

HOMO AND BIMETALLIC DINUCLEAR MACROCYCLIC COMPLEXES OF 1,4,5,8,11,14,15,18,19,21, DECAAZA- 2,3,6,7,12,13,16,17,-OCTAPHENYL-20-THIA-UNDODECANE- 1,3,5,7,11,13,15,17-OCTAENE (DOTUO): ITS SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL PROPERTIES

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Abstract: A series of homo- and bimetallic dinuclear macrocyclic Schiff base metal complexes, using different transition metal ions such as Cu(II), Ni(II) and Co(II) with the titled ligand has been prepared. The ligand and its 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 ligand as well as the metal complexes exhibited antimicrobial activities against the pathogenic fungus *Aspergillus Niger*, *Helminthosporium Oryzae* and *Fusarium Oxysporium*.

Keywords: Schiff Base, Macrocyclic complex, Pathogenic Fungus, Biological Properties, Transition Metal.

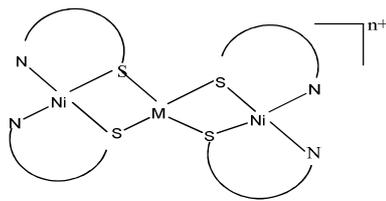
INTRODUCTION

The designing and synthesis of a new ligand is perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity possibly due to electron donor, electron acceptor, structural, functional groups or the position of the ligand in the coordination sphere [1,2] and widening the scope for further research.

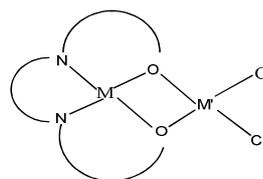
Reports on the direct synthesis of bimetallic metal complexes bound to the same ligand framework are scanty. Their preparation involves multi steps of reaction. In the first step a mono nuclear complex is prepared which subsequently reacts with the hetero metal ions giving rise to bimetallic complexes. The precursor complex is called metallo ligand as the mono nuclear complex acts as a ligand for the second metal ion.

Coordinated thio and phenoxy atoms have non-bonding electron pairs which are sufficiently nucleophilic to form bridges for various metal ions [3-6] as depicted below.

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[Fig-1]



[Fig-2]

Similarly the mono nuclear metal complexes of dihydrazones of diacetyl, benzil and glyoxal have pendant free -NH_2 groups suitably oriented for condensation reaction. They have been used to prepare macrocyclic complexes with formaldehyde [7-9].

In the present study, we report the synthesis and characterization and biological properties of some homo- and bimetallic dinuclear macrocyclic complexes with the titled ligand (DOTUO). The bimetallic complexes have been isolated in multi-step reactions. In the first step of the reaction two mononuclear complex units with homo or hetero metal ions have been interacted. The resulting dinuclear complexes contain pendant -NH_2 groups in close locality are encapsulated by carbondisulphide in the third step resulting in the formation of macrocyclic complexes.

EXPERIMENTAL

All the chemicals and solvents used are either of Glaxo or Merck grade. The solvents were purified before its use in the reaction. The metal contents of all the complexes were estimated by standard methods [10]. 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 Gouy method with mercury tetra thiocyanatocobalt (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 $0.63 \times 10\text{G}$.

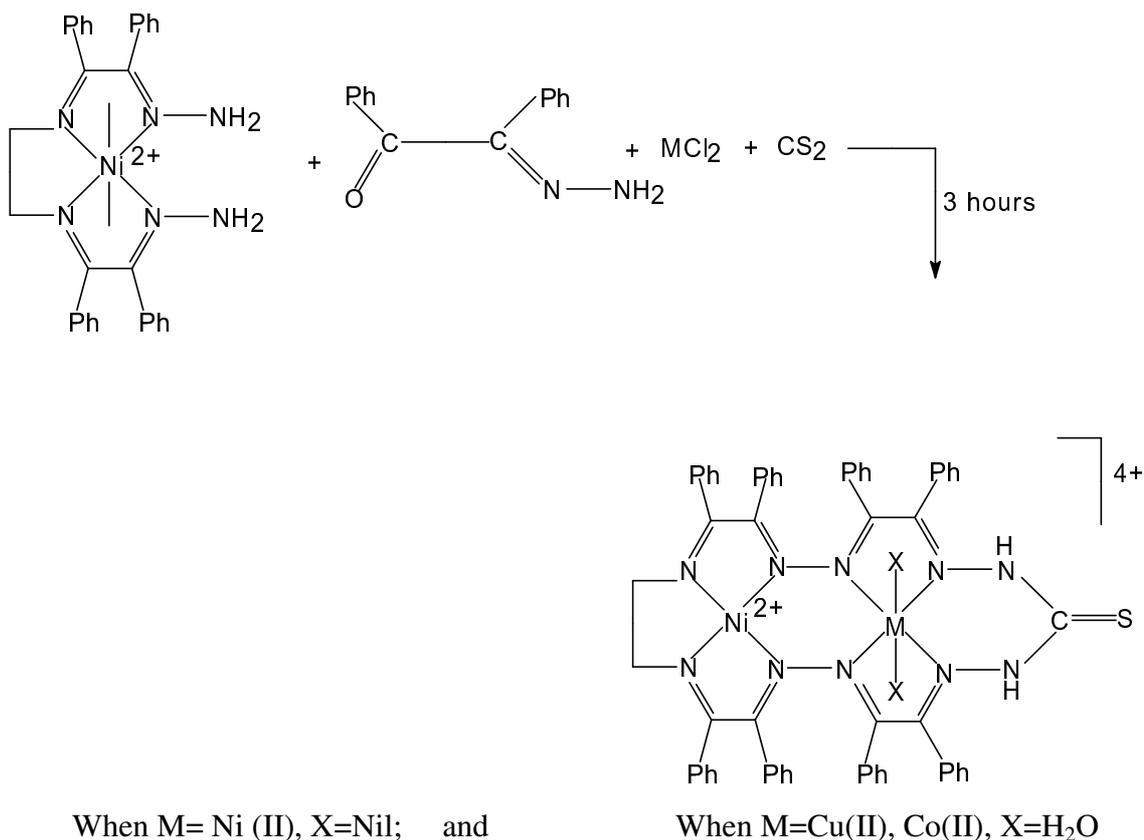
Synthesis of the ligand and its metal complexes:

Benzil monohydrazone (BMH) and Ethylenediamine-bis-(benzil) nickel (II) chloride precursor complexes were prepared according to literature methods [11,12].

Preparation of homo dinuclear Nickel (II) complexes of DOTUO

In a 100 mL round bottomed flask, the precursor complex [Ni (BED)] Cl₂ (0.153g, 0.0025 mol) was suspended in minimum volume of ethanol and was refluxed for 30 minutes. To the resulting solution, benzilmonohydrazone (1.12 g, 0.005 mol) was added followed by NiCl₂.6H₂O (0.59g, 0.0025 mol) in absolute ethanol and was refluxed for 3 hours. To the resulting deep red solution, a few drops of CS₂ were added. It was then further refluxed for 1 hour. A deep red solution was obtained. The solution was then cooled to room temperature, when a deep red compound was formed. The precipitate was then filtered and washed with cold ethanol and kept over fused CaCl₂ in a dessicator till dryness.

The proposed mechanism of the reaction is presented below [Scheme: 1]



[Scheme: 1]

Similarly the other homo and bimetallic dinuclear complexes were prepared in an identical method by adding appropriate metal salts in definite proportions. The analytical data of the complexes are recorded in Table:-1.

Table:-1 Analytical and molar conductance data of the metal complexes:

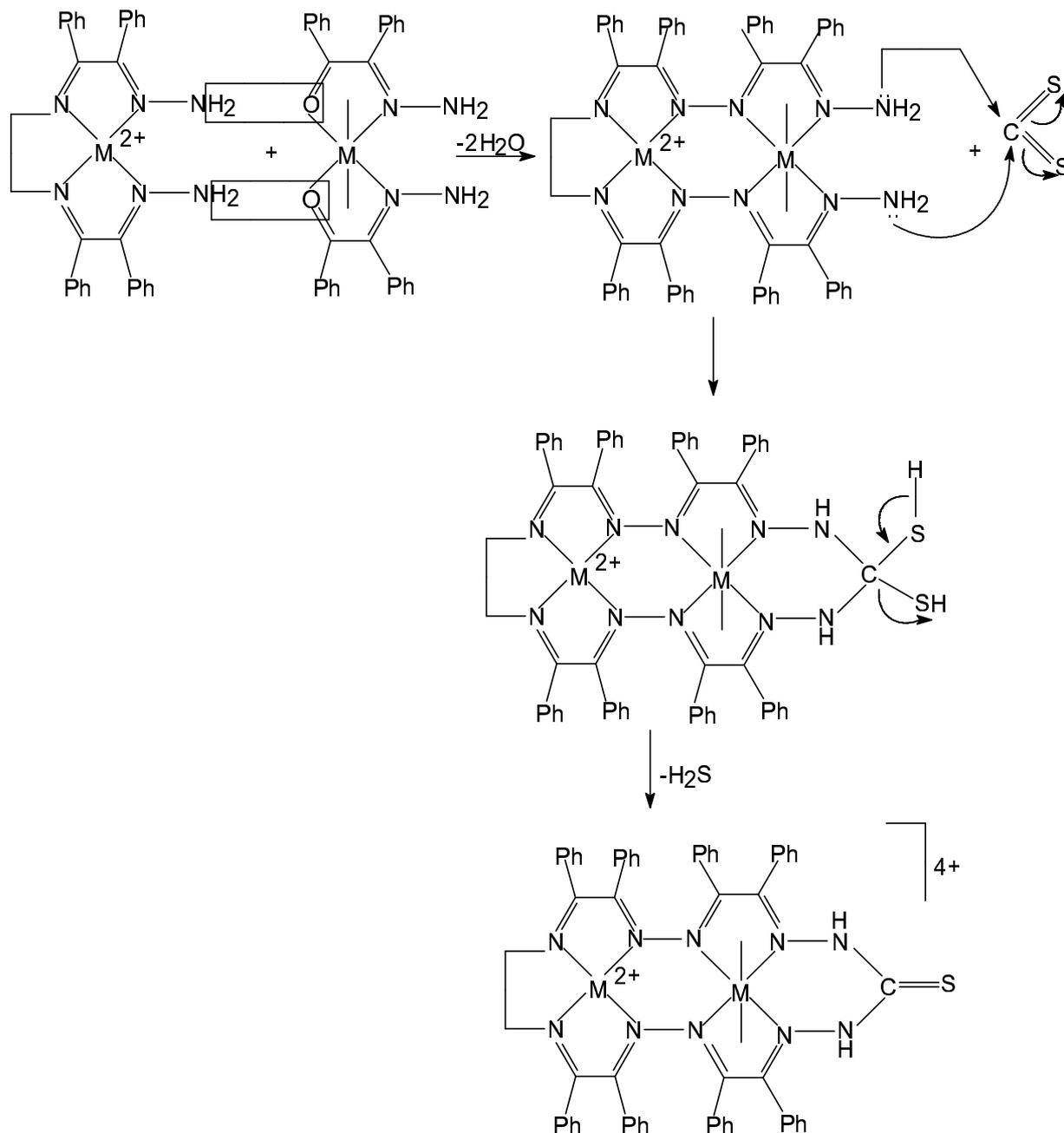
Complexes	Colour	MP In $^{\circ}\text{C}$	% of Metal		%of C found (Calc)	% of H found (Calc)	% of N found (Calc)	λ in $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
			M	M'				
[Ni-Ni-DOTUO]Cl ₄	Deep red	>250	11.24 (11.29)	--	68.04 (67.90)	4.39 (4.41)	13.39 (13.42)	155
[Ni- Co(DOTUO)(H ₂ O) ₂]Cl ₄	Dirty grey	>250	5.63 (5.59)	5.70 (5.64)	37.82 (67.86)	4.33 (4.40)	13.39 (13.41)	165
[Ni- Cu(DOTUO)(H ₂ O) ₂]Cl ₄	Light yellow	>250	5.59	6.11 (6.06)	67.53 (67.56)	4.42 (4.38)	13.42 (13.36)	162

M = Ni (II); M' = Ni (II), Cu (II) and Co (II)

RESULTS AND DISCUSSION

The complexes are highly coloured and have melting point above 250° . They are insoluble in common organic solvents but are soluble in polar solvents like DMF, DMSO and Dioxane. They show high molar conductance values ($155 - 165 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) suggesting them to be electrolytic in nature.

It is envisaged that in the first step of the reaction, the precursor complexes containing homo or bimetal ions will undergo Schiff base reaction in the presence of homo/bimetal ion, which again subsequently undergo condensation reaction with CS₂. The mechanism of the reaction is presented below in [Scheme: 2].



[Scheme: 2]

The complexes have been characterized by the following physico-chemical methods.

IR Spectra

The Infrared spectra of the dinuclear complexes have been studied along with the precursor complexes, benzilmonohydrazone and other related Schiff bases. Some of the important IR bands of structural importance are recorded in Table-2 and Table-3. The entire complexes exhibit identical spectral pattern suggesting them to be isostructural. They are highly complicated. However efforts have been made to identify certain important bands which furnished vital information on the nature of metal-ligand bond.

Table:-2 Structurally Important Infrared Bands of BMH and Nickel (II) complexes of ethylenediamine-bis-(BMH)

Complexes	$\nu_{\text{asym}} \text{NH}_2$ $\nu_{\text{sym}} \text{NH}_2$	ν_{NH}	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=C}}$ (Phenylic)	$\nu_{\delta-} \text{NH}_2$	$\nu_{\omega-} \text{NH}$	ν_{CH} out of plane	$\nu_{\text{M-N}}$
BMH	3380 3260 3180	3025	1645	1625	1585 1480 1425	1525	760	720 710	
Ni [EDMBH]Cl ₂	3365 3260 3175	3025	--	1610	1580 1470 1450	1530	760	720 710	460

Table:-3 Structurally Important Infrared Bands of the macrocyclic complexes.

Complexes	$\nu_{\text{H}_2\text{O}}$	ν_{NH}	$\nu_{\text{C-N}}$	$\nu_{\text{C=S}}$	$\nu_{\text{C=C}}$ phenylic	$\nu_{\text{C=N}}$	$\nu_{\text{M=N}}$	$\nu_{\text{M-N}}$
[Ni-Ni(DOTUO)] Cl ₄	--	3061	2365	1676	1571 1488 1443	1592	1072	476
[Ni-Cu(DOTUO)(H ₂ O) ₂]Cl ₄	3339	3061	2356	1678	1571 1490 1444	1595	1072	483
[Ni-Co(DOTUO)(H ₂ O) ₂]Cl ₄	3337	3061	2365	1678	1572 1444 1488	1593	1073	478

The characteristic symmetric and asymmetric vibrations for primary amine -NH₂ group of benzilmonohydrazone appears as a triplet in the vicinity of 3380, 3260 and 3180 cm⁻¹. The $\nu_{\text{C=O}}$ stretching of benzil which occurs at 1650 cm⁻¹ suffers a red shift and appears at 1645 cm⁻¹ in benzilmonohydrazone. A significant band that is absent in benzil appears as a triplet in the vicinity of 1530 cm⁻¹ is the deformation vibration of -NH₂ groups. Another remarkable but sharp band appears ~1610 cm⁻¹ in benzilmonohydrazone and has been assigned to the $\nu_{\text{C=N}}$ vibration originating from the precursor Ni(II) complex, the $\nu_{\text{C=O}}$ stretching frequency due to benzilmonohydrazone spectacularly disappears. This therefore suggests that, the reaction between -NH₂ group of diamine and carbonyl group of benzilmonohydrazone has taken place.

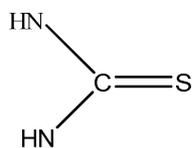
Appearance of a single ($>\text{C=N}$) stretching band clearly implies that all the imine (C=N) groups are of equal vibrational energy. The other stretching vibrations due to -NH₂ group do not undergo any significant change in the precursor complex.

Reaction of precursor complexes with CS₂ in the presence of metal ions brings about drastic change in the spectra of the product. The most significant features of the spectra is the disappearance of the band due to -NH₂ stretching and deformation vibration. Only one band ~3061cm⁻¹ appears which is assigned to νNH. Again band due to (>C=O) of benzil monohydrazone disappeared which indicate that reaction between the precursor complexes followed by CS₂ has taken place. At around 1590 cm⁻¹ a band has appeared which is assigned due to the νC=N. The appearance of a single band suggests that, all the imino groups are of same vibrational energy and their shifting to lower frequency region indicate participation in complexation. Besides a multiple band system in the region 1440-1600 cm⁻¹ is observed in all the complexes suggesting there by the presence of C=C skeletal diagnostic of aromatic structure.

The metal-nitrogen vibration νM-N bands which are clearly distinguishable in the precursor and in the binuclear complexes are observed in the region 460 and 480 cm⁻¹ respectively [13, 14].

In addition to the above bands, all the complexes except Ni-Ni system, show a strong board band at about 3450 cm⁻¹, which is due to νOH band of coordinated water [15,16].The width of the band suggest inter\intra molecular hydrogen bonding.

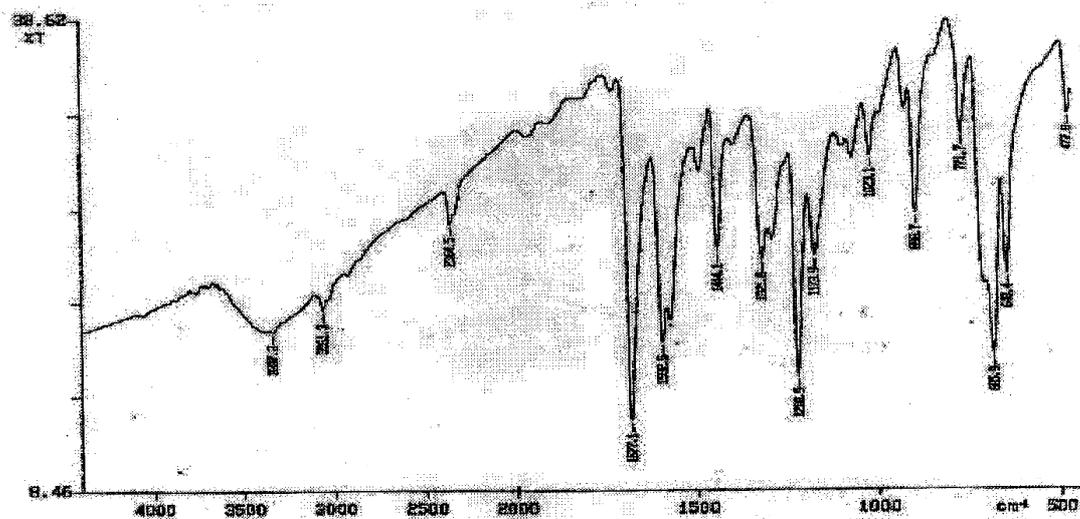
A new band at ~1677 cm⁻¹ in the complexes due to νC=S indicate the presence of a



which is clearly evidenced from the structure. The bands at 3337 cm⁻¹ further and 1617 cm⁻¹ show that C=S group is attached to the two NH groups.

In the lower frequency region a band at ~476 cm⁻¹ due to νM-N suggests the presence of M-N bond in the complexes. Absence of band at around 2570 cm⁻¹ due to νS-H indicate that the ligand frame work in the complex predominantly exist in the thioketo form.

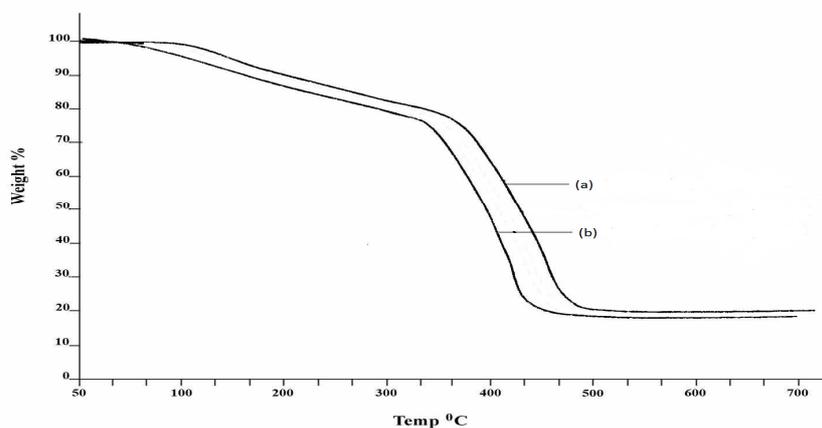
The IR spectrum of the complex [Ni-Co(DOTUO)(H₂O)₂]Cl₄ is given below.

IR Spectrum of $[\text{NiCo}(\text{DOTUO})(\text{H}_2\text{O})_2]\text{Cl}_2$

[Fig-3]

Thermogravimetric analysis:

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



[Fig-4]

Where (a) = $[\text{Ni-Cu}(\text{DOTUO})(\text{H}_2\text{O})_2]\text{Cl}_4$, (b) = $[\text{Ni-Co}(\text{DOTUO})(\text{H}_2\text{O})_2]\text{Cl}_4$

In Ni-Cu chloro system, there was no mass loss up to 110°C , indicating the absence of lattice water [17]. The complex loses weight at $\sim 120^\circ\text{C}$ with a weight loss of 2.89 % which corresponds to the loss of two water molecules (2.93 % theoretical) in a single step. Such behaviour is characteristic of coordinated water in the same chemical environment [18]. The

decomposition proceeds slowly at around 180°C with a residue of 12.51% (12.58% theoretical) ~470°C which corresponds to the formation of metal oxide. The thermal stability of the complexes are in the order Ni-Cu > Ni-Co system.

The thermo analytical data of the complexes are given in Table -4.

Table 4. Thermo analytical data of the complexes

Complex	Temperature range of decomposition	% of Wt. loss found (Calc)	Remarks
[Ni-Cu(DOTUO)(H ₂ O) ₂]Cl ₄	120°C	2.89	Loss of two water molecules
		(2.93)	
	180°C	12.51	Formation of metal oxides
		(12.58)	
[Ni-Co(DOTUO)(H ₂ O) ₂]Cl ₄	120°C	2.91	Loss of two water molecules
		(2.94)	
	180°C	12.19	Formation of metal oxides
		(12.25)	

Electronic spectra and magnetic properties of the precursor complex:

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

The en-bis-(BMH) Ni(II) precursor complex shows two bands one near 19000 cm⁻¹ and the other at higher frequency region near 29000 cm⁻¹. The former band has a lower intensity than that one in the UV region. These transitions has been assigned to ¹A_{2g} → ¹A_{1g} transition under a square planar environment for Ni(II) ion. The more intense band is believed to arise due to charge transfer (CT) transition. The precursor complexes are diamagnetic corresponding to square planar geometry.

The [NiNi(DOTUO)]X₄ complexes are diamagnetic which is further supported by the electronic spectra of the complexes. All the Ni-Ni complexes exhibit an identical pattern. The precursor band at 19000 cm⁻¹ is shifted to 22,335 cm⁻¹ and has been assigned to ¹A_{2g} → ¹A_{1g} transitions. Occurrence of a single band is not unexpected because both the nickel centers have Ni-N₄ chromophoric group in an identical chemical environment.

The electronic spectra of [NiCu(DOTUO)(H₂O)₂]X₄ display mainly two broad bands at 22727 cm⁻¹ and 14315 cm⁻¹ followed by a CT band at 28995 cm⁻¹. This type of spectral features reveal that the former band arises may be due to inner Ni (II) centre in

square planar environment shifted to higher frequency compared to precursor complex, whereas the latter band is a broad envelop due to the outer Cu(II) centre in a approximately distorted octahedral environment. However, instead of getting three band 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 that all the ν_1 , ν_2 and ν_3 bands are superimposed due to small energy difference into a single band, analogous to ${}^2E_{1g} \rightarrow {}^2T_{2g}$ transition. The width and asymmetry of the band provide evidence for Jahn-Teller distortion [19]. Further non-occurrence of bands below $10,000\text{ cm}^{-1}$ rules out the possibility of tetrahedral or pseudo tetrahedral geometry for the Cu(II) centre.

The observed magnetic moment values of the complexes lie in the range 1.77 to 1.85 BM which is commensurate with spin free hexacoordinated Cu (II) centres [20].

A close examination of the electronic spectra of $[\text{NiCo}(\text{DOTUO})(\text{H}_2\text{O})_2]\text{X}_4$ reveals the following characteristic features:

1. A broad band in the region $10,055\text{ cm}^{-1}$ is observed. This can be assigned to ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ (ν_1) transition due to outer Co(II) ion in an octahedral symmetry[21]. The broad unsymmetrical nature of the band led us to suggest the other bands are superimposed by the ν_1 band.
2. A doubly split band in the region $18,700\text{ cm}^{-1}$ and $17,550\text{ cm}^{-1}$ was observed. This may be due to split component of ν_3 band due to ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ transition of the outer Co(II) centers. The multiplicity of such band can be interpreted due to six coordinated Co(II) centre of an approximately C_2 symmetry [22].
3. A shoulder at $15,450\text{ cm}^{-1}$ is also observed. This may be due to either ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$ transition.
4. Besides the above bands, a more intense band at $22,220\text{ cm}^{-1}$ is also observed due to ${}^1A_{2g} \rightarrow {}^1A_{1g}$ transition. This can be safely assigned to Ni (II) centre under square planar environment shifted to higher frequency region.

The room temperature magnetic moment values lies in the range 4.3 to 4.5 BM. These values are lower than those expected for high spin octahedral Co(II) complexes. This values may arise due to distorted six coordinated Co(II) centre of approximately C_2 -symmetry, the inner Ni(II) centre being diamagnetic. Under C_2 symmetry, the degeneracy of the ground stat of Co(II) is shifted from ${}^4T_{1g} \rightarrow {}^4A_{1g} + {}^4B_{1g}$. Thus the new ground state being an orbital singlet, will give rise to magnetic moment values lower than that observed for octahedral Co(II) complexes. However, in the ν_1 band region, no splitting is observed as

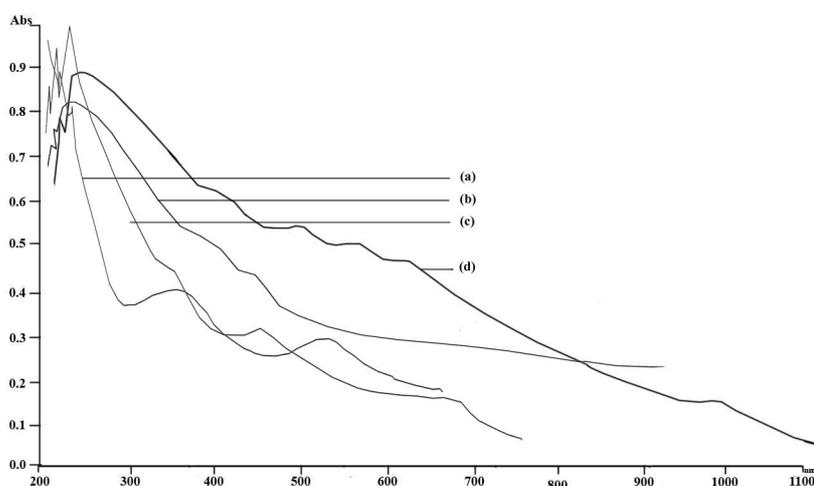
expected. Nevertheless, the appearance of the band as broader one suggests superimposition of different component into single one.

The electronic spectral data of the precursor and thi dinuclear metal complexes are given in table-5.

Table 5: Electronic spectra and magnetic properties of complexes.

Complexes	Band Position in cm^{-1}	Assignment	μ_{Eff} in BM
[Ni(EDBMH)Cl ₂]	19000	$^1A_{2g} \rightarrow ^1A_{1g}$	Diamagnetic
	29000	CT	
[Ni-Ni(DOTUO)Cl ₄]	22325	$^1A_{2g} \rightarrow ^1A_{1g}$	Diamagnetic
	29000	$^1A_{2g} \rightarrow ^1B_{2g}$ $^1A_{2g} \rightarrow ^1T_{2g}$ CT	
[Ni-Cu(DOTUO)(H ₂ O) ₂]Cl ₄	22727	$^1A_{2g} \rightarrow ^1A_{1g}$	1.81
	14315	$^2E_g \rightarrow ^2T_{2g}$	
	29000	CT	
[Ni-Co(DOTUO)(H ₂ O) ₂]Cl ₄	10055	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$	4.42
	18700	$^4T_{1g}(F) \rightarrow ^4T_{2g}(P)$	
	17550		
	22727	$^1A_{2g} \rightarrow ^1A_{1g}$	
	29000	CT	

The electronic spectra of the complexes are represented below [Fig-3].



[Fig-5] Wavelength (nm)

Where (a) = [Ni-(EDBMH)Cl₂], (b) = [NiNi (DOTUO)Cl₄], (c) = [Ni-Cu(DOTUO)(H₂O)₂]Cl₄, (d) = [Ni-Co(DOTUO)(H₂O)₂]Cl₄

ESR spectra of copper (II) complexes:

The ESR spectra of the polynuclear copper (II) complex exhibit well resolved anisotropic signals in parallel and perpendicular ⁶³Cu region. The values of g_{\parallel} , g_{\perp} and A_{\parallel} have been used for the calculation of α^2 , covalency parameter [23] which for this complex lies in the range 2.292 - 2.301 and 180×10^{-4} - 190×10^{-4} cm⁻¹ respectively. The observed data show that g_{\parallel} and g_{\perp} values are closer to 2 and $g_{\parallel} > g_{\perp}$ and $A_{\parallel} > A_{\perp}$. This clearly suggests major distortion in the copper(II) complex from O_h symmetry to D_{4h} symmetry [24]. The complex has $g_{\parallel} > 2.3$, which indicate an ionic or lesser covalent environment around the complex [25]. The value of covalency parameter α^2 (0.886) which is more than the α^2 values of the precursor complex. This suggests that the macrocyclic complex is less covalent than the precursor complex. The α^2 value is commensurate with considerable covalent character in σ -bonding involving metal ion and ligand [26, 27]. The ESR spectral data indicate that the unpaired electron of copper (II) complex spend about ~11.34 -14.82% of its time in the ligand donor sites.

CONCLUSION

Thus from all the above observations, we conclude that,

1. The ligand molecule DOTUO acts as octadentate ligand satisfying four coordination numbers around each metal centre.
2. The precursor metal ion i.e. Ni(II) occupy the 'inner' core of the complexes with N₄ - chromophore, while the other metal centre occupy the 'outer' core also having N₄ - chromophore.
3. The fifth and sixth coordination numbers of the binuclear complexes other than the homo binuclear complexes are satisfied by water molecules leading to cationic complexes as evidenced from higher molar conductance values.

From the above physico-chemical investigations the following tentative structure for the complexes have been proposed [Fig-6].

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 Tabl-6. The homo dinuclear nickel (II) complexes are found to be more active than the hetero dinuclear complexes and the precursor (Metallo ligand). The activity order is Ni-Cu > Ni-Co > Ni₂ > metallo ligand. The statistical calculations adopting two ways ANOVA test [36] have also indicated significant difference with respect to different treatment of complexes.

Table 6
Antifungal screening data of trinuclear metal complexes

Complexes	A.niger			H. oryzae			F. oxysporium		
	25	50	100	25	50	100	25	50	100
[Ni(EDBMH)(NO ₃) ₂]	7	8	10	8	10	11	10	12	14
[Ni(EDBMH)Cl ₂]	8	9	11	9	11	12	11	14	16
[Ni-Ni(DOTUO)](NO ₃) ₄	10	11	14	11	13	14	12	16	19
[Ni-Ni(DOTUO)Cl ₄]	11	12	14	12	13	15	13	18	20
[Ni-Co(DOTUO)(H ₂ O) ₂](NO ₃) ₄	12	13	15	13	15	16	14	19	21
[Ni-Co(DOTUO)(H ₂ O) ₂]Cl ₄	14	16	19	15	17	19	16	20	23
[Ni-Cu(DOTUO)(H ₂ O) ₂](NO ₃) ₄	13	15	19	15	18	19	16	21	24
[Ni-Cu(DOTUO)(H ₂ O) ₂]Cl ₄	15	17	20	16	19	21	17	23	25

REFERENCES

- [1] J. Balsells, L. Meorado, M. Phillips, F. Ortega, G. Aguirre, R. Somanathan, P.J Walsh, *Tetrahedron Asymm* 1998, **9**, 4135.
 [2] J. Sima J, Crao. *Chem. Acta* 2001, **74**, 593.

- [3] T. Thanvasiri & E. Sinn, *J.Chem. Soc, Dalton* (1989) 1187 and reference there in.
- [4] E.L. Blinn, P. Bulter, M.M. Chapman & S. Haris *Inorg. Chim. Acta.* 1977, **24**,139.
- [5] R.E. De Simane, T. Ontko, L. Wardman& E.L. Blinn, *InorgChem*, 1975, 14, 1313.
- [6] D. Fenton, U. Casellato, P.A. Vigato & M. Vidali, *Inorg. Chim. Acta.* 1982, 62, 57.
- [7] B. Sahoo, A.K. Rout, & B. Sahoo *Indian.J. Chem*, 1986, **25A**, 609.
- [8] B.K.Mohapatra & B. Sahoo, *Indian.J. Chem*, 1984, **23A**, 844.
- [9] A.K. Panda, D.C Dash & P. Mishra, *Indian J. Chem*, 1996, **35A**, 848-851.
- [10] A. I. Vogel “A Hand Book of Qualitative Inorganic Analysis”, 2nd ed., Longmans and ELBS, 1966, 466.
- [11] D.G. Brown, *Progr. Inorg. Chem.*, 1953, **18**, 177.
- [12] N.S. Bush and I.S. Woolsey, *J. Chem. Soc.*, 1972, **94**, 4107.
- [13] K. Nakamoto, “Infrared and Raman spectra of inorganic and coordination compounds”, (wiley, New York) (1997), 3rd edn.
- [14] M. Thomas, M.K.M. Nair, R.K. Radhakrishnan, *Synth.React.Inorg. Met.Org*, 1995, **25**, 471-479.
- [15] K.Y. El-Baradie, *Montash.Chem*, 2005, 136.
- [16] L.J. Bellamy, “The Infrared Spectra of complex molecules”, Chapman and Hall, London (1978).
- [17] P. R. Shukla, V. K. Singh and J. Bhargava, *J. Indian Chem. Soc.* , 1982, **59**, 620.
- [18] A. K. Panda, S. Rout and H. Mohanty, *Indian J. Chem., Sect. A*, 1994, **33**, 788.
- [19] A.B.P. Lever, “Inorganic electronic spectroscopy”, Elsevier publ. 1968, 337.
- [20] D.P. Graddon and I.C. Watton, *J. Inorg. Nucl. Chem.*, 1961, **21**, 49.
- [21] A.B.P. Lever, “Inorganic electronic spectroscopy” Elsevier publ., 1968, 308.
- [22] J. Ballhausen, “Introduction to Ligand field theory” (McGraw Hill, New York), 1962.
- [23] R.L. Dutta and A. Syamal. “Elements of Magnetochemistry”, (S.Chand, New Delhi), 1982, 178.
- [24] M. Shakir, S.P.Varkey and P.S. Hameed, *Polyhedron*, 1993, **12**, 2775.
- [25] R.K. Ray and G.B. Kauffman, *Inorg. Chem. Acta*, 1990, 207.
- [26] E.L. Gordon and J.B. Rayner, “*Topics in Inorg. Radiochem*”, 1970, **13**, 136.
- [27] R.S. Drago, “Physical methods in inorganic chemistry”, (Affiliated East-West, New Delhi), 1991, 355.
- [28] R. Nair, A. Shah, S. Baluja and S. Chanda Synthesis and antibacterial activity of some Schiff base complexes, *J. Serb. Chem .Soc.* 2006, **71**, 733-744

- [29] J. Parekh, P. Inamdhar, R. Nair, A. Shah, S. Baluja and S. Chanda, *J. Serb. Chem. Soc.* 2005, **70**, 1155-1161.
- [30] Y.K. Vaghasia, R. Nair, M. Soni, S. Baluja and S.Chanda, *J. Serb. Chem. Soc.* 2004, **69**, 991-998.
- [31] N. Dharamraj, P. Viswanathamurty and K. Natrajan, *Trans. Met. Chem.*, 2001, **26**, 105.
- [32] B .G. Tweedy, *Phytopathology*, 1964, **55**, 910,
- [33] S. Ankri, T. Miron, A. Rabonkov, M. Wilchek and D. Mirelman, *Antimicrob Agents Chemother.* 1997, **41**, 2286
- [34] G.J. Tortora, B.R. Funka and C.L .Case. "Microbiology- An Introduction" 6th Edn. Addison Wesley Longman, Inc., 1998.
- [35] J.G. Horsfall, *Bot Rev*, 1945, **11**, 357.
- [36] G.W.Snedecor and G.W. Cochran, *Statisticals methods* (Iowa Unipress, Iowa, USA) 1967.