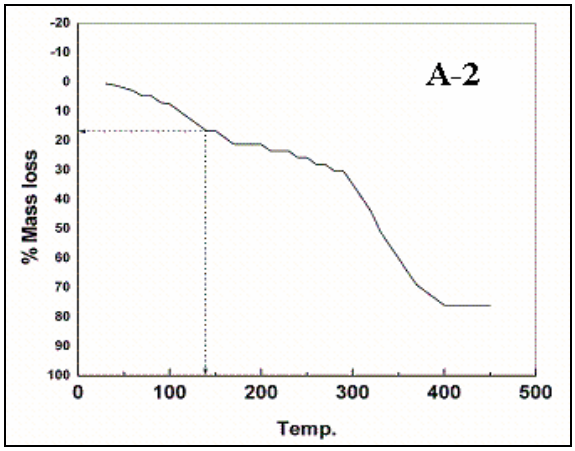
MATERIALS AND METHODS: 1) Synthesized Chemicals: Set A: 1 to 6 and Set B: A1 to A6. 2) Diluents: Sterile distilled water [10 ml in each 7 tubes. 3) Nutrient agar medium [Cruickshank *et al* 1975] plates- 18 in numbers. 4) Fresh 24 Hrs old nutrient broth cultures of test bacterial organism. *a) Bacillus subfilis – Gram positive in nature. b) Staphylococcus aureus - Gram positive in nature. c) Escherichia coli - Gram negative in nature. d) Yeast - Canadian albicaus. f) Molds- Aspergillus, Penecillium chrysogenum.* 5) Well borer and glass spreader. 6) Sterile1 ml. capacity glass pipette/micropipette.

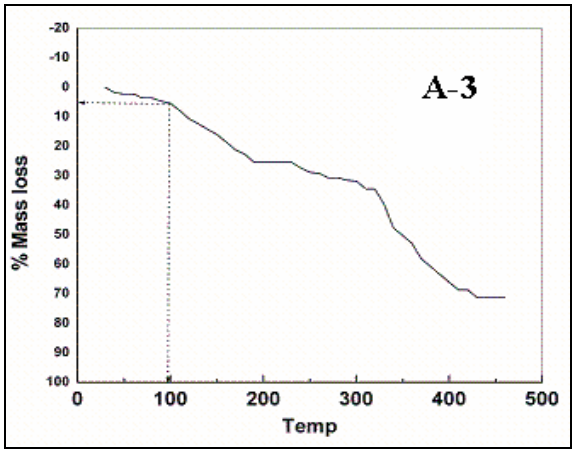
1. Using sterile distilled water diluents 1% solution of each chemical was prepared.
2. For every chemical solution three nutrient agar plates were used and labeled for above three bacterial cultures. In total 12 sets of plates [3 plates in each set] were prepared.
3. In each set of plates 0.5 ml. of above bacterial cultures were spread, inoculated and incubated at 37^oC for 30 minutes to adsorb the culture on medium surface.
4. Using well borer, a well was bored at center of medium in each plate, aseptically.
5. 0.1 ml. of each chemical solution was poured aseptically in each respective well and incubated for diffusion at 4^0C for 1 hrs.
6. All the plates were incubated at 37^0C for 48 hrs and results were recorded.

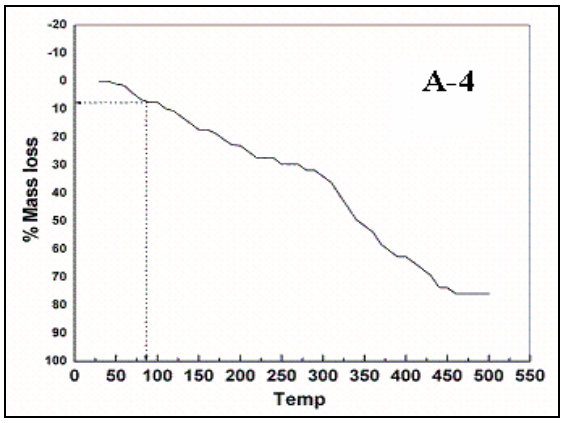
RESULT AND DISCUSSION:

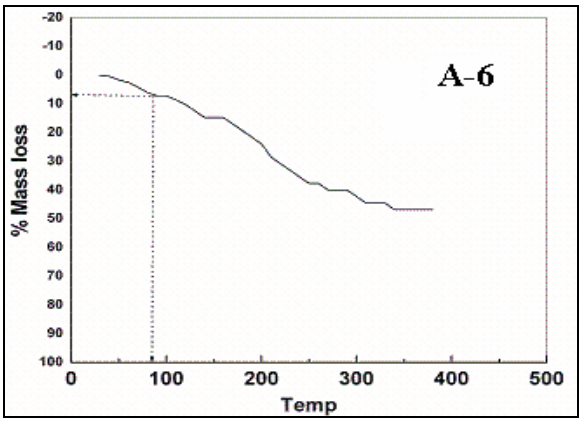
Characterization of precursors: Figure 1 shows the TGA curves of Cu-Ni Tartarate











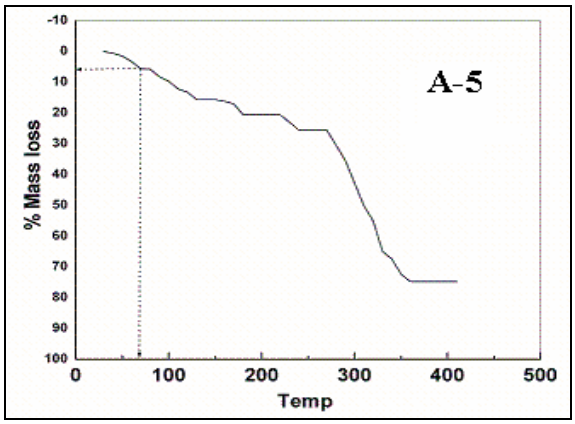


FIGURE 1: TGA OF Cu-Ni TARTARATE

The elemental analysis made in Wt % of tartarate precursors are very well matched with the calculated ones (**Table 1**).

The X-ray powder diffraction pattern of these precursors (**Fig. 2**) showed broad as well as sharp line indicating that sample were polycrystalline in nature and the 'd' spacing values calculated for respective precursors are given in the **table 3**.

TABLE 1: ELEMENTAL ANALYSIS

	Formula	C		H		Cu		Ni	
Complex	**weight**	**Calcd**	**Found**	**Calcd**	**Found**	**Calcd**	**Found**	**Calcd**	**Found**
A_1 Cu(0.8)Ni(0.2) $(C_4H_4O_6)*H_2O$	236.54	20.29	20.22	2.50	2.42	24.86	24.35	4.95	4.84
A_2 Cu(0.6)-Ni(0.4) $(C_4H_4O_6)*H_2O$	227.6	21.09	20.95	2.64	2.61	16.74	16.80	10.31	10.02
A_3 Cu(0.4)-Ni(0.6) $(C_4H_4O_6)*H_2O$	226.63	21.18	21.14	2.65	2.56	11.21	10.87	15.53	14.85
A_4 Cu(0.2)-Ni(0.6) $(C_4H_4O_6)*H_2O$	335.65	21.27	21.22	2.66	2.59	5.62	5.13	20.8	20.18
A_5 Cu $(C_4H_4O_6)*H_2O$	229.54	20.91	20.65	2.61	2.51	27.68	27.02	--	--
A_6 Ni $(C_4H_4O_6)*H_2O$	224.69	21.36	21.31	2.67	2.85	--	--	26.12	25.98

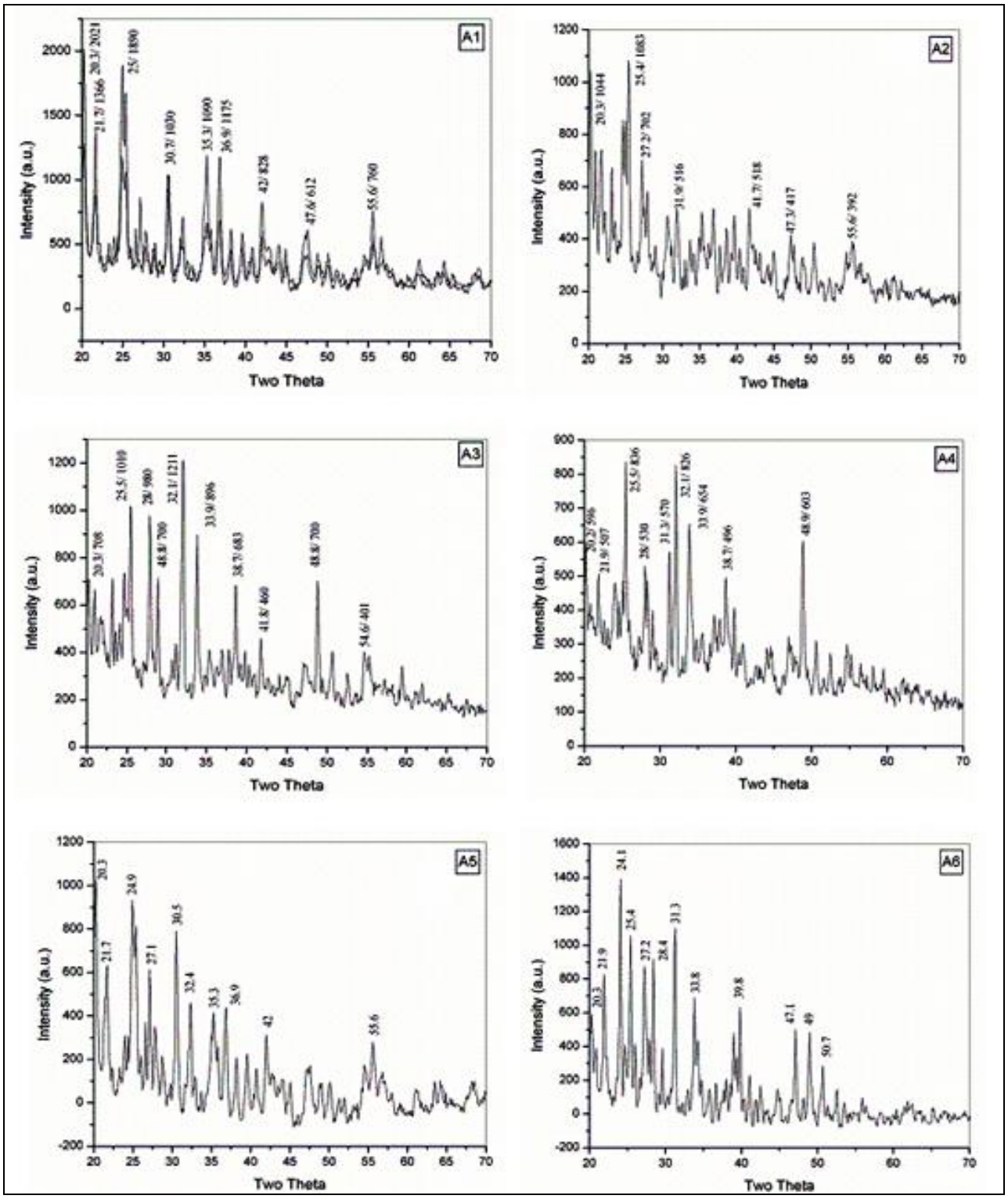


FIGURE 2: X-RAY DIFFRACTION PATTERNS OF Cu-Ni TARTARATES

The C, H analysis done on Thermoquest model FLASH EA 1112. Nicollet NEXUS 7000C spectrometer is used for taking IR of the precursors (A1-A6).

The infrared spectra showed (**Fig. 3**) frequencies corresponding to carboxylate group, hydroxyl group, metal-oxygen, carbon-hydrogen etc.

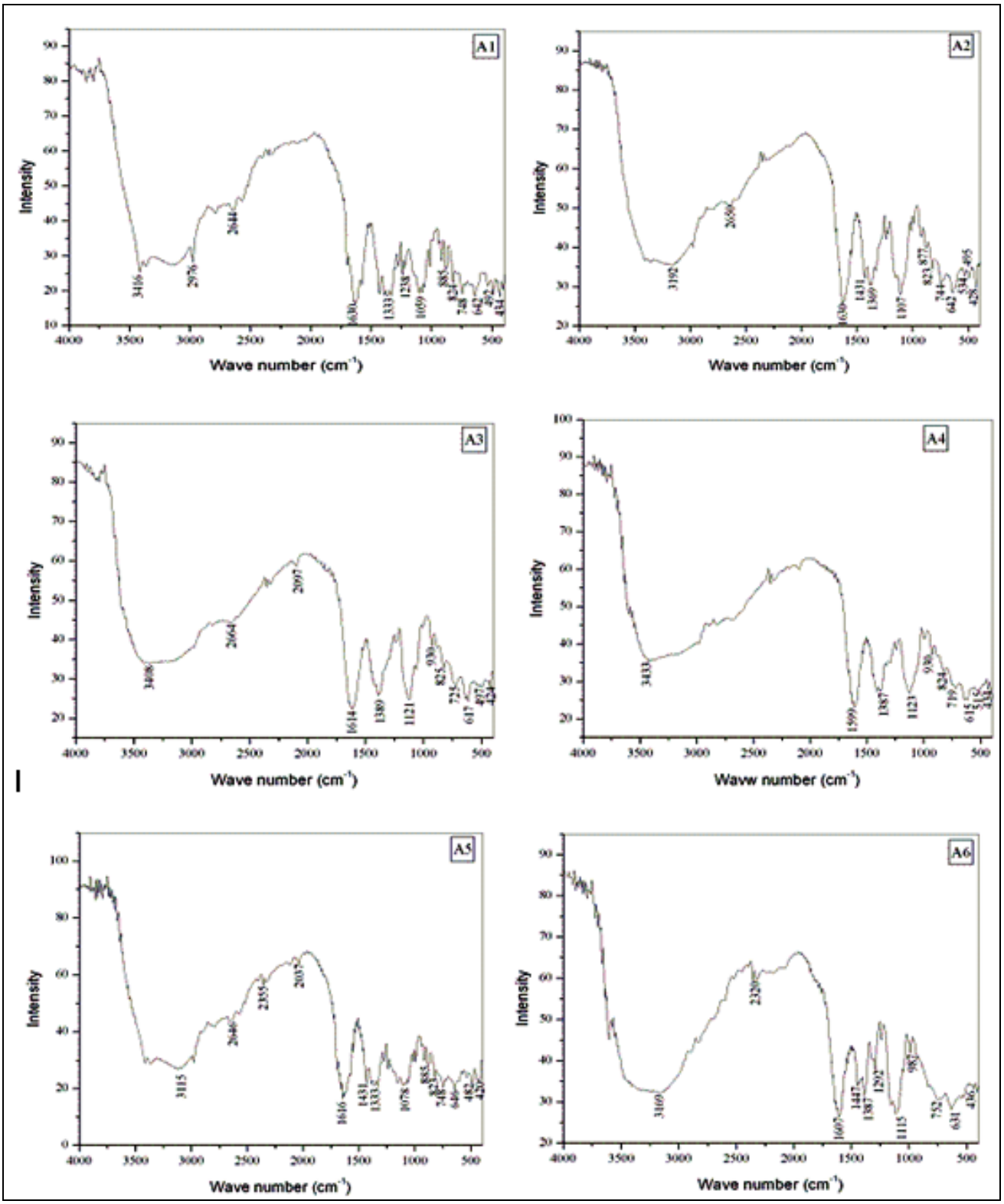


FIGURE-3: INFRA-RED SPECTRA OF TRANSITION METAL COMPLEXES A_1-A_6

The bidentate linkage of tartarate group with metal was confirmed on the basis of the difference between antisymmetric and symmetric stretching frequencies (**Table 2**).

The TGA data of Cu-Ni tartarates is summarized in **Table 4**. **Table 5** describes the compositions of Cu-Ni tartarates.

TABLE 2: INFRA-RED SPECTRAL BANDS AND THEIR PROBABLE ASSIGNMENTS

S. no.	A1	A2	A3	A4	A5	A6	ASSIGNMENT
	Cu0.8Ni0.2 $(C_4H_4O_6)*H_2O$	Cu0.6-Ni0.4 $(C_4H_4O_6)*H_2O$	Cu0.4-Ni0.6 $(C_4H_4O_6)*H_2O$	Cu0.2-Ni0.6 $(C_4H_4O_6)*H_2O$	Cu $(C_4H_4O_6)*H_2O$	Ni $(C_4H_4O_6)*H_2O$	
1	3416	3192	3408	3433	3115	3169	ν(O-H)- stretch
	2976						ν(C-H)
2.	2644	2650	2664	2630	2646	2320	ν(O-H) carboxylic acid
			2097		2355		ν
					2037		ν
3.	1630	1630	1614	1599	1616	1607	ν(C-O)
4.	1333	1431	1389	1387	1431	1447	ν(C=O)
		1369			1333	1387	ν
5.	1238					1292	ν
6.	1059	1107	1121	1123	1078	1115	νC-O(alcohol)
7.	885	877	930	930	885	987	ν C-O(sym)
			825	824	823		
8.	748	744	725	719	748	752	νsym(C-C)
9.	642	642	617	615	646	631	ν(C-H)
10.	492	495	497	515	482	436	ν(M-O)
11.	434	428	424	434	420		ν

TABLE 3: OBSERVED D-SPACING VALUES (A˚):

A_1 Cu0.8Ni0.2 $(C_4H_4O_6)*H_2O$	A_2 Cu0.6Ni0.4 $(C_4H_4O_6)*H_2O$	A_3 Cu0.4Ni0.6 $(C_4H_4O_6)*H_2O$	A_4 Cu0.2Ni0.6 $(C_4H_4O_6)*H_2O$	A_5 Cu $(C_4H_4O_6)*H_2O$	A_6 Ni $(C_4H_4O_6)*H_2O$
0.77856	1.1613	1.1613	1.2323	1.1613	4.3718
16.6149	5.7831	4.2185	0.7711	4.5419	0.7719
2.1986	0.8965	0.7776	4.2185	3.573	4.093
0.8266	3.2136	1.1516	0.7776	0.9253	3.5046
1.9802	0.8473	2.2967	13.304	3.246	0.8966
0.92069	0.7733	0.8139	2.2967	2.7609	3.4824
0.79266	1.6867	1.6055	0.8139	0.8266	2.8551
1.6869		0.8682	1.605	2.6953	0.8291
		1.1516	1.1936	2.15	2.505
		0.9311		0.7749	1.9282
				1.8215	1.3025
					1.9874

Observed particle size (D=0.89λ/B.cosθ):

A_1	A_2	A_3	A_4	A_5	A_6
287.153 A˚	631.87 A˚	442.31 A˚	175.59 A˚	541.96 A˚	629.03 A˚

TABLE 4: TGA DATA OF CU-NI TARTARATES UNDER STATIC AIR

Complex	% mass loss Obsd	% mass loss2 Calcd	Temp. Range ˚C
	11		30-150
A_1-> $Cu_{0.8}$-$Ni_{0.2}(C_4H_4O_6)*H_2O$	19.5	7.60%	150-240
	25.5		240-320
	8.5		30-95
A_2-> $Cu_{0.6}$-$Ni_{0.4}(C_4H_4O_6)*H_2O$	25.5	7.60%	95-175
	35.5		175-320
	18.5		30-145
A_3-> $Cu_{0.4}$-$Ni_{0.6}(C_4H_4O_6)*H_2O$	28.5	7.60%	145-220
	31.2		220-280

A_4-> $Cu_{0.2}$-$Ni_{0.6}(C_4H_4O_6)*H_2O$	16.5 19.8 24.0	7.60%	30-130 130-175 175-240
A_5-> $Cu(C_4H_4O_6)*H_2O$	9.0 15.0 38.0	7.60%	30-80 80-135 135-255
A_6-> $Ni(C_4H_4O_6)*H_2O$	9.5 15.5 24.8	7.60%	30-100 100-190 190-280

TABLE-5: Cu-Ni TARTARATES COMPLEX COMPOSITIONS

Complex/ Composites	Molecular Weight	Amount of $CuSO_4.5H_2O$ taken	Amount of $NiSO_4$ $7H_2O$ taken	Tartarate solution added
A_1 Copper Nickel $Cu_{0.8}Ni_{0.2}(C_4H_4O_6).H_2O$	236.54	4.02 gm	1.12 gm	10 %
A_2 Copper Nickel $Cu_{0.6}Ni_{0.4}(C_4H_4O_6).H_2O$	227.6	4.53 gm	3.36 gm	10 %
A_3 Copper Nickel $Cu_{0.4}Ni_{0.6}(C_4H_4O_6).H_2O$	226.63	2.51 gm	4.21 gm	10 %
A_4 Copper Nickel $Cu_{0.2}Ni_{0.8}(C_4H_4O_6).H_2O$	335.65	1.255 gm	5.6 gm	10 %
A_5 Copper Nickel $Cu_{1.0}Ni_{0.0}(C_4H_4O_6).H_2O$	229.54	7 gm	0 gm	10 %
A_6 Copper Nickel $Cu_{0.0}Ni_{1.0}(C_4H_4O_6).H_2O$	224.69	0 gm	7 gm	10 %

Rigaku D/Max-2A Diffractometer with Cu, K alpha radiation and Ni filter is used for taking XRD of these precursors. Particle size is also calculated using formula ($D=0.89\lambda/B \cos\theta$). The probable structure of compound Copper Nickel Tartarate is shown by **figure 4**.

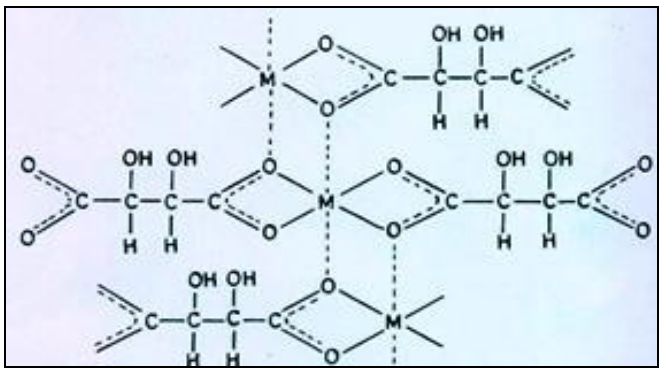


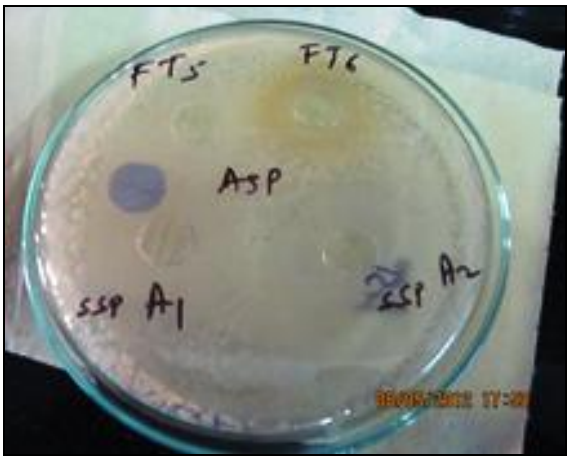
FIGURE 4:

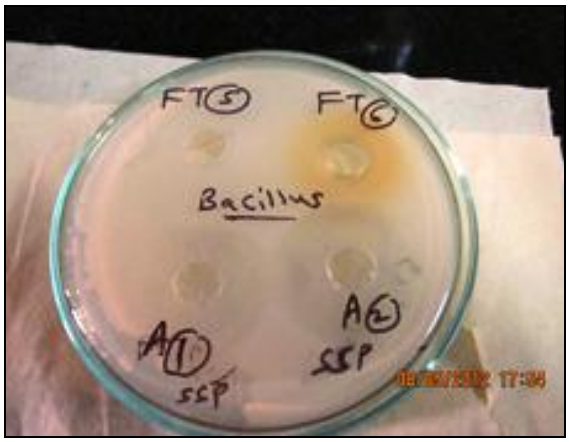
All the precursors shows loss of water molecule at about 100°C. The percentage loss for one water molecule is well matched with the theoretical loss. The oxidative decomposition of the ligand is observed between 150 to 400°C.

Biological Activity: All these complexes (i.e. A_1 to A_6) showed antibacterial and antifungal activity against microorganism (**Table 6**).

Table 6: Antibacterial and antifungal activity studies of synthesized chemicals: Zone of Inhibition [in mms]

S. No.	Complex	*E. coli*	*B. subtilis*	*S. aureus*	*C. albicans*	*A. niger*	*P. chrysogenum*
1	A1	30	21	17	9	19	7
2	A2	25	25	19	22	28	8
3	A3	16	19	17	25	10	22
4	A4	15	16	22	14	8	17
5	A5	14	34	27	34	5	9
6	A6	16	12	20	17	17	17
7	Control [Sterile distilled water]	0	0	0	0	0	0





PHOTOGRAPHS OF SOME ACTIVITY PETRI-DISHES:

All these complexes (A_1 to A_6) possess potential to inhibit gram positive as well as gram negative bacteria selected indicating their possible to use as bacterial agent. Out of these, sample A_5 showed highest antibacterial and antifungal effects.

CONCLUSION:

1. The elemental analysis for complexes (A_1 to A_6) is well matched with expected ones.

2. The Infra-Red study suggests that the tartarate ligand is a bidentate ligand.

3. The -ray patterns of these complexes (A_1 to A_6) suggest that they are polycrystalline in nature.

4. Thermogram provides the information about the presence of one water molecule and oxidative decomposition of the ligand.

5. Above study suggest that the metal chelate exhibited polymeric octahedral structure (Fig-4).

6. Antimicrobial and Antifungal activity: The study reveals that these complexes possess antimicrobial as well as antifungal activity.

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