

Synthesis, characterization and antimicrobial activities of homo- and bimetallic trinuclear complexes of a 30-membered macrocyclic ligand [30] 1,4,5,9,10,13,16,19,20,24,25,28-dodecaaza-2,3,11,12,17,18,26,27-octaphenyl-6,8,21,23-tetramethylcyclotriaconta-1,3,5,8,10,12,16,18,20,23,25,27-dodecaene (L)

S. K. Tripathy^a, A. Panda^a, P. K. Das^b, N. K. Behera^a and A. K. Panda^{*a}

^aSchool of Chemistry, Sambalpur University, Jyotivihar, Burla-768 019, Odisha, India

E-mail : ashokspanda@yahoo.co.in

^bG. M. College (Autonomous), Sambalpur, Odisha, India

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Abstract : A series of homo- and bimetallic trinuclear macrocyclic Schiff base metal complexes, with different transition metal ions such as Cu^{II}, Ni^{II} and Co^{II} with the titled ligand has been prepared using ethylenediamine-bisbenzilmonohydrazone Ni^{II} complexes as metallo-ligand. The metal complexes have been characterized on the basis of analytical and spectral data, thermal analysis, magnetic and conductivity measurements. Based on the results, tentative structures of the complexes have been proposed. The metallo-ligand as well as the macrocyclic complexes is found to have good antimicrobial activities against the pathogenic fungus *Aspergillus niger*, *Helminthosporium oryzae* and *Fusarium oxysporium*.

Keywords : Macrocyclic complex, thermal analysis, antimicrobial activity, conductivity measurements.

Introduction

A large number of macrocycles have been synthesized on the basis of equilibrium template effect, enunciated by Thompson and Busch¹⁻⁵. These macrocycles provide some illuminating attractions from structural considerations and can be classified into two categories, namely macrocycles with benzenoid units and non-benzenoid macrocycles apart from some unusual macrocycles. Amongst the benzenoid macrocycles, self condensation of *o*-aminobenzaldehyde represents a classical example which, even in the absence of metal ions, undergo condensation at a slow rate to give products containing anhydrotrimers and tris-anhydrotetramers⁵⁻⁷. The subject matter has been thoroughly investigated^{8,9} and macrocyclic complexes of nickel(II) have been found where condensation of *o*-aminobenzaldehyde showed complexes containing trimeric and tetrameric units in the macrocyclic frames¹⁰⁻¹². Several other reports have appeared containing structurally different benzenoid units and the sub-

ject matter has been reviewed¹³⁻¹⁹. Other macrocyclic compounds designed with pyridine as part of the structural units have also been synthesized in coordination with a range of metal ions²⁰. Complexes have been synthesized with various structural modification of the main skeleton of the macrocyclic ring by introducing various substituents in the ring frame. A large number of such macrocycles have been reported with different structural features and a variety of substituents on the macro ring²¹⁻²³.

Herein, we report the synthesis, characterization and antimicrobial activity of a new series of homo- and bimetallic trinuclear macrocyclic complexes. Our objective is to change the ligand field strength around the metal centres of the macrocycle, so as to affect and alter some physico-chemical behavior of the complexes. It is observed that the structural characteristics of macrocyclic ligands exhibit metal based redox behaviour even on introducing α -diimine and isolated β -diimine functions. Attention was focussed to synthesize macrocyclic ligands

containing wider electron delocalization, particularly coupled with α -diimino groups.

Benzilmonohydrazone²⁴ was chosen as the model starting material and it was envisaged that the carbonyl function can be condensed with amine groups and a new series of complexes containing the open chain ligands could be derived. *In situ* condensation of benzilmonohydrazone and benzil in presence of Ni^{II} ion has been effective with 1,2-diaminoethane giving rise to the precursor complexes. Ethylenediimino-bis-(benzilmonohydrazone) nickel(II), (Fig. 1(a)) and ethylenediimino-bis-(benzil) nickel(II), (Fig. 1(b)) respectively.

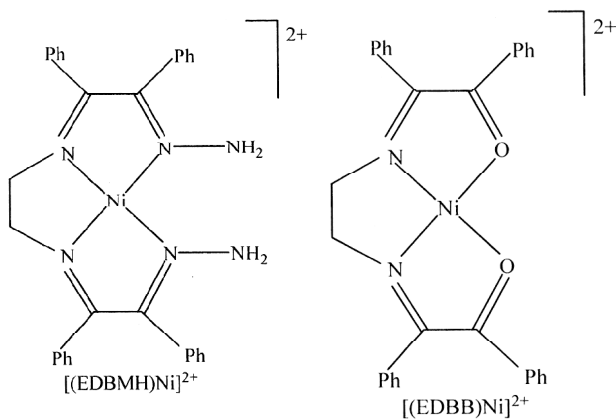


Fig. 1(a)

Fig. 1(b)

The terminal pendant -NH_2 groups and the coordinated carbonyl groups of [1(a)] and [1(b)] respectively are now in suitable geometrical orientation to undergo further condensation with ketone and amine functions leading to the formation of the homo and polymetallic macrocyclic complexes.

Based on the above facts, we focus on designing new trinuclear Schiff base metal complexes. The present communication deals with the synthesis of a series of homo and polymetallic trinuclear metal complexes with the titled ligand derived from the metallo ligand ethylenediamine bis-(benzilmonohydrazone) Ni^{II} and pentane-2,4-dione (acetylacetonate) in a template reaction. The complexes were investigated for antimicrobial activity.

Experimental

All the chemicals and solvents used are either of Glaxo or Merck grade. The solvents were purified before use in the reaction. The metal contents of all the complexes were estimated by standard methods²⁵. The percentage of nitrogen was calculated by combustion method. The values obtained were also supported by semi micro Kjeldahl's method. Carbon and hydrogen were estimated with CHN micro analyser. The IR spectra of the metal complexes were recorded on a Varian spectrophotometer, Australia, in KBr pellets in the region $4000\text{--}400\text{ cm}^{-1}$. The electronic spectra of the complexes in DMSO were recorded on a Perkin-Elmer-398 spectrophotometer. The conductivity of the complexes in DMF was measured with a Philips conductivity bridge (model CLO-06, cell constant 0.5 cm^{-1}) using $1 \times 10^{-3}\text{ M}$ solution of the complex in DMF. The room temperature magnetic moment values are determined by Guoy method with mercury tetra thiocyanatocobaltate(II), $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The electron spin resonance spectra were recorded as powder sample (poly crystalline) on an E-112EPR spectrophotometer with field set at 3200G, scan range $2.0 \times 1\text{ kg}$, modulation frequency 100 KHz, microwave frequency 9.4 GHz receiver gain 10×10^2 and modulation amplitude $0.63 \times 10\text{ G}$. The thermogravimetric analysis was carried out in a DTA/TG instrument STA 409C in nitrogen atmosphere.

Synthesis of the ligand and its metal complexes :

The precursor and the trinuclear metal complexes were prepared in following three steps.

(a) Preparation of ethylenediamine-bis-(benzilmonohydrazone) :

Ethylenediimino-bis-(benzilmonohydrazone) [EDBMH] was prepared following the literature method²⁶.

(b) Preparation of mono nuclear metal(II) complexes :

The mono nuclear metal(II) complexes of BED (precursor complexes) were prepared according to literature method²⁷. The analytical data of the precursor complexes are given in Table 1.

Table 1. Analytical data of precursor complexes

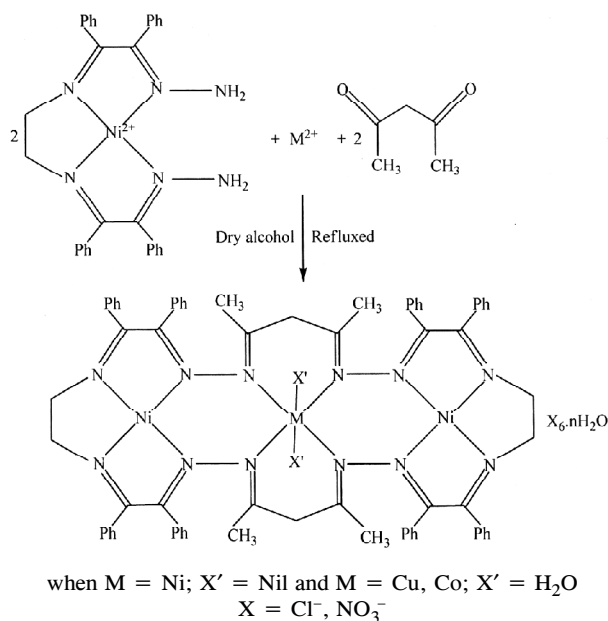
Complexes	Colour	Mol. wt.	Analysis (%) : Found (Calcd.)				
			Ni	C	H	N	Cl
[Ni(EDBMH)Cl ₂]	Yellow	601.7	9.76 (9.55)	59.83 (59.68)	4.65 (4.49)	–	11.80 (11.68)
[Ni(EDBMH)(NO ₃) ₂].5H ₂ O	Pink	681.7	8.61 (8.38)	52.81 (52.62)	4.55 (4.42)	16.43 (16.36)	– –

(c) Preparation of homo and bimetallic trinuclear complexes :

Ethylenediimino-bis-(benzilmonohydrazone) nickel(II) nitrate (0.53 g, 1.0 mmol), suspended in ethanol and Ni(NO₃)₂.6H₂O (0.15 g, 0.5 mmol) was taken in a 100 mL two necked round bottom flask fitted with a reflux condenser. The mixture was refluxed for 3 h, then pentane-2,4-dione (acetylacetonone) (0.10 g, 1.0 mmol) was added to it and was again refluxed for another 3 h. On cooling to room temperature a cabinet grey colored precipitate was obtained. It was filtered and washed several times with ethanol and finally dried over fused calcium chloride in a desiccator.

The other homo and bimetallic trinuclear nitrate or chloride complexes were prepared in an identical method by taking appropriate metal salts and the corresponding precursor complexes in stoichiometric amounts. The analytical data of the complexes are incorporated in Table 2.

The scheme of the reaction is given below.



Results and discussion

The complexes are highly coloured and have melting

Table 2. Analytical data of trinuclear complexes

Complexes	Colour	Analysis (%) : Found (Calcd.)					
		Ni	M	C	H	N	Cl
[Ni ₃ L](NO ₃) ₆ .5H ₂ O	Cabinet grey	10.62 (10.55)	–	41.68 (41.57)	4.40 (4.33)	14.59 (14.54)	–
[Ni ₃ L]Cl ₆	Yellowish white	11.98 (11.92)	–	49.54 (49.34)	4.41 (4.38)	11.62 (11.51)	15.10 (14.59)
[Ni ₂ CoL(H ₂ O) ₂](NO ₃) ₆ .2.5H ₂ O	Pale yellow	6.89 (6.84)	3.51 (3.45)	49.9 (49.5)	4.11 (4.06)	15.00 (14.86)	–
[Ni ₂ CoL(H ₂ O) ₂]Cl ₆	Spring green	7.82 (7.77)	4.10 (3.92)	56.9 (56.3)	4.31 (4.29)	11.35 (11.26)	14.80 (14.20)
[Ni ₂ CuL(H ₂ O) ₂](NO ₃) ₆ .1.5H ₂ O	Brick red	7.08 (7.04)	3.91 (3.85)	51.05 (51.01)	3.90 (3.82)	15.60 (15.30)	–
[Ni ₂ CuL(H ₂ O) ₂]Cl ₆	Lemon green	8.11 (7.94)	4.39 (4.34)	57.8 (57.5)	4.18 (4.10)	11.80 (11.50)	14.66 (14.58)

L = 1,4,5,9,10,13,16,19,20,24,25,28-dodecaaza-2,3,11,12,17,18,26,27-octaphenyl-6,8,21,23-tetramethylcyclotriaconta-1,3,5,8,10,12,16,18,20,23,25,27-dodecaene.

point above 250 °C. They are insoluble in common organic solvents but are soluble in polar solvents like DMF, DMSO and dioxane. They show high molar conductance values ($140\text{--}150 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) suggesting them to be electrolyte in nature.

The structures of the complexes have been established on the basis of different spectral studies and magnetic properties as discussed subsequently and a tentative structure for the complexes has been suggested.

IR spectra :

In the present investigation, the IR spectra of the trinuclear macrocyclic complexes are compared with the precursor ethylenediamine-bis-(benzilmonohydrazone) nickel(II) complexes. They exhibit identical spectral pattern suggesting them to be isostructural. Formation of trinuclear macrocyclic complexes brings about drastic changes in the spectral pattern of the precursor complex²⁸. The IR spectra become more complicated. However, efforts have been made to identify certain bands, which provide vital information on the mode of bonding of the ligand framework with the metal ions. The IR spectra of $[\text{Ni}_3\text{L}]\text{Cl}_6$ is shown in the Fig. 2 given below.

It is observed that the precursor bands due to $\nu\text{C}=\text{O}$

and νNH_2 are totally absent in the trinuclear complexes. Rather the band in the precursor complex due to $\nu\text{C}=\text{N}$ in the vicinity of 1590cm^{-1} which is observed for ethylene-bis-(benzilmonohydrazone) is split into a doublet with higher intensity indicating the presence of more than one $\text{C}=\text{N}$ groups in different chemical environment²⁹. This amply suggests that Schiff base condensation reaction has taken place. The fundamental frequencies due to N-N have also been observed in the range of $1178\text{--}1186 \text{cm}^{-1}$.

In addition to these bands, Ni_2Co complexes show a very broad band with its centre of gravity $\sim 3480 \text{cm}^{-1}$ which has been assigned to νOH arising out of coordinated water. The presence of coordinated water is further supported by another band at 1025cm^{-1} due to $\delta\text{wH}_2\text{O}$. The broadness of the band is probably due to presence of inter/intra molecular hydrogen bonding.

In order to ascertain the nature of the NO_3^- group (coordinated or free), the spectra of the nitrate complexes were recorded. However, no bands in the vicinity of 1285 and 1040cm^{-1} due to coordinated NO_3^- groups were observed. In the lower frequency region a band $\sim 478 \text{cm}^{-1}$ assignable³⁰ to $\nu\text{M-N}$ were observed for all the complexes. Thus from the IR spectral data it is concluded that,

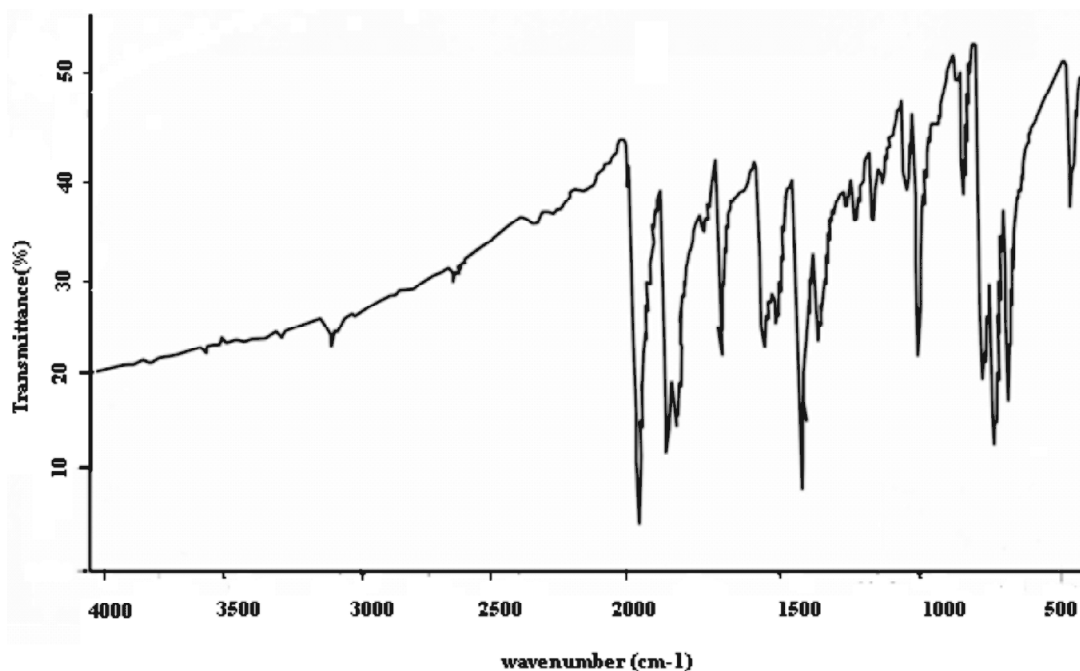


Fig. 2. IR spectra of $[\text{Ni}_3\text{L}]\text{Cl}_6$.

- (i) All the metal centers, in homo and bimetallic complexes, are coordinated to the ligand framework through azomethine ($>C=N$) nitrogen satisfying four coordination numbers of the metal ions.
- (ii) The Ni_2Co and Ni_2Cu bimetallic complexes contain water molecules which are linked to the central metal ion in trans-axial positions satisfying its 5th and 6th coordination numbers. The IR spectral data of the complexes are given in Table 3.
- nates the possibility of the presence of lattice water³¹. The weight loss at a comparatively higher temperature of ~ 180 °C corresponding to the loss of two water molecules³² suggests that they are coordinated, in conformity with our earlier observation from IR spectral investigations. The endothermic peaks occurring in the second and third step at 350 and ~ 490 °C, respectively, correspond to the decomposition of organic constituents, leaving behind the respective metal oxides.

Table 3. IR spectral data of trinuclear complexes

$[Ni_3L]Cl_6$	$[Ni_2CoL(H_2O)_2](NO_3)_6$ nH ₂ O	$[Ni_2CuL(H_2O)_2]Cl_6$	Assignments
-	3480	3450	vO-H of coordinated water
3036	3039	3042	vN-H
1025	1021	1023	δwH_2O
478	480	484	vM-N
1178	1182	1186	vN-N
1595	1590	1593	Azomethine group

Thermal analysis :

The thermograms of Ni_2Co and Ni_2Cu complexes follow the same pattern of thermal decomposition. The complexes remain almost unaffected upto 160 °C, which elimi-

Electronic spectra and magnetic properties :

The electronic spectra of the precursor complexes are dominated by intense bands observed in the visible and UV region. However, the electronic spectra of the

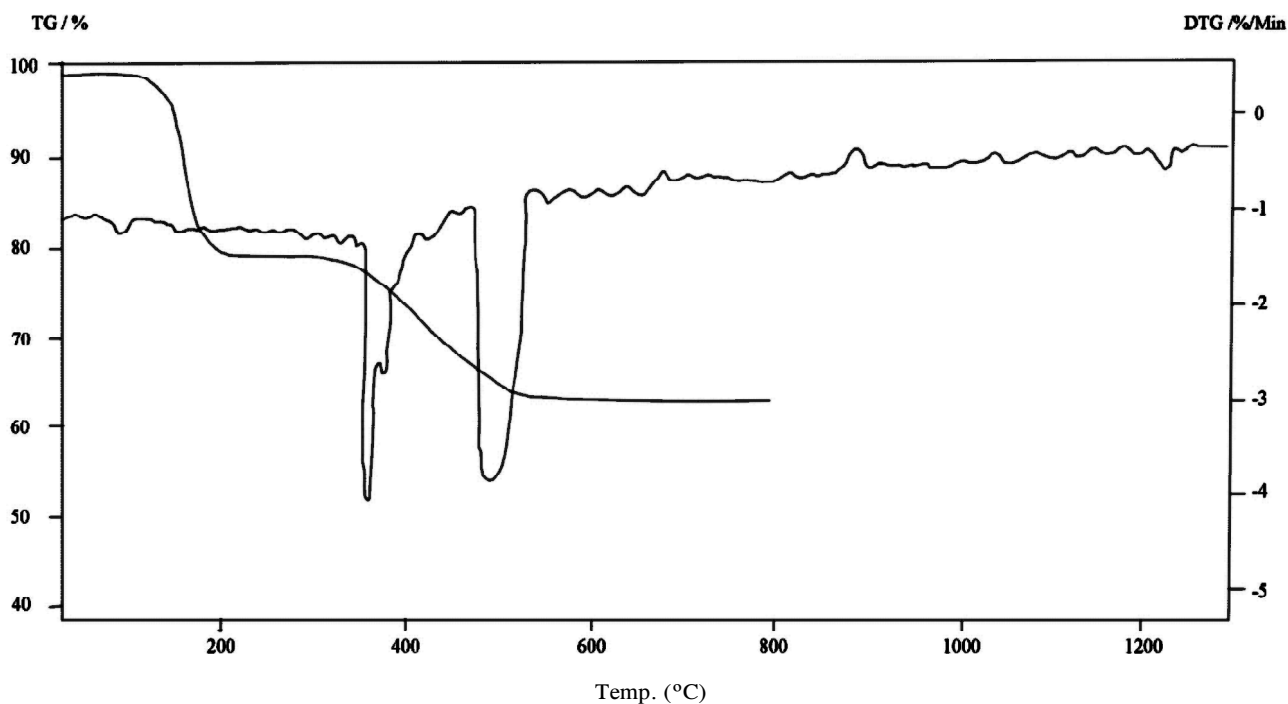


Fig. 3. Thermogram of $[Ni_2CuL(H_2O)_2]Cl_6$.

trinuclear complexes exhibit additional features in addition to the precursor complexes. The precursor complexes show two bands near 19000 cm^{-1} and the other at a higher frequency region near 29000 cm^{-1} . The former band has a lower intensity than one in the UV-region. These have been assigned to ${}^1A_{2g} \rightarrow {}^1A_{1g}$ transition under a square planar environment for Ni^{II} ion³³⁻³⁵. The more intense band is believed to arise from L→M charge transfer transition. The precursor complexes are diamagnetic corresponding to square planar geometry.

The electronic spectral band of $[\text{Ni}_3\text{L}]\text{X}_6 \cdot n\text{H}_2\text{O}$ exhibit only one band at 22730 cm^{-1} . The width of the band manifests that the band represents a group of two to three transitions arising out of ${}^1A_{2g} \rightarrow {}^1A_{1g}$, ${}^1A_{2g} \rightarrow {}^1B_{2g}$ and ${}^1A_{2g} \rightarrow {}^1E_g$ transition under a square planar environment and superimposed into a single one³⁶. This is confirmed from diamagnetic nature of the complexes.

The complex $[\text{Ni}_2\text{CoL}(\text{H}_2\text{O})_2]\text{X}_6$ is paramagnetic. The electronic spectra of this complex was found to exhibit four bands at 10000 cm^{-1} (ν_1), 15400 cm^{-1} (ν_2), 17480 cm^{-1} and 18900 cm^{-1} (ν_3) [a doublet] and, at 22200 cm^{-1} (ν_4). The first band is due to central cobalt(II) ion in an octahedral symmetry³⁷ assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition. The second band at 15400 cm^{-1} was due to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition. The third band appears as a doubly split band due to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition of the cobalt(II) centre. The multiplicity of such band can be interpreted due to six coordinated cobalt(II) centre of an approximately C_2 symmetry³⁸. From the spectroscopic bands assigned for Co^{II} in the trinuclear complex, the interelectronic repulsion parameter B , the crystal field parameter D_q and nephelauxetic parameters β and β^0 have been calculated³⁹ which are incorporated in the Table 4. The value of (ν_3) has been recorded as 18150 cm^{-1} which is the mean of the doublet appearing at 17480 cm^{-1} and 18900 cm^{-1} for calculation of above parameters.

tion of d -electrons onto the ligand orbitals on complexation.

Besides the above bands, a more intense band at 22200 cm^{-1} is also observed due to ${}^1A_{2g} \rightarrow {}^1A_{1g}$ transition assigned to nickel(II) centre under square planar environment shifted to higher frequency region compared to the precursor. The room temperature magnetic moment values of these complexes lie in the range 4.38 to 3.42 B.M. These values are lower than those expected for high spin octahedral cobalt(II) complexes and may arise due to distorted six coordinated cobalt(II) centre of approximately C_2 symmetry, the inner nickel(II) centre being diamagnetic. Under C_2 symmetry the degeneracy of the ground state of cobalt(II) is lifted from ${}^4T_{1g} \rightarrow {}^4A_{1g} + {}^4B_{1g}$. Thus the new ground state being an orbital singlet will give rise to magnetic moment value lower than that observed for octahedral cobalt(II) complexes. The electronic spectral data of the complexes as discussed above provide evidence for the above facts.

The electronic spectra of the complexes $[\text{Ni}_2\text{CuL}(\text{H}_2\text{O})_2]\text{X}_6$ display two broad bands at 23810 and 14285 cm^{-1} . This type of spectral features reveal that the former band might be due to nickel(II) centre in square planar environment shifted to higher frequency region compared to precursor complex, whereas the later band is a broad envelope due to the central copper(II) ion in an approximately distorted octahedral environment. However, instead of getting three bands due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1), ${}^2B_{1g} \rightarrow {}^2B_{2g}$ (ν_2) and ${}^2B_{1g} \rightarrow {}^2E_g$ (ν_3) transitions, only one broad band is observed suggesting thereby all the ν_1 , ν_2 and ν_3 bands are superimposed due to small energy difference into a single band, analogous to ${}^2E_g \rightarrow {}^2T_{2g}$ transition. The width and symmetry of the band provide evidence for Jahn-Teller distortion. Further non-occur-

Table 4. Interelectronic repulsion parameter, crystal field parameter and nephelauxetic parameters of Co^{II} complex

Complex	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	B (cm^{-1})	D_q (cm^{-1})	β	β^0 (%)
$[\text{Ni}_2\text{CoL}(\text{H}_2\text{O})_2]\text{Cl}_6$	10000	15400	18150	614	1105	0.633	36.7

The above data reveal that the interelectronic repulsion in Co^{II} gets significantly reduced due to delocaliza-

rence of bands below 10000 cm^{-1} rules out the possibility of tetrahedral geometry for the Cu^{II} centre. The observed

Table 5. ESR spectral data of Ni-Cu-Ni macrocyclic complexes

Complexes	$g_{ }$	g_{\perp}	g_{av}	$A_{ } \times 10^{-4}$	$A_{\perp} \times 10^{-4}$ (cm^{-1})	$A_{av} \times 10^{-4}$ (cm^{-1})	α^2	$1 - \alpha^2$	% of covalency
[NiCuNiL]Cl ₆	2.32	2.08	2.18	184	107	145.5	0.90	0.10	10.0
[NiCuNiL](H ₂ O) ₂ (NO ₃) ₆	2.31	2.06	2.16	181	102	141.5	0.875	0.125	12.50

magnetic moment values of the complexes lie in the range 1.78 to 1.84 B.M. which is commensurate with spin free hexa coordinated Cu^{II} centres⁴⁰, inner Ni^{II} centre being diamagnetic.

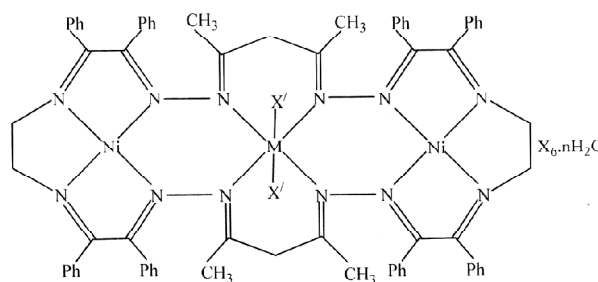
ESR spectra :

The ESR parameters $g_{||}$, g_{\perp} and $A_{||}$, A_{\perp} corresponding to Ni-Cu-Ni complexes are calculated as reported by Goodman and Rayner⁴¹ and recorded in Table 5. The data show that $g_{||}$ and g_{\perp} values are closer to 2 and $g_{||} > g_{\perp}$ and $A_{||} > A_{\perp}$. The value correspond to copper(II) center having D_{4h} symmetry⁴². It also suggest that d_{z^2} orbital is stabilized by Jahn-Teller effect and the unpaired electron is present in $d_{x^2-y^2}$ orbital with major distortions in octahedral environment of copper(II) complex which causes g values to approach to 2. Thus for a tetragonal or square planar complex $\Delta E (d_{x^2-y^2} - d_{xy})$ and $\Delta E (d_{x^2-y^2} - d_{xy}, d_{xz})$ becomes very large as a result of $g_{||}$ and g_{\perp} becoming small. The covalency parameter α^2 is calculated from $g_{||}$, g_{\perp} and $A_{||}$ values⁴³ by using the following equation,

$$\alpha^2 = (g_{||} - 2.0023) + 3/7 (g_{\perp} - 2.0023) + (A_{||}/0.036) + 0.04$$

The α^2 value lie in ~ 0.875 – 0.911 indicates that the unpaired electron of copper(II) complexes spend about 12.5–8.9% of its time in the ligand donor sites. The complexes under study show $g_{||} > 2.3$ indicate a comparatively anionic or less covalent environment around the metal centre⁴⁴. The values are related by the expression $G = (g_{||} - 2)/(g_{\perp} - 2)$, which measures the exchange interaction between copper centres in polycrystalline solid. If $G > 4$, exchange interaction is negligible and $G < 4$ indicate considerable exchange interaction in the solid complexes. In the present case the axial symmetry parameter G lies in the range 4.00–6.00 indicates that the exchange integral is negligible.

Based on the above studies and the observations obtained we propose the following structure (Fig. 4) for the trinuclear metal complex.



when M = Ni (Homonuclear) M = Cu, Co (Heteronuclear)
 $X' = \text{Nil}$ $X' = \text{H}_2\text{O}$
 $X = \text{Cl}^-, \text{NO}_3^-$

Fig. 4

Fungicidal activities :

The fungicidal activity of the precursor and the trinuclear metal complexes was carried out. It was 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 activity^{45–47}. The observed antifungal activity of the ligand and its metal complexes find support from the literature^{48–50} because 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 antifungal activities of the complexes were tested against the organisms *Aspergillus niger*, *Helminthosporium*

Table 6. Antifungal screening data of trinuclear metal complexes

Complexes	<i>A. niger</i>			<i>H. oryzae</i>			<i>F. oxysporium</i>		
	25	50	100	25	50	100	25	50	100
Conc. ($\mu\text{g mL}^{-1}$)	25	50	100	25	50	100	25	50	100
[Ni(EDBMH)(NO ₃) ₂]	8	9	12	9	11	12	11	14	15
[Ni(EDBMH)Cl ₂]	9	11	14	10	12	13	12	16	18
[Ni ₃ L(NO ₃) ₆]	11	13	17	12	14	15	13	19	21
[Ni ₃ L]Cl ₆	13	15	18	14	16	21	15	21	23
[Ni ₂ CoL(H ₂ O) ₂](NO ₃) ₆	12	14	18	13	15	16	14	21	23
[Ni ₂ CoL(H ₂ O) ₂]Cl ₆	14	16	19	15	17	22	16	22	24
[Ni ₂ CuL(H ₂ O) ₂](NO ₃) ₆	13	15	19	14	16	18	15	23	25
[Ni ₂ CuL(H ₂ O) ₂]Cl ₆	15	18	20	16	19	24	17	24	26

oryzae and *Fusarium oxysporium* by the method of Horsfall⁵¹. The evaluation was carried out at a different concentration of dioxane in ppm. 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.

The results are given in Table 6. The activity order among the trinuclear complex is found to be Ni₂Cu > Ni₂Co > Ni₃ > metallo-ligand. With respect to the anion, the homo/hetero trinuclear complexes follow the trend Cl⁻ > NO₃. which is in conformity with corresponding acid strength. The statistical calculations adopting two ways ANOVA test⁵² have also indicated significant difference with respect to different treatment of complexes.

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