

Synthesis, characterization and antimicrobial studies of mono and bimetallic trinuclear transition metal complexes of bis(N_2, N_2' -acetylacetonehydrazone)- N_1, N_1' -benzil dihydrazone (BAHBD) with Cu^{II} , Ni^{II} and Co^{II} ions

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Abstract : A few mono and bimetallic trinuclear metal complexes of the type $[MCuM(BAHBD)_2X_2(H_2O)_4]$, where $M = Cu^{II}, Ni^{II}, Co^{II}$; $X = Cl, Br, NO_3$ and BAHBD = bis(N_2, N_2' -acetylacetonehydrazone)- N_1, N_1' -benzil dihydrazone have been isolated in a stepwise reaction from the precursor copper bis(benzil dihydrazone) complex. These have been characterized on the basis of elemental analysis, spectral and magnetic properties, conductivity measurements and thermal analyses. The ligand as well as the metal complexes exhibited good antimicrobial activities against the pathogenic fungus *Aspergillus niger*, *Helminthosporium oryzae* and *Fusarium oxysporium*.

Keywords : Trinuclear metal complex, fungicidal screening, thermal analysis, electronic spectra.

Introduction

There is no report so far on the direct synthesis of bimetallic (hetero) poly nuclear complexes. These have been prepared in a stepwise reaction of metal complexes containing either a coordinating atom with nonbonded electron pair which are sufficiently nucleophilic^{1,2} [structure **1(a)**, Fig. 1] or a functional group³, which can further coordinate to another metal centre [structure **1(b)**, Fig. 1].

Taking these aspects into consideration, we have chosen the dihydrazone complex systems of benzil, in our continued effort for the synthesis of homo and bimetallic complexes.

The dihydrazones of benzil and diacetyl exist in *trans*

configurations. In the presence of the metal ions, they attain a *cis* configuration thereby allowing the NH_2 groups to become proximal to the metal ion for coordination. Transition metal complexes involving such vicinal dihydrazones⁴⁻¹⁰ have been used as intermediates to prepare macrocyclic metal complexes by template condensation with aldehydes and ketones¹¹⁻¹³.

Hydrazone derivatives are found to possess antimicrobial¹⁴, antitubercular¹⁵, anticonvulsant¹⁶ and anti-inflammatory¹⁷ activities. The antibacterial and antifungal properties of hydrazones and their complexes with some transition metal ions have been studied and reported by Carcelli *et al.*¹⁸.

In the present communication, we have made an at-

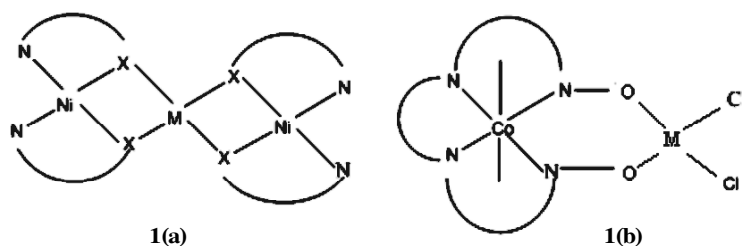


Fig. 1. Structure [1(a)] and structure [1(b)].

tempt to use bis(benzil dihydrazone)copper(II) complexes as precursor for the isolation of homo/hetero bimetallic trinuclear complexes from its reaction with acetyl acetone in the presence of copper(II), nickel(II) and cobalt(II) salts and have studied their antifungal activities.

Experimental

Materials and methods :

All the chemicals used in the synthesis were of AR grade. The solvents were purified before use by standard procedure.

Synthesis of metal complexes :

Benzil dihydrazone was prepared according to literature method¹⁹. The nickel(II) and cobalt(II) bromides were prepared by dissolving the respective metal carbonates in minimum volume of hydrobromic acid followed by crystallization. All other metal salts were used as such.

The precursor bis(benzyl dihydrazone)copper(II) complexes were prepared at low temperature in a similar manner as reported earlier¹⁰. Both homo/bimetallic trinuclear complexes were prepared by the following method.

An ethanolic solution of bis(benzil dihydrazone)-copper(II) complex (0.5 mmol) and acetylacetone (2 mmol) were refluxed for 2 h and to this was added metal salts of nickel(II), cobalt(II) and copper(II) (1 mmol) in ethanol dropwise. After 1 h of refluxing a clear solution was obtained. It was cooled to room temperature and then a calculated amount of NaOH (2 mmol) was added when an intensely coloured precipitate was obtained. It was filtered, washed several times with water followed by ethanol and dried over fused CaCl₂.

Analysis and physical measurement :

The metal contents in the complexes were estimated using standard methods²⁰. Carbon, hydrogen and nitrogen contents in the complexes were determined using a MLW-CHN micro analyzer. The molar conductivity measurements were carried out at room temperature with a Systronics 321 conductivity bridge using $1 \times 10^{-3} M$

FTIR spectrophotometer. The electronic spectra of the complexes in DMSO were obtained using Perkin-Elmer 983 spectrophotometer. The ESR spectrum of the complex was recorded using EPR 112 spectrophotometer. The thermal decomposition pattern of the complexes was studied using Mettler Toledo thermal analyzer. The measurements were carried out using sample weight of 100 mg. The rate of temperature increase of $10 \text{ }^\circ\text{C min}^{-1}$ was chosen for all the measurements. The magnetic susceptibility measurements at room temperature were carried out by Guoy method using Hg[Co(NCS)₄] as the calibrant.

Fungicidal screening :

The antifungal activities of the complexes were tested against the organisms *Aspergillus niger*, *Helminthosporium oryzae* and *Fusarium oxysporium* by the method of Horsfall²¹. The evaluation was carried out at a different concentration in dioxane. The amount of germination or growth inhibition was determined after inoculation of the fungal spores into Czapekdox agar-agar media. Spores were also inoculated onto the agar-agar media containing the test sample. The whole system was kept in an incubator for five days. The percentage of inhibition was calculated as follows :

$$\% \text{ of inhibition} = 100 (P - Q)/P$$

where P = area of colony growth without test sample, and Q = area of the colony growth with the test sample.

Results and discussion

The elemental analysis data of the compounds are presented in Table 1, which show a good agreement between the experimental and calculated values (using Fig. 6). The complexes are highly stable under normal conditions, slowly attacked by dilute acids and alkalis, and are soluble in DMF, DMSO and dioxane. The TLC in water-dioxane mixture shows a single spot ensuring the purity of the compound. They have low molar conductance values in dioxane and have high melting point ($>250 \text{ }^\circ\text{C}$). The scheme of reaction for the preparation of the complexes is depicted below (Fig. 2).

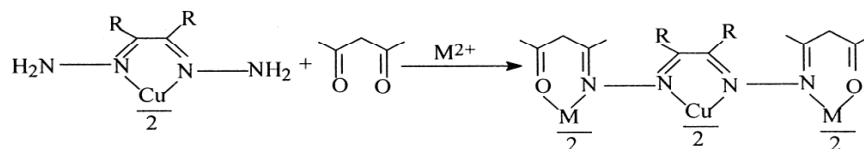


Fig. 2. Scheme of reaction.

solution of complexes in dioxane. The FTIR spectra of the complexes in KBr pellets were recorded on a Varian

where $R = \text{Ph}$. When $M = \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}$, the complexes are called bimetallic trinuclear complexes with the hetero at-

Table 1. Analytical data of the complexes of BAHBD

Compds.	Mol. wt. Found (Calcd.)	Found (Calcd.) %							Λ_m in mho cm ² mol ⁻¹
		Ni	Cu	Co	N ^a	C	H	X	
[Cu ₃ (BAHBD) ₂ Cl ₂ (H ₂ O) ₄] (Greenish blue)	1140 (1134)	-	17.01 (16.81)	-	9.72 (9.88)	51.22 (50.81)	4.91 (4.94)	6.32 (6.26)	11.13
[Cu ₃ (BAHBD) ₂ Br ₂ (H ₂ O) ₄] (Blue)	1229 (1222)	-	15.85 (15.59)	-	9.19 (9.16)	47.46 (47.11)	4.62 (4.58)	13.28 (13.07)	11.42
[Cu ₃ (BAHBD) ₂ (NO ₃) ₂ (H ₂ O) ₄] (Greenish blue)	1198 (1188)	-	16.26 (16.03)	-	11.89 (11.77)	48.65 (48.45)	4.81 (4.71)	-	13.24
[Ni ₂ Cu(BAHBD) ₂ Cl ₂ (H ₂ O) ₄] (Greenish yellow)	1128 (1123)	10.52 (10.44)	6.16 (5.65)	-	10.23 (9.96)	51.95 (51.25)	4.66 (4.27)	6.82 (6.30)	15.35
[Ni ₂ Cu(BAHBD) ₂ Br ₂ (H ₂ O) ₄] (Greenish yellow)	1120 (1213)	9.99 (9.68)	5.42 (5.23)	-	9.34 (9.23)	48.13 (47.49)	4.26 (3.95)	13.48 (13.17)	15.68
[Ni ₂ Cu(BAHBD) ₂ (NO ₃) ₂ (H ₂ O) ₄] (Green)	1185 (1177)	10.12 (9.97)	5.48 (5.39)	-	9.82 (9.51)	48.23 (48.93)	4.27 (4.07)	-	16.66
[Co ₂ Cu(BAHBD) ₂ Cl ₂ (H ₂ O) ₄] (Yellow ochre)	1129 (1124)	-	5.86 (5.65)	10.55 (10.46)	10.11 (9.96)	51.08 (51.23)	5.02 (4.98)	8.42 (8.30)	19.35
[Co ₂ Cu(BAHBD) ₂ Br ₂ (H ₂ O) ₄] (Grey)	1222 (1213)	-	5.29 (5.23)	9.86 (9.71)	9.46 (9.23)	47.52 (47.47)	4.69 (4.61)	13.26 (13.17)	20.13
[Co ₂ Cu(BAHBD) ₂ (NO ₃) ₂ (H ₂ O) ₄] (Grey)	1187 (1177)	-	5.37 (5.39)	10.18 (10.01)	10.28 (9.51)	49.12 (48.93)	4.62 (4.07)	-	21.68

^aIncluding nitrogen of nitrate groups where ever present.

oms occupying the terminal positions and when M = Cu^{II}, it is called a homo trinuclear complex.

IR spectra :

The spectra of the precursor and the trinuclear metal complexes were compared with the spectra of isostructural bis(benzil dihydrazone)nickel(II) complexes¹⁰. The IR spectra of the precursor are identical with the corresponding nickel(II) complexes. The IR spectral data of the com-

plexes are presented in Table 2.

Thermal analysis :

The IR spectra of the complexes indicated the presence of coordinated water molecules. In order to confirm it, thermal analyses were carried out. The thermograms of the complexes exhibit almost an identical pattern, displayed in Fig. 3.

In Cu-Cu-Cu chloro system, there was no mass loss

Table 2. Infrared spectral data of complexes²²⁻²⁴

[Ni ₂ Cu(BAHBD) ₂ Cl ₂ (H ₂ O) ₄]	[Ni ₂ Cu(BAHBD) ₂ Br ₂ (H ₂ O) ₄]	[Ni ₂ Cu(BAHBD) ₂ (NO ₃) ₂ (H ₂ O) ₄]	Assignments
3460	3460	3460	vO-H of coordinated water
1630	1625	1623	Due to azomethine group
1470	1465	1463	vC-O
1020	1021	1023	δ_w H ₂ O
-	-	1035	NO ⁻ group
		1285	(Coordinated)
		1495	
485	485	484	vM-N
375	370	373	vM-O

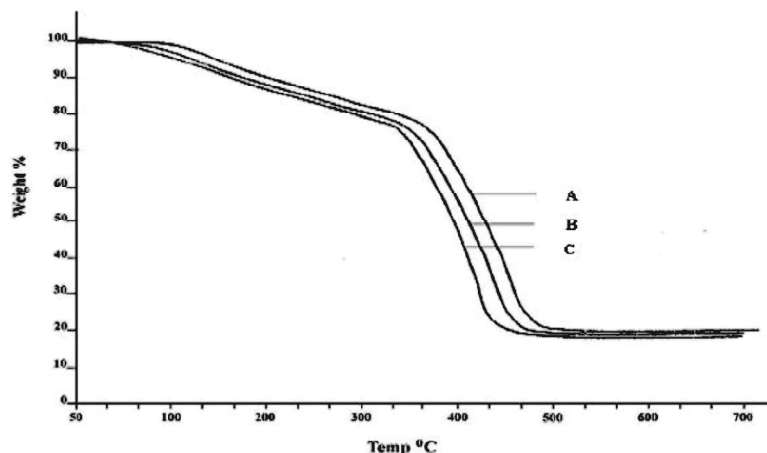


Fig. 3. Thermograms of the complexes, sample weight : 100 mg; heating rate : 10 °C min⁻¹; where, (A) = [Cu₃(BAHBD)₂Cl₂(H₂O)₄], (B) = [Co₂Cu(BAHBD)₂Cl₂(H₂O)₄], (C) = [Ni₂Cu(BAHBD)₂Cl₂(H₂O)₄].

up to 110 °C, indicating the absence of lattice water²⁵. The complex loses weight at ~130 °C with a weight loss of 6.21% which corresponds to the loss of four water molecules (6.35% theoretical) in a single step. Such behaviour is characteristic of coordinated water in the same chemical environment²⁶. The complex exhibits thermal stability upto 370 °C after which an accelerated weight loss occurs which may be due to the decomposition of organic component present in the complex. This trend continues until 470 °C with a residue of 20.91% (21.06% theoretical) which corresponds to the formation of metal oxide. The same thermal behavior is exhibited by the Ni-Cu-Ni as well as Co-Cu-Co systems. The thermal stabi-

lity of the complexes are in the order Cu-Cu-Cu > Co-Cu-Co > Ni-Cu-Ni systems. The thermo analytical data of the complexes are given in Table 3.

Electronic spectra :

The Cu-Cu-Cu systems exhibited an additional band at ~15385 cm⁻¹ (650 nm), and have magnetic moment values in the range 1.52–1.56 B.M. per copper(II) ion (Table 4). The substantial decrease of μ_{eff} as compared to the mononuclear [Cu(BDH)X₂(H₂O)₂] complex may be attributed to weak antiferromagnetic couplings of unpaired electrons, one on each Cu^{II} ion in the Cu-Cu-Cu system at room temperature²⁷. This corroborates the polynuclear nature of the complex^{28,29}.

Table 3. Thermoanalytical data of complexes

Complex	Temperature range of decomposition (°C)	% of Wt. loss		Remarks
		Found	(Calcd.)	
[Cu ₃ (BAHBD) ₂ Cl ₂ (H ₂ O) ₄]	130	6.21	(6.35)	Loss of four water molecules
	480	20.91	(21.06)	Formation of metal oxides
[Co ₂ Cu(BAHBD) ₂ Cl ₂ (H ₂ O) ₄]	120	6.29	(6.41)	Loss of four water molecules
	460	20.97	(21.11)	Formation of metal oxides
[Ni ₂ Cu(BAHBD) ₂ Cl ₂ (H ₂ O) ₄]	100	6.38	(6.41)	Loss of four water molecules
	430	20.98	(21.12)	Formation of metal oxides

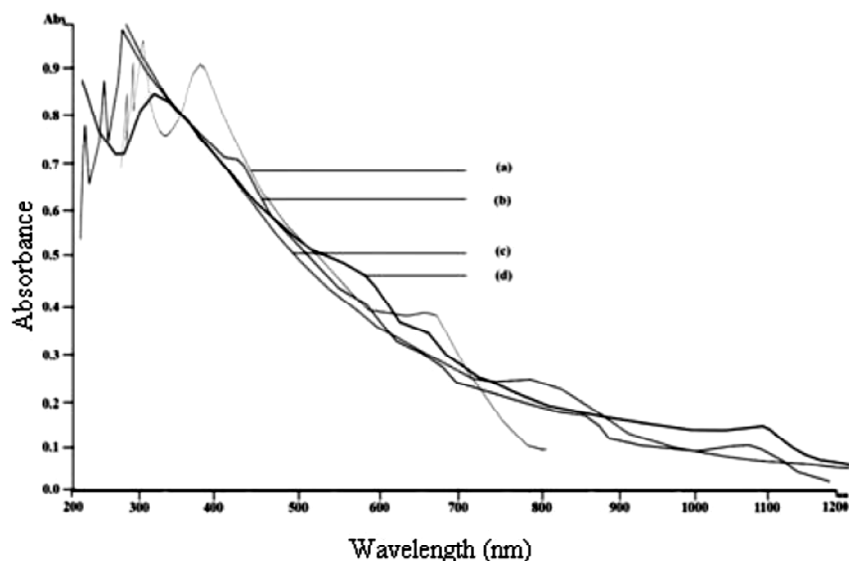


Fig. 4. Electronic spectra of complexes : (a) = $[\text{Cu}_3(\text{BAHBD})_2\text{Cl}_2(\text{H}_2\text{O})_4]$, (b) = $[\text{Ni}_2\text{Cu}(\text{BAHBD})_2\text{Cl}_2(\text{H}_2\text{O})_4]$, (c) = $[\text{Cu}(\text{BDH})\text{X}_2(\text{H}_2\text{O})_2]$, (d) = $[\text{Co}_2\text{Cu}(\text{BAHBD})_2\text{Cl}_2(\text{H}_2\text{O})_4]$.

Table 4. Electronic spectral data and magnetic moment values of copper complexes

Complexes	μ_{eff} in B.M. ^a	Ligand field band positions in cm^{-1} (${}^2E_g \rightarrow {}^2T_{2g}$)
$[\text{Cu}(\text{BDH})\text{X}_2(\text{H}_2\text{O})_2]$	1.83–1.87	14085
$[\text{Cu}_3(\text{BAHBD})_2\text{X}_2(\text{H}_2\text{O})_4]$ ^a per Cu.	1.52–1.56	15385

The Table 5 incorporates electronic spectral data, magnetic moment, crystal field and nephelauxetic param-

eters of hetero bimetallic trinuclear complexes involving Co^{II} while Table 6 and Table 7 record the electronic spectral data and tetragonal parameters of Ni^{II} complexes respectively.

The Co-Cu-Co system exhibit bands in the region $\sim 9090 \text{ cm}^{-1}$ (1100 nm), 15625 cm^{-1} (640 nm) and 17857 cm^{-1} (560 nm) and are assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3), transitions respectively (Table 5) in an approximately octahedral field around cobalt(II) centers³⁰. The ligand

Table 5. Electronic spectral data, magnetic moment, crystal field and nephelauxetic parameters of cobalt complexes

Complexes	μ_{eff} in B.M. ^a	Ligand field band positions in cm^{-1}						
		${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1)	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2)	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3)	$10 Dq$ (cm^{-1})	B (cm^{-1})	β	β^0 (%)
$[\text{Co}_2\text{Cu}(\text{BAHBD})_2\text{Cl}_2(\text{H}_2\text{O})_4]$	4.73	9090	15625	17857	9982	665	.594	40
$[\text{Co}_2\text{Cu}(\text{BAHBD})_2\text{Br}_2(\text{H}_2\text{O})_4]$	4.75	9300	16000	18500	10342	689	.616	38
$[\text{Co}_2\text{Cu}(\text{BAHBD})_2(\text{NO}_3)_2(\text{H}_2\text{O})_4]$ ^a per Cu and per Co.	4.79	8900	16300	19100	9908	762	.681	32

Table 6. Electronic spectral data (in cm^{-1}) and magnetic moment values of nickel complexes

Complexes	μ_{eff} in B.M. ^a	${}^3B_{1g} \rightarrow {}^3B_{2g}$	${}^3B_{1g} \rightarrow {}^3E_g$	${}^3B_{1g} \rightarrow {}^3A_{2g}$	${}^3B_{1g} \rightarrow {}^3E_g$	${}^3B_{1g} \rightarrow {}^3A_{2g}$
		(${}^3T_{2g}$)	(${}^3T_{2g}$)	(${}^3T_{1g}$)	(${}^3T_{1g}$)	(${}^3T_{1g}(P)$)
$[\text{Ni}_2\text{Cu}(\text{BAHBD})_2\text{Cl}_2(\text{H}_2\text{O})_4]$	2.98	9175	11365	14815	17240	24390
$[\text{Ni}_2\text{Cu}(\text{BAHBD})_2\text{Br}_2(\text{H}_2\text{O})_4]$	3.12	8530	10780	14740	17000	25500
$[\text{Ni}_2\text{Cu}(\text{BAHBD})_2(\text{NO}_3)_2(\text{H}_2\text{O})_4]$ ^a per Cu and per Ni.	3.41	8570	10830	15000	17500	25900

Table 7. Tetragonal parameters D_t , D_q^E , D_q^A and D_s of Ni^{II} complexes

Complexes	D_t (cm ⁻¹)	D_q^E (cm ⁻¹)	D_q^A (cm ⁻¹)	D_s (cm ⁻¹)
[Ni ₂ Cu(BAHBD) ₂ Cl ₂ (H ₂ O) ₄]	250	918	480 (H ₂ O)	-352
[Ni ₂ Cu(BAHBD) ₂ Br ₂ (H ₂ O) ₄]	257	853	403 (H ₂ O)	-323
[Ni ₂ Cu(BAHBD) ₂ (NO ₃) ₂ (H ₂ O) ₄]	258	857	405 (H ₂ O)	-363

ESR spectra :

The complex [Cu₃(BAHBD)₂Cl₂(H₂O)₄] was examined by ESR spectroscopy (Fig. 5) and the value of g_{II} and g_I were determined for the proper magnetic field parameters required on octahedral symmetry for the copper(II) complex. The ESR spectral data is given in Table 8.

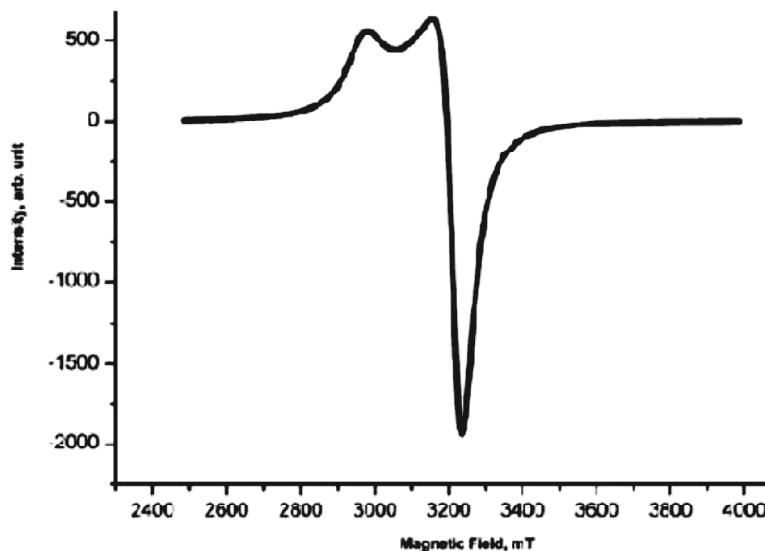


Fig. 5. ESR spectra of the complex [Cu₃(BAHBD)₂Cl₂(H₂O)₄].

filed parameters have been calculated by the crystal field approximation³¹ which agrees with the proposed geometry. The magnetic moment value of the complexes lie in the range 4.73–4.79 B.M. The increase in the values of B and β suggest that the order of the extent of delocalization of d electrons in the complexes is chloro > bromo > nitro.

In Ni-Cu-Ni system, new bands at ~ 9175 cm⁻¹ (1090 nm), 11365 cm⁻¹ (880 nm), 14815 cm⁻¹ (675 nm), 17240 cm⁻¹ (580 nm) and 24390 cm⁻¹ (410 nm) are observed. These may be due to tetragonally distorted nickel(II) species³² and are assignable to ${}^3B_{1g} \rightarrow {}^3B_{2g}$ (${}^3T_{2g}$), ${}^3B_{1g} \rightarrow {}^3E_g$, ${}^3B_{1g} \rightarrow {}^3A_{2g}$, ${}^3B_{1g} \rightarrow {}^3E_g$ (${}^3T_{1g}$), and ${}^3B_{1g} \rightarrow {}^3A_{2g}$ [${}^3T_{1g}(P)$] transitions respectively (Table 6). The values of tetragonal parameters calculated by known methods³³ indicate that the ligand BAHBD creates a stronger crystal field than the axial water molecules. The room temperature magnetic moment values lie in the range 2.98–3.41 B.M. per nickel(II) ion.

Based on the foregoing observations, the following tentative structure may be proposed.

Table 8. ESR spectral data of copper complex

Complex	g_{II}	g_I	H_{II}	H_I
[Cu ₃ (BAHBD) ₂ Cl ₂ (H ₂ O) ₄]	2.2648	2.1129	298.063	319.491

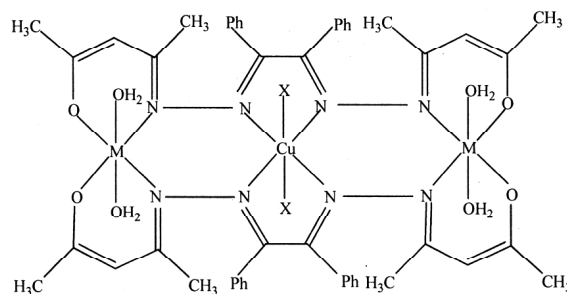


Fig. 6. Structure of the metal complexes; where M = Cu^{II}, Ni^{II}, Co^{II} and X = Cl, Br, NO₃.

Antifungal activity :

The antifungal screening tests reveal that all the compounds are antifungal active. The result is reported in Table 9.

It is generally observed that metal chelates have higher antifungal activity than the free ligand due to an increase in cell permeability. The lipid membrane which surrounds the cell favours only the passage of lipid soluble materials and it is known that liposolubility is an important factor controlling antifungal activity³⁴⁻³⁶. Such screening of various organic compounds and identifying the active agents are essential because the successful prediction of a lead molecule and the drug like properties at the onset of drug design will pay off later in drug development. The observed antifungal activity of the ligands and their metal complexes find support from the literature³⁷⁻⁴⁰ because of the operation of the following factors.

Chelation increases the liposolubility of the complexes which enhances the penetration of the complexes into the lipid membrane. The organic skeleton of the complexes function as a lipophilic group to drive the compound through the semipermeable membrane of the cell and blocks the metal binding sites in the enzymes of microorganisms. The complexes also disturb the respiration process of the cell blocking the synthesis of proteins which restrict the further growth of the organisms.

The extension of chelation in the metal complexes as compared to the precursor one tends to render these complexes more active towards antifungal behavior. The homo trinuclear complexes are found to exhibit greater antifungal activity than the hetero trinuclear counter parts. The relative order of such activity for the complexes is Cu-Cu-Cu > Ni-Cu-Ni > Co-Cu-Co > [Cu(BDH)₂]. Further, it is observed that for a given system, the bromo complexes exhibit maximum effect towards antifungal growth while the nitrate complexes have minimum. Thus with respect to the anion, the homo/hetero trinuclear complexes follow the trend Br > Cl > NO₃ which is in conformity with corresponding acid strength.

The statistical calculations adopting two ways ANOVA test⁴¹ have also indicated significant difference with respect to different treatment of complexes.

Table 9. Fungitoxicity of the complexes of BAHBD at different concentration levels

Complex	% Inhibition over control														
	<i>Aspergillus niger</i>			<i>Helminthosporium oryzae</i>			<i>Fusarium oxysporium</i>								
Concentration (µg mL ⁻¹)	100	200	400	800	1000	100	200	400	800	1000	100	200	400	800	1000
[Cu(BDH) ₂]	19.46	24.38	33.47	43.56	48.67	23.42	32.67	38.76	43.87	48.67	26.56	35.56	43.26	49.37	54.87
[Cu ₃ (BAHBD) ₂ Cl ₂ (H ₂ O) ₄]	23.33	30.18	38.56	47.22	52.61	26.84	37.77	42.15	48.52	52.23	30.15	39.68	46.29	53.17	59.32
[Cu ₃ (BAHBD) ₂ Br ₂ (H ₂ O) ₄]	29.33	37.54	46.29	52.43	57.77	34.26	44.69	48.34	54.28	63.39	35.62	43.89	51.62	59.17	65.37
[Cu ₃ (BAHBD) ₂ (NO ₃) ₂ (H ₂ O) ₄]	20.13	25.47	34.81	40.26	48.92	22.51	29.36	34.87	43.66	51.28	29.46	38.02	44.56	51.29	57.59
[Ni ₂ Cu(BAHBD) ₂ Cl ₂ (H ₂ O) ₄]	20.99	26.87	32.63	43.18	51.25	20.62	28.93	31.25	43.34	50.52	28.63	37.77	43.83	50.78	56.68
[Ni ₂ Cu(BAHBD) ₂ Br ₂ (H ₂ O) ₄]	25.83	32.19	38.75	50.23	52.95	22.44	30.18	34.63	48.59	54.32	33.23	42.76	48.33	53.68	56.11
[Ni ₂ Cu(BAHBD) ₂ (NO ₃) ₂ (H ₂ O) ₄]	17.54	23.17	28.52	35.91	19.55	19.55	27.69	29.62	41.13	49.59	26.38	33.29	41.85	49.68	54.53
[Co ₂ Cu(BAHBD) ₂ Cl ₂ (H ₂ O) ₄]	19.58	25.64	30.35	42.29	50.67	19.69	29.38	30.11	42.28	48.53	25.61	36.29	41.74	49.98	55.39
[Co ₂ Cu(BAHBD) ₂ Br ₂ (H ₂ O) ₄]	23.55	31.73	37.32	49.11	51.38	21.58	31.11	32.29	45.75	52.87	32.18	41.36	46.39	52.55	55.84
[Co ₂ Cu(BAHBD) ₂ (NO ₃) ₂ (H ₂ O) ₄]	16.26	22.24	28.11	34.84	43.82	18.36	26.33	28.61	40.62	47.53	24.66	35.39	39.36	46.52	53.22

Conclusion

The experimental findings and the supporting evidences lead us to the following conclusions.

- (i) The substantial reduction in the μ_{eff} value of the copper complex at room temperature and very low molar conductance values of the complexes indicate that the complexes are polynuclear and neutral in nature.
- (ii) The presence of four water molecules in the co-ordination sphere of all the complexes is evidenced by their degradation pattern, as observed in the thermograms which is amply supported by their IR spectra.
- (iii) The thermal stability of the complexes are in the order Cu-Cu-Cu > Co-Cu-Co > Ni-Cu-Ni systems.
- (iv) The spectroscopic evidences such as IR, Visible and ESR are adequately in favour of nearly octahedral coordination of ligands around the metal ions.
- (v) The antimicrobial activity of metal complexes is imputed to large chelating environment around the metal ions. The relative order of activity is found to be Cu-Cu-Cu > Ni-Cu-Ni > Co-Cu-Co > [Cu(BDH)₂].

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