

**SYNTHESIS AND CHARACTERISATION OF NICKEL (II) COMPLEXES USING  
HEPTANEDIONEDIOXIME AND AMINES**

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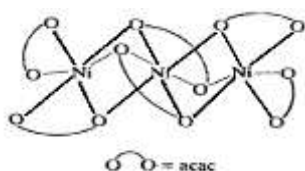
**ABSTRACT**

In recent years, there has been an unprecedented increase in the number of interesting binuclear, trinuclear and of even higher nuclearity (up to 24) nickel (II) complexes that have been structurally characterized by single crystal X-ray crystallography and the absolute size of the materials ascertained. Particularly, planar ligands with imine or amine donors and bridging phenolic oxygens, which are usually referred to as Robson-type ligands. In this paper we studied about synthesis and characterisation of nickel (ii) complexes using heptanedionedioxiime and amines

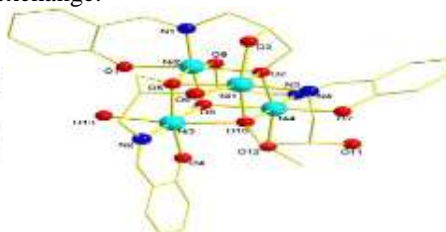
**Keywords:** Nickel (II), Heptanedionedioxiime, Coordination Chemistry.

**INTRODUCTION**

Trinuclear nickel (II) complexes showing ferromagnetic exchange behavior are rare and these have received much attention in recent years<sup>1-11</sup>. Bis(acetylacetonato)nickel(II), a linear trimer, is so far the only trinuclear complex (Fig-1.1) for which the magnetic behavior has been studied over the temperature range 1.6-290 K and it has been found to have parallel spin alignment in its ground state. It is also one of the rare examples which exhibit both positive ( $J=26\text{ cm}^{-1}$ ) and negative ( $J=-7\text{ cm}^{-1}$ ) intracluster exchange integrals. A series of cubane type tetrameric acetate of nickel (II) of the type  $\text{Ni}_4(\text{OCH}_3)_4(\text{L})_4(\text{CH}_3\text{OH})_4$  (L= acetylacetonate or salicylaldehyde anion) (Fig-1.2) have been reported<sup>12-15</sup>. Magnetic studies show that the nickel tetramers have intramolecular ferromagnetic exchange. A few Ni(II) dimers  $[\text{Ni}_2(\text{en})_4\text{X}_2]$  (X=Cl<sup>-</sup> or Br<sup>-</sup>) and  $[\text{Ni}_2(\text{en})_4(\text{SCN})_2]_2$  have also been reported which exhibit intracluster ferromagnetic exchange.<sup>16</sup>

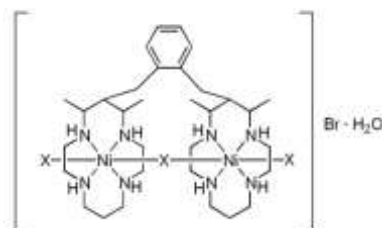


**Fig-1.1**

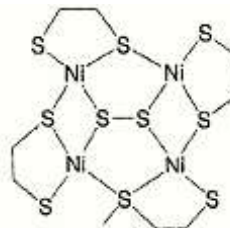


**Fig-1.2 : Cubane type tetrameric acetate of nickel (II)**

In recent years, there has been an unprecedented increase in the number of interesting binuclear, trinuclear and of even higher nuclearity (up to 24) nickel (II) complexes that have been structurally characterized by single crystal X-ray crystallography and the absolute size of the materials ascertained. A few representative examples have been shown in Figs (1.3-1.9).



**Fig 1.3 : Dinuclear bis macrocyclic complex**



**Fig-1.4 : Tetranuclear macrocyclic complexes**

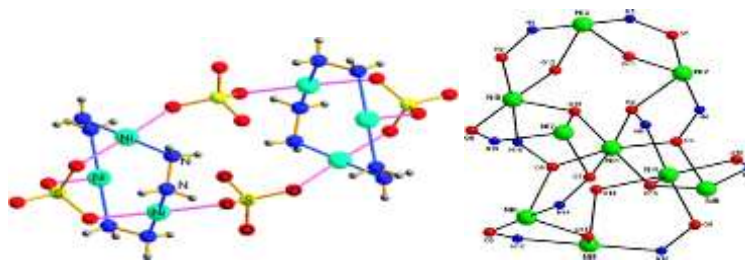


Fig 1.5 : Hexanuclear Ni(II) macrocyclic complexes

Fig 1.6 : Heptanuclear Ni(II) macrocyclic complexes

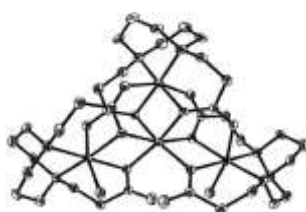


Fig 1.7 : Nonanuclear macrocyclic complexes



Fig-1.8 : Dodecanuclear Ni(II) complexes

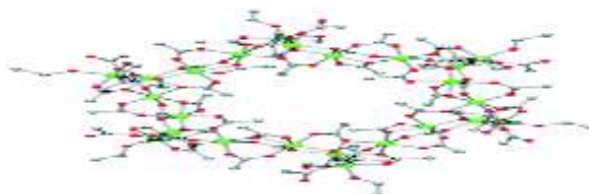


Fig-1.9 : High-nuclearity homometallic iron and nickel clusters: Fe<sub>22</sub> and Ni<sub>24</sub> complexes

The rich chemistry of complexes of dicompartmental ligands binding identical metals and to a lesser extent different metals has been applied to the investigation of magnetic exchange interactions between the two metal ions, the stabilization of mixed-valent species, and the activation of small molecules. Particularly, significant examples (Fig 1.10 and 1.11) of this type are planar ligands with imine or amine donors and bridging phenolic oxygens, which are usually referred to as Robson-type ligands.<sup>3</sup> The complexes formed from these macrocyclic ligands are also used as models for protein-metal binding sites in biological systems, as synthetic ionophores, as therapeutic reagents in chelate therapy for treatment of metal toxication, in catalysis and to investigate the mutual influence of two metal centers on their physicochemical properties.

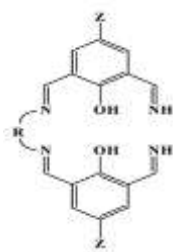


Fig-1.10

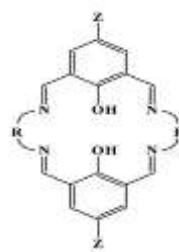
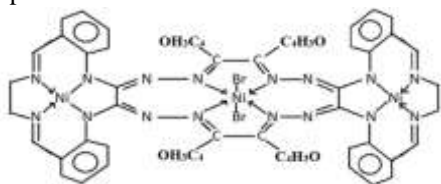


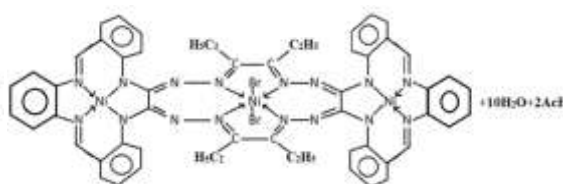
Fig-1.11

Nickel(II) is recognized as a transition metal of considerable biological importance forming the active site of a variety of metalloproteins such as hydrogenase, carbonmonoxide dehydrogenase, methyl-S-coenzyme-M methylreductase and urease.<sup>1-3</sup> Discoveries of dinuclear cores at the active sites of some metalloproteins have aroused interest in the investigation of multimetallic systems.<sup>4,5</sup> Dinucleating macrocyclic ligands which are designed to bind two similar or dissimilar metal ions in close proximity have received considerable attention.<sup>6,7</sup> This is particularly fascinating for a family of phenol-based macrocyclic ligands, derived from the [2 + 2] template condensation of 2,6-diformyl-p-cresol (DFPC) with a diamine (e.g. 2,2-dimethyl-1,3-propanediamine) in the presence of metal ions. Consequently we, in the present programme, in continuation of our earlier interest in the field, (Fig-1.12)<sup>13-15</sup> propose to synthesize and characterize a series of trinuclear complexes with a

compartmental ligand derived by the Schiff base condensation of unutilized carbonyl and amine functional groups of precursors.



**Fig-1.12** : A 40-membered tricompartamental (isolated) macrocyclic of nickel(II)



**Fig-1.13** : A 40-membered tricompartamental (isolated) macrocyclic of nickel(II)

Another series of trinuclear complexes of Ni(II) with 3,5-heptanedionedioxime have also been synthesized and magnetic interaction studied over a range of temperature. Before presenting outcome of the present investigation it would be appropriate to present first an elaborate account of earlier work done in the field. Nickel clusters showing ferromagnetic exchange behavior are few and these have received much attention in recent years<sup>1-5</sup>. Bis(acetylacetonato) nickel(II) complex, a linear trimer is so far the only trinuclear complex for which the magnetic behavior has been studied over the temperature range 1.6-296 K and it had been found to have parallel spin alignment in its ground state. It is also one of the rare example which exhibit both positive ( $J = 26 \text{ cm}^{-1}$ ) and negative ( $J = -7 \text{ cm}^{-1}$ ) intracuster exchange integrals. A series of 'cubane' type tetrameric clusters of Ni(II) of the type,  $\text{Ni}_4(\text{OCH}_3)_4(\text{L})(\text{CHOH})_4$  ( $\text{L} = \text{acetylacetonato}$  or salicylaldehyde anion) have been reported. Magnetic studies show that the nickel tetramers have intramolecular ferromagnetic exchange. Recently few Ni(II) dimers ( $\text{Ni}_2\text{en}_4\text{X}_2$ ) and  $[\text{Ni}_2\text{en}_4(\text{SCN})_2]_2$  have been reported ( $\text{X} = \text{Cl}^-$  or  $\text{Br}^-$ ) which exhibit intracuster ferromagnetic exchange. We report here the isolation of a few trinuclear cluster of Ni(II) with 3,5-heptanedionedioxime of the type  $\text{Ni}_3(\text{HDDO})_2\text{X}_2(\text{H}_2\text{O})_8 \cdot 2\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$  or  $\text{NO}_3^-$ ) which show ferromagnetic spin coupling between adjacent pairs of nickel ions.

## MATERIALS AND MERHODS

All the chemicals used were BDH or E. Merck reagents. The dioxime was prepared by the literature method and its melting point agreed well with the reported value. Bis(heptanedionedioximato)nickel(II) dichloride and dibromide were prepared by reacting ethanolic solutions of the respective metal halides with an ethanolic solution of 3,5-heptanedionedioxime in 1:2 molar ratio. Di-3,5-heptanedionedioximato-dichlorido(octaquo)-trinickel(II) dihydrate was prepared by adding nickel (II) chloride hexahydrate (1.2 g, 0.005 mole) in 30 ml of ethanol to a solution of 3,5-heptanedionedioxime (1.6 g, 0.01 mole) in 70 ml of ethanol when a deep bluish violet solution was obtained. The solution was subsequently treated with nickel acetate tetrahydrate (2.5 g, 0.01 mole) and stirred for several minutes when a clear solution was obtained. The solution was allowed to concentrate at room temperature when a green crystalline product was obtained after a few days. It was filtered, washed with small quantities of ethanol, finally with solvent ether and dried in vacuo. The bromide, iodide and nitrate complexes were prepared in a similar manner. Analytical data of the compounds are recorded in Table-4.1. Physical measurements were carried out as reported earlier.

**Table-4.1:** Analytical Data of the complexes

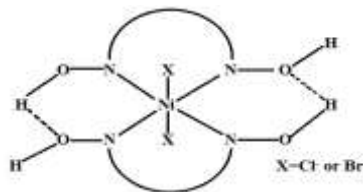
Comp.	Ni (%)		C(%)		H(%)		N(%)		X(%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$\text{Ni}(\text{HDDOH}_2)_2 \text{Cl}_2$	12.98	13.04	37.28	37.33	7.05	7.11	12.34	12.44	15.73	15.78
$\text{Ni}(\text{HDDOH}_2)_2 \text{Br}_2$	10.89	10.91	31.15	31.22	5.90	5.94	10.34	10.41	29.64	29.71
$\text{Ni}_3(\text{HDDO})_2 \text{Br}_2 \cdot 10\text{H}_2\text{O}$	21.12	21.17	20.15	20.19	5.70	5.77	6.68	6.73	19.15	19.21
$\text{Ni}_3(\text{HDDO})_2 \text{Cl}_2 \cdot 10\text{H}_2\text{O}$	23.65	23.70	22.58	22.61	6.40	6.46	7.47	7.53	9.48	9.55
$\text{Ni}_3(\text{HDDO})_2 \text{I}_2 \cdot 10\text{H}_2\text{O}$	22.90	22.96	10.89	10.95	4.35	4.43	3.58	3.65	32.91	32.98
$\text{Ni}_3(\text{HDDO})_2(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$	22.00	22.12	20.95	21.10	5.98	6.03	10.49	10.55	32.90	32.45

## RESULTS AND DISCUSSION

### IR SPECTRA

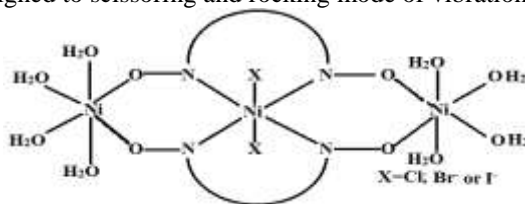
It is remarkable to observe that the IR spectra of all the trinuclear complexes resemble each other very closely but differ strikingly from that of the mononuclear complex. 3,5-heptanedionedioxime shows a strong and broad band at  $3290 \text{ cm}^{-1}$  which may be assigned to hydrogen bonded  $\nu\text{OH}$  of the NOH groups. In the mononuclear complex,  $\text{Ni}(\text{HDDOH}_2)_2 \text{Cl}_2$ , a sharp band at  $3280 \text{ cm}^{-1}$  and relatively broad band at  $3245 \text{ cm}^{-1}$  are observed. The relative intensity and the shape of the latter band are comparable to those of the  $\nu\text{OH}$  band of the free ligand. This indicates the presence of both hydrogen-bonded and free OH in the monomeric complex, the band at  $3380$

$\text{cm}^{-1}$  may be assigned to  $\nu\text{OH}$  of free OH group while that at  $3245 \text{ cm}^{-1}$  may be due to hydrogen-bonded  $\nu\text{OH}$ . These results are consistent with the proposed structure (Fig-4.1) for the mononuclear complex. Bands at  $1600 \text{ cm}^{-1}$  ( $\nu\text{C}=\text{N}$ )  $980$  and  $960 \text{ cm}^{-1}$  ( $\nu\text{N}-\text{O}$ ) in the ligand shift to  $1675$  and  $1060$  and  $990 \text{ cm}^{-1}$  respectively in the monomeric complex.



**Fig-4.1**

The trinuclear metal complexes are found to possess the stoichiometry  $\text{Ni}_3(\text{HDDO})_2\text{X}_2(\text{H}_2\text{O})_8\cdot 2\text{H}_2\text{O}$  where both the protons of the dioxime have been replaced by metal ion. The IR spectra of the cluster exhibit some characteristic differences from those of the ligand as well as the mononuclear complex. In the region  $3500\text{-}3400 \text{ cm}^{-1}$ , all the complexes show a strong and broad band at  $3480 \text{ cm}^{-1}$  which can be unequivocally assigned to the  $\nu\text{O}-\text{H}$  of the water molecules. None of the complexes exhibit any band in the region  $3400\text{-}3200 \text{ cm}^{-1}$  indicating ionization of all the protons of NOH groups of 3,5-heptanedionedioxime. The CN and NO bands appear at  $1650$ ,  $1020$  and  $975 \text{ cm}^{-1}$  respectively which are precisely in the regions intermediate with respect to the mononuclear complex and the free ligand vibrations. The shift of the bands towards the low frequency region as compared to the mononuclear complex indicates wider delocalization of the electronic charge in the newly formed chelate rings on account of coordination of both nitrogen and oxygen atoms of the oxime groups to adjacent nickel ions. Structure (Fig-4.2) is tentatively assigned to the complex which is further supported by magnetic data. Besides the characteristics  $\nu\text{C}-\text{N}$ ,  $\nu\text{NO}$  and other ligand vibrational bands, the trimers show two additional bands, the first a strong and broad band at  $1540 \text{ cm}^{-1}$  and second a sharp band of medium intensity at  $900 \text{ cm}^{-1}$ , which may be assigned to scissoring and rocking mode of vibration of coordinated water.



**Fig-4.2**

### ELECTRONIC SPECTRA

The electronic spectra of the mononuclear complexes,  $\text{Ni}(\text{HDDOH}_2)_2 \text{X}_2$  ( $\text{X} = \text{Cl}^-$  and  $\text{Br}^-$ ) shows a symmetric band at  $14700 \text{ cm}^{-1}$  which may be reasonably assigned to the  $\nu_2$  transition [ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ] for octahedral  $\text{Ni}(\text{II})$ . In sharp contrast to mononuclear complexes, the trinuclear clusters shows a group of three bands well separated from each other in this region. Spectra of the complexes have been also examined in different solvents like dimethyl sulphoxide, methyl cyanide, ethanol and water and found to be very similar except some minor vibration in band positions. The observed bands are due to d-d transitions since their extinction coefficients lie in the range  $10\text{-}40$  and can be reasonable interpreted by assigning tetragonal distortion of the crystal field for the central nickel ion and an approximately octahedral crystal field for the terminal nickel ions with chromophores  $\text{NiN}_4\text{X}_2$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ ) and  $\text{NiO}_6$  respectively. The first band which is observed at  $13000 \text{ cm}^{-1}$  can be assigned to the transitions [ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ] for the terminal chromophores,  $\text{NiO}_6$ . The next two bands at  $14500$  and  $17500 \text{ cm}^{-1}$  corresponds to the two components into which the transition [ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ] of octahedral field is split upon tetragonal distortion. The suggested assignments are show in table-4.2. The position of the bands and magnitude of axial field splitting are comparable to those in the case of dihydrazinophthalazine nickel(II) complexes where the arrangement of the ligand atoms is trans-  $\text{NiN}_4\text{X}_4$  and level are split by some  $4000\text{-}5000 \text{ cm}^{-1}$  by the tetragonal distortion. Alternatively, the three bands can be assigned to the transitions from the ground ( ${}^1\text{A}_{2g}$ ) to the three orbitally singlet components that will be produced from the  ${}^3\text{A}_{1g}(\text{F})$  state under still lower rhombic ( $\text{D}_{2h}$ ) symmetry for both the chromophores  $\text{NiN}_4\text{O}_2$  and  $\text{NiO}_6$  the bands mutually overlapping each other.

Table-4.2

Compound	Solvent	Transitions				
		${}^3A_{2g} \rightarrow {}^3T_{1g}$	${}^3B_{1g} \rightarrow {}^3A_{2g}$	${}^3A_{2g} \rightarrow {}^3T_{1g}$	${}^3B_{1g} \rightarrow {}^3E_g$	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Ni(HDDOH) <sub>2</sub> Cl <sub>2</sub>	Ethanol			15400		25300
Ni(HDDOH) <sub>2</sub> Br <sub>2</sub>	Ethanol			15600		25600
Ni(HDDO) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) 8.2 H <sub>2</sub> O	DMSO	13000	14900		16100	Strong CT band above 20000
	MeCN		14900		16700	Strong CT band above 20000
	Nujol	13000	14900	14900	16700	25000
Ni(HDDO) <sub>2</sub> Br <sub>2</sub> (H <sub>2</sub> O) 8.2 H <sub>2</sub> O	Ethanol	13200	14900		16600	
	DMSO	13100	14800		17500	
Ni(HDDO) <sub>2</sub> I <sub>2</sub> (H <sub>2</sub> O) 8.2 H <sub>2</sub> O	Ethanol	13100	15400		17200	
	Water	13100	15000		17200	
Ni(HDDO) <sub>2</sub> (NO <sub>3</sub> ) (H <sub>2</sub> O) <sub>8.2</sub> H <sub>2</sub> O	DMSO	13100	14500		17200	

**MAGNETIC SUSCEPTIBILITY**

The magnetic properties of the trinuclear clusters may be discussed in terms of Heisenberg-Dirac Van-vleck spin coupling Hamiltonian. For an isolated linear trimer the spin-spin Hamiltonian H is given by Eq. (1).

$$H = -2[J_{12}S_1S_2 + J_{23}S_2S_3 + J_{13}S_1S_3] \dots \dots \dots (1)$$

Where J<sub>ij</sub> is the exchange coupling constant between ith and jth paramagnetic centres and S<sub>i</sub> is the spin angular momentum operator for the ith centre. The spin angular momentum operator S<sub>i</sub>(i=1-3) have the same expectation values and may be written as S. The characteristic values of S<sub>i</sub>.S<sub>i</sub>=S(S+1) and by taking S<sub>13</sub>=S<sub>1</sub>+S<sub>3</sub> and S<sub>123</sub>= S<sub>1</sub>+S<sub>2</sub>+S<sub>3</sub>, the energy levels for the Hamiltonian are described by Eq. (2).

$$E(S_{123}, S_{13}) = -J[S_{123}(S_{123}+1) - S_{13}(S_{13}+1) - S(S+1)] - J_{13}[S_{13}(S_{13}+1) - 2S(S+1)] \dots \dots \dots (2)$$

For the nickel triad with two unpaired spins on each metal ion, the energy values are recorded in Table-4.3. When the system is subjected to external magnetic field, the energy levels are further split into (2S<sub>123</sub>+1) levels, i.e, the first order Zeeman term gM<sub>s</sub> βH is added to the energy where g is Lande splitting factor and M<sub>s</sub> takes the values S<sub>123</sub>, S<sub>123</sub>-1, ..., -S<sub>123</sub>.

The molar susceptibility is given by Eq. 3.

$$\chi_m = \frac{N}{H} [\sum_i \frac{E_i}{H} \exp(-\frac{E_i}{kT}) / \sum_i \exp(-\frac{E_i}{kT})] \dots \dots \dots (3)$$

**Table-4.3:** The energy values for the Nickel triad

S <sub>12</sub>	S <sub>123</sub>	E <sub>i</sub>
2	3	-4f-2f <sub>13</sub>
2	2	-2f-2f <sub>12</sub>
1	2	-2f+2f <sub>13</sub>
2	1	-6f-2f <sub>12</sub>
1	1	2f+2f <sub>12</sub>
0	1	4f <sub>13</sub>
1	0	4f+2f <sub>13</sub>

In the present case g βH < kT in the temperature range studied, the susceptibility values listed in Table-4.4(a) have been corrected for diamagnetism using Pascal's constants and the temperature independent paramagnetism. The effective magnetic moments has been calculated at each temperature employing the expression μ<sub>eff</sub>=2.828 (T<sub>A</sub>-N<sub>a</sub>)<sup>1/2</sup>. The value 200×10<sup>-6</sup> c.g.s/e.m.u. per nickel ion has been used for N<sub>a</sub>, the temperature independent paramagnetism.

**Table-4.4(a)**

T/K	X <sub>A</sub> ×10 <sup>6</sup>	μ <sub>eff</sub> (B.M)
305.0	4330	3.11
285.0	4687	3.11
270.0	5123	3.14
250.0	5670	3.11
240.0	6100	3.14
200.0	6505	3.15
190.0	6698	3.21
175.0	7396	3.25
145.0	9898	3.38
135.0	10710	3.58
125.0	12539	3.45
110.0	14900	3.56
101.0	15833	3.56

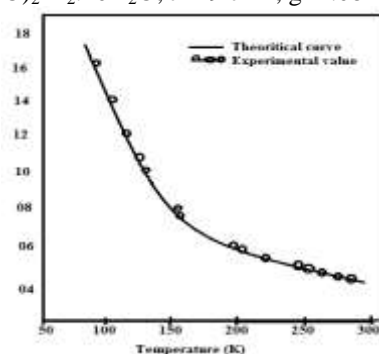
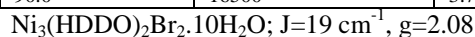
$$Ni_3(HDDO)_2Cl_2 \cdot 10H_2O; J = 18 \text{ cm}^{-1}, g = 2.05$$

At room temperature, a μ<sub>eff</sub> value of 3.3 B.M. is observed for each compound and it gradually increases as the temperature is lowered. Comparison with Kambe's theoretical curve-4.1 indicated that exchange coupling constant J must be positive. The best fit value for J and the Lande' splitting factor g were derived for the each

compound and are recorded in Table-4.4(b). The magnetic susceptibilities observed for the compounds were compared with the predicted ones obtained by graphical procedure. The monotonic increase in moment together with positive exchange coupling constant provide evidence in support of a trimeric structure of the complexes and for the existence of ferromagnetic interaction between different subsets of spins in the trinuclear clusters.

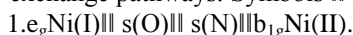
**Table-4.4(b)**

T/K	$\chi_A \times 10^6$	$\mu_{\text{eff}}(\text{B.M})$
305.0	4380	3.17
288.0	4647	3.19
275.0	5123	3.25
260.0	5630	3.30
250.0	6600	3.36
240.0	7005	3.45
210.0	7998	3.50
185.0	9996	3.56
150.0	11898	3.60
120.0	14710	3.65
100.0	14939	3.70
90.0	16500	3.75

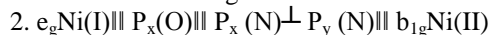


**Curve-4.1**

The major contribution to ferromagnetism in the trinuclear 3,5-heptanedionedioxime nickel (II) complexes is due to super-exchange through –OH bridging groups rather than direct overlap of metal-metal orbitals. The ferromagnetic spin coupling can be reasonably understood from the consideration of symmetry relationship between metal orbitals containing unpaired spins and s and p orbitals of O and N atoms which constituted the polyatomic bridging system. For the terminal metal ion in the trimer, the unpaired electron may be considered to occupy the  $e_g$  orbitals in an octahedral ligand field. For the central ion, tetragonal distortion occurs and under  $D_{4h}$  symmetry the set of d orbitals may be considered to split with the following decreasing order of energy  $b_{1g}$  ( $d_{x^2-y^2}$ ) >  $b_{2g}$  ( $d_{xy}$ ) ≥  $a_{1g}$  ( $d_{z^2}$ ) and <  $e_g$  ( $d_{yz}$ ,  $d_{xz}$ ) with the unpaired electrons occupying orbital of  $b_{1g}$  and  $b_{2g}$  representation. Since super-exchange mechanism is well known for  $180^\circ$  and  $90^\circ$  interactions we assume an idealized geometry with –O-N-Ni(2) angle of  $90^\circ$ . The contribution to J may be, considered by the following 1,2, and 3 exchange pathways. Symbols || and  $\perp$  indicate overlap and orthogonality respectively.

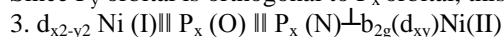


The  $e_g$  orbitals of terminal nickel ions and  $b_{1g}$  orbital of central nickel ion mutually overlap with the spherically symmetrical 2s orbitals of the bridging O and N atom. This super-exchange pathway will lead to antiferromagnetic coupling. If the terminal nickel ion has  $\alpha$  spin than  $\beta$  spin will arise on the central ion and the contribution to J would be negative



The unpaired spin density (say  $\alpha$ ) at the  $e_g$  orbitals of the terminal nickel ions may be first transferred to  $P_x$  orbitals of O and N and subsequently to  $b_{1g}$  orbital of Ni(II) through  $P_y$  of N.

Since  $P_y$  orbital is orthogonal to  $P_x$  orbital, this interatomic direct exchange would be ferromagnetic.



The third pathway is Anderson's true direct exchange effect between unpaired spins occupying mutually orthogonal orbitals. It is always ferromagnetic and originates from coulomb repulsion of the overlap charge. A true direct exchange between terminal and centered nickel ions occurs because the unpaired spins in  $e_g$  and  $b_{2g}$  sets respectively are in mutually orthogonal orbitals and coupling between  $e_g$  and  $b_{2g}$  subset centered on nickel(1) and (2) would be ferromagnetic. The magnitude and sign of J would be the resultant of the terms 1-3. The contribution of each pathway will be influenced by the magnitude of the relevant overlap integrals, interatomic distances and angles and the relative energies of the orbitals. In the present case the combined effect

of pathways 2 and 3 predominates over the antiferromagnetic term 1 with the result that the spins of adjacent metal ions in the trimers interact ferromagnetically.

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