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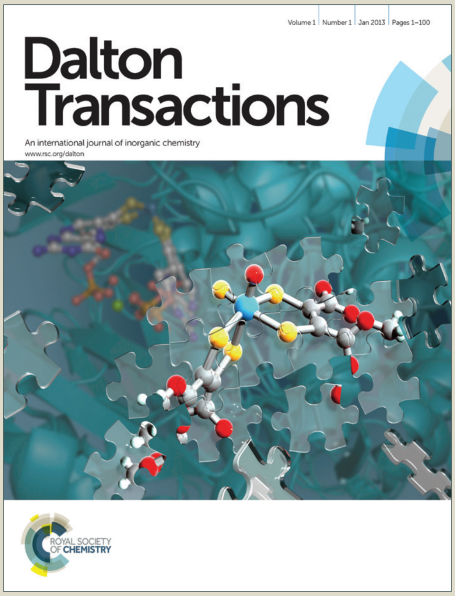

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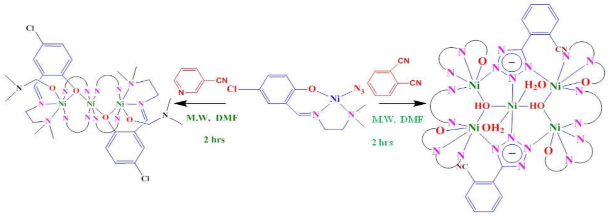
The [2+3] cycloaddition reaction between metal coordinated azide [Ni(L)(N_3)] and different organonitriles afforded tetrazolate bridge tri- and pentanuclear nickel (II) complexes revealing antiferromagnetic interactions.



Limiting nuclearity in formation of polynuclear metal complexes through [2+3] cycloaddition: synthesis and magnetic properties of tri- and pentanuclear metal complexes generated through bridging tetrazolate moiety

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* *Supporting Information*

A tridentate ligand *p*-chloro-2-{(2-(dimethylamino)ethylimino)methyl}phenol (HL) was used to generate an octahedral nickel complex [Ni(L)Cl(H_2O)$_2$] **1** which was further converted into a square-planar nickel complex [Ni(L)(N_3)] **2**. The [2+3] cycloaddition reaction between metal coordinated azide **2** and different organonitriles under microwave irradiation afforded tri- and pentanuclear nickel (II) complexes **4a**-**4c**. Reaction with benzonitrile and 3-cyano pyridine furnished the trinuclear species [Ni_3L_2(5-Phenyltetrazolato)$_4$(DMF)$_2$] **4a** and [Ni_3L_2{5-(3-pyridyl)-tetrazolato}$_4$(DMF)$_2$]$\cdot$2H_2O **4b**, respectively. The nickel centers were found to be linearly disposed to each other and the complex is formed by a 2,3-tetrazolate bridge and a phenoxo bridge between central and terminal nickel atoms. Compound **2** when treated with 1,2-dicyanobenzene under identical conditions furnished a pentanuclear complex [Ni_5L_4{5-(2-cyanophenyl)-tetrazolato}$_4$(OH)$_2$(H_2O)$_2$]$\cdot$3$H_2O\cdot$DMF **4c**. In this pentanuclear compound two dimeric nickel units are connected to the central nickel center by a μ_3-hydroxo bridge and a tetrazolate ligand operating *via* a relatively rare 1,2,3-bridging mode. The compounds were characterized by IR, elemental analysis, thermogravimetric analysis and single crystal X-ray crystallography. The magnetic susceptibility data for compound **4a**-**4c** shows dominant antiferromagnetic interactions between the nickel centers for all the

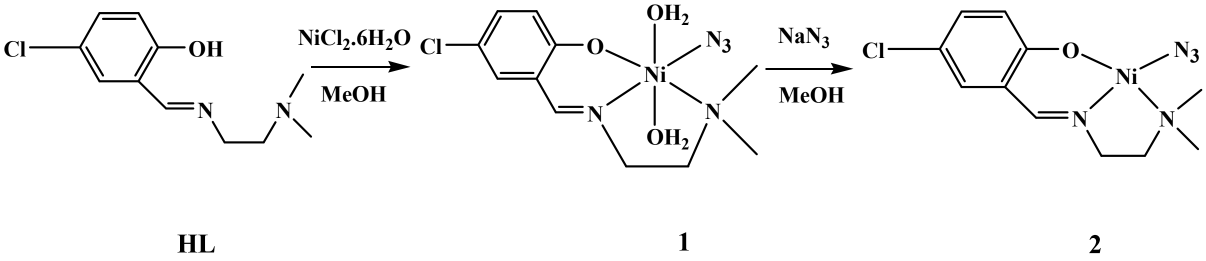
complexes. DFT calculations were performed to investigate the magnetic parameter in one of the complex **4b** by Broken Symmetry approach.

Introduction

Generation of coordination polymers using tetrazole ligands is now a popular method as tetrazoles can act as a very good bridging ligand for the formation of multidimensional coordination polymers exhibiting great structural diversity sometimes with interesting catalytic, optical, magnetic, membrane and absorption property[1]. However, the synthetic procedure largely depends upon solvothermal synthesis, which generates polymers in an uncontrolled way irrespective of whether the tetrazoles were used as a starting material or generated *in situ* by cycloaddition pathway between azide and organonitriles in presence or absence of supporting ligands.[2] Limiting nuclearity to a finite level is a challenging task from the synthetic viewpoint as polynuclear complexes can many times show unusual magnetic or catalytic properties.[3] Only a handful polynuclear complexes have been synthesized under different reaction conditions where tetrazoles acts as bridging ligands.[4] To further explore[5] the metal mediated cycloaddition reactions involving organonitriles and coordinated azide for the synthesis of novel 5-substituted tetrazole complexes, preferably under mild conditions, we have focused our interest to generate polynuclear compounds with limiting nuclearity in presence of an additional tridentate ligand. Herein, we investigate the reaction of monoazido nickel compound $[Ni(L)(N_3)]$ (**2**) [HL = *p*-chloro-2-{(2-(dimethylamino)ethylimino)methyl}phenol] with various organonitriles. Two of the reported compounds exhibit linear trinuclear structure while the other compound shows pentanuclear structure.

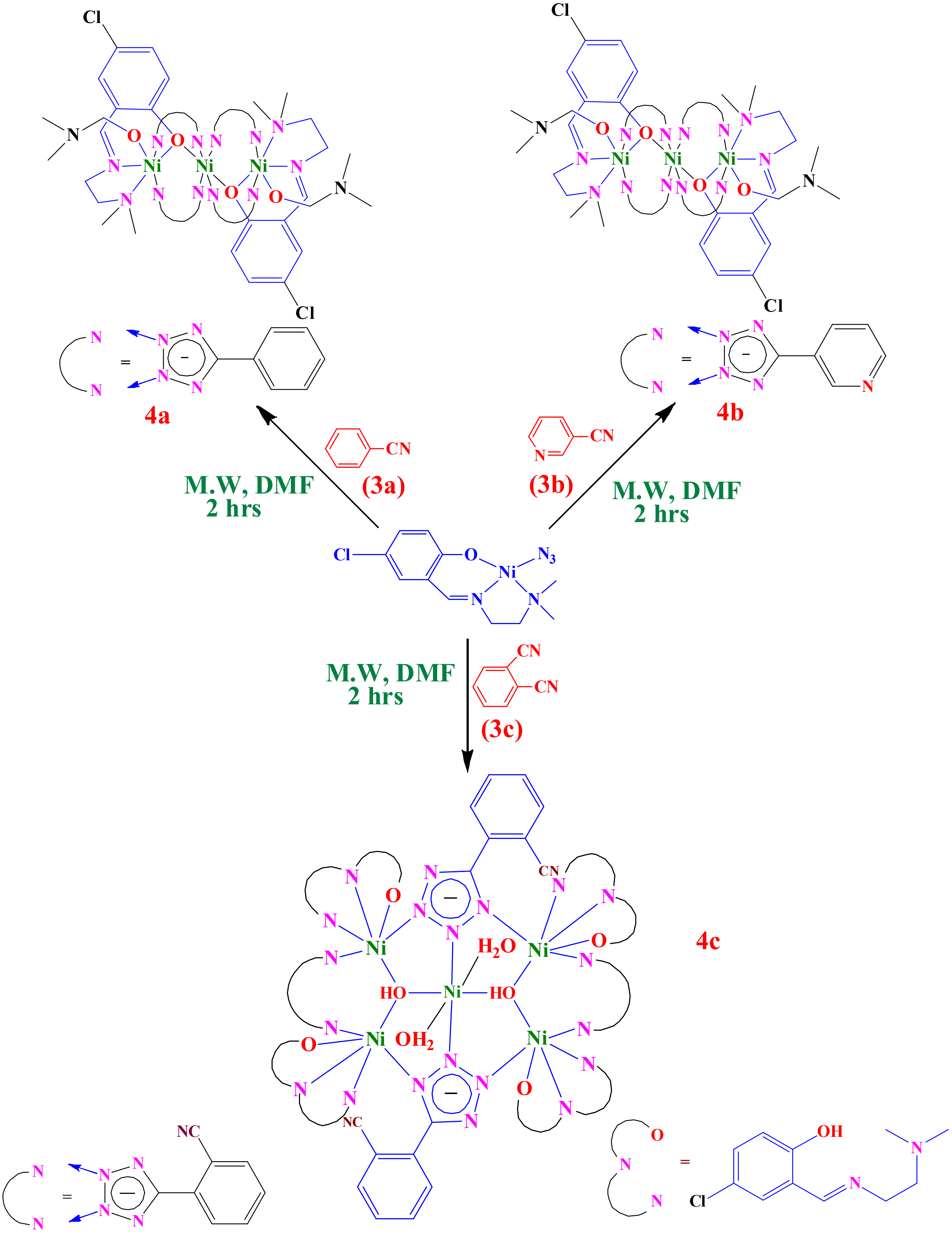
Results and Discussions

To target the formation of polynuclear compounds a square-planar monoazido nickel complex has been synthesized. This complex with a limited number of coordinated ligands demonstrates a natural tendency to expand its coordination number when more prospective coordination sites have been supplied through formation of polydentate tetrazole ligand by *in situ*-cycloaddition of coordinated azide and nitrile.



Scheme 1 Schematic representation for the synthesis of the complex [Ni(L)(N$_3$)].

A methanolic solution of the iminophenol [HL = *p*-chloro-2-{(2-(dimethylamino)ethylimino)methyl}phenol] was treated with nickel chloride (1 eq), at room temperature for 3 h to furnish a chloro-diaquo-complex [Ni(L)Cl(H$_2$O)$_2$] **1**. Subsequent treatment of complex **1** with NaN$_3$ at room temperature replaces the chloride ligand with azide and liberates the coordinated water molecules to yield [Ni(L)(N$_3$)] **2** (Scheme 1).[6] Compound **1** and **2** were isolated in good yields**.** Treatment of the monoazido complex **2** under microwave irradiation with different organonitriles RCN **3** [R = C$_6$H$_5$ (**3a**), 3-NC$_5$H$_4$ (**3b**), 2CN-C$_5$H$_4$ (**3c**)] gives the corresponding polynuclear complexes [Ni$_3$L$_2$(5-Phenyltetrazolato)$_4$(DMF)$_2$] (**4a**), [Ni$_3$L$_2${5-(3-pyridyl)-tetrazolato}$_4$(DMF)$_2$]·2H$_2$O and [Ni$_5$L$_4${5-(2-cyanophenyl)-tetrazolato}$_4$(OH)$_2$(H$_2$O)$_2$]·3H$_2$O·DMF (**4c**), respectively (Scheme 2). In all the cases the compound was isolated as reddish-brown powder which has been further recrystallized from suitable solvents.



Scheme 2 Synthetic route of the complexes **4a-4c** .

All the complexes (**1**, **2** and **4a**-**4c**) have been characterized by elemental analyses, IR and TGA analyses (except **2**). Complex **1** is further characterized by ESI-MS spectroscopy and in the case of complexes **2** and **4a**-**4c,** by single crystal X-ray crystallography . IR spectra of all the compounds have a couple of prominent bands at ca. 1635 and 1535 cm^{-1} region assignable to ν(C=N) and ν(C-O/phenolate) stretching modes, respectively.[7] In the high frequency region, a broad band of medium intensity around 3420-3500 cm^{-1} indicates the presence of coordinated water molecule in complex **1** and **4c**.[7] The IR spectrum of compound **2** displays a strong band at 2051 cm^{-1} due to the asymmetric stretching vibration of coordinated azido group.[8] Complexes **4a–4c** show a strong band *ca.* 1650 cm^{-1}, attributed to the coordinated tetrazolate group.[5] Moreover, complex **4c** exhibits a band at 2229 cm^{-1} indicating the presence of free nitrile group which is not involved in the cycloaddition. In conclusion, the infrared spectral data of the complexes **2** and **4a–4c** are found to be consistent with crystal structure analyses.

The thermal stabilities of complexes **1** and **4a-4c** were examined by thermogravimetric analysis. For complex **1** (Figure 1, Supporting Information), the first weight loss of 10.11 % is observed in the temperature range 30-100 ºC which corresponds to the loss of the two coordinated water molecules. Further heating to 700 ºC results in the slow decomposition of the sample. The polycrystalline complex **4a** shows a rapid decomposition in the temperature range 30-300° C (Figure 2, Supporting Information). The complex **4b** exhibits two thermal steps which were followed by a continuous weight loss above 270° C (Figure 3, Supporting Information). The first weight loss of 2.72 % in the temperature range 40-120°C corresponds to the loss of two water of crystallization. The anhydrous complex further undergoes weight loss of 10.29 % in the range 150-190 °C which corresponds to the loss of two coordinated *N*,*N*-Dimethylformamide (DMF) molecules. The TGA graph of complex **4c** shows a two step weight loss. The initial weight loss of 4.26 % in the temperature range 60-130°C, corresponds to the loss of five water molecules (three water of crystallization and two coordinated water molecule) which is followed by the weight loss of 3.56 % due to loss of one DMF molecule in the temperature range of 140-200 °C (Figure 4, Supporting Information). A continuous weight loss was recorded above 270 °C for complex **4c**.

Table 1 Crystal data and structure refinement information for compounds **2** and **4a-4c**.

	2	**4a**	**4b**[a]	**4c**[a]
Empirical formula	$C_{11}H_{14}N_5ONiCl$	$C_{28}H_{31}N_{11}O_2Ni_{1.5}Cl$	$C_{52}H_{62}N_{26}O_2Ni_3Cl_2$	$C_{79}H_{85}N_{29}O_{12}Ni_5Cl_4$
Formula weight	326.43	677.15	1394.27	2067.95
Wavelength(A)	0.71073	0.71073	0.71073	0.71073
Temperature(K)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Color and shape	Brown needle	Green needle	Green needle	Green needle
Space group	P 21 /c	P - 1	P 21 /c	P 21 /c
a/Å	9.4997(3)	11.0194(11)	15.6896(18)	10.5420(10)
b/Å	12.1258(4)	12.2772(12)	15.8934(17)	22.598(3)
c/Å	11.8494(4)	12.3400(13)	16.5290(15)	21.861(2)
α/degree	90	79.470(8)	76.751(9)	90
β/degree	100.933(3)	76.251(9)	89.705(9)	91.357(9)
γ/degree	90	79.852(8)	69.725(10)	90
Volume($Å^3$)	1340.18(8)	1578.8(3)	3750.9(7)	5206.5(10)
Z	4	2	2	2
D_{calcd} /mg m^{-3}	1.618	1.424	1.231	1.384
μ(Mo Kα)/mm^{-1}	1.646	1.033	0.875	1.062
F(000)	672	702	1436	2220
Crystal size/mm	0.32 x 0.28 x 0.22	0.32 x 0.26 x 0.21	0.23 x 0.16 x 0.13	0.26 x 0.21 x 0.18
θ range(°)	3.03 to 25.00	3.15 to 25.00	3.15 to 25.00	2.94 to 25.00
Limiting indices	-11<=h<=9 -14<=k<=12 -14<=l<=14	-12<=h<=13 -14<=k<=14 -14<=l<=14	-18<=h<=18 -18<=k<=18 -19<=l<=18	-11<=h<=12 -26<=k<=23 -25<=l<=25
Total/ unique no. of reflns.	8391 / 2357	10777 / 5547	30207 / 13183	41030 / 9170
R_{int}	0.0214	0.0533	0.0866	0.1220
Data/restr./params.	2357 / 0 / 174	5547 / 0 / 398	13183 / 0 / 813	9170 / 0 / 623
GOF(F^2)	1.153	1.038	1.142	1.041
R1, wR2	0.0478, 0.1408	0.0563, 0.1516	0.1086, 0.3015	0.0837, 0.2231
R1, wR2 (all data)	0.0492, 0.1416	0.0733, 0.1743	0.1491, 0.3507	0.1318, 0.2817

Peak and hole (e Å^{-3n})	2.069 and -0.498	0.925 and -0.886	2.160 and -0.889	1.120 and -0.663

[a] The "SQUEEZE" software was applied to subtract the contribution of disordered solvent from diffraction data of **4b** (two water molecules) and **4c** (one DMF and three water molecules). Refinement was carried out after solvent electron density was removed by the SQUEEZE routine in PLATON.

Crystal structures of [Ni(L)(N_3)] (2), [Ni_3L_2(5-Phenyltetrazolato)$_4$(DMF)$_2$] (4a), [Ni_3L_2{5-(3-pyridyl)-tetrazolato}$_4$(DMF)$_2$]·2H_2O (4b) and [Ni_5L_4{5-(2-cyanophenyl)-tetrazolato}$_4$(OH)$_2$(H_2O)$_2$]·3H_2O·DMF (4c).

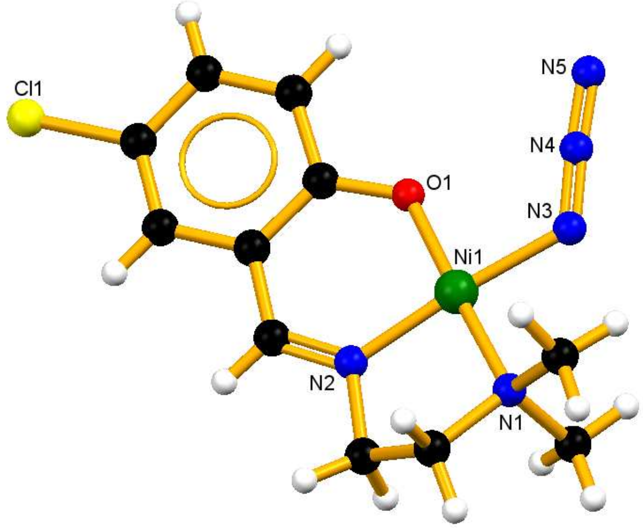


Figure 5 Molecular structure of [Ni(L)(N_3)] **2** with atomic numbering scheme.

The monoazide compound **2** crystallizes in space group P2$_{1/c}$ (Table 1). In [Ni(L)(N_3)] **(2),** the central metal ion is coordinated to the tridentate Schiff-base ligand L and one azide ion to give a distorted square planar geometry (Figure 5). The Ni-N bond lengths range from 1.856(4) to 1.955(4) Å and together with the Ni-O distance (1.837(3) Å) (Table 2) are well within the ranges of related square planar nickel complexes.[6,9] The N_3 group is almost linear

[N5-N4-N3 175.9(5)°] and is not coaxial with the Ni1-N3 bond as shown by the Ni1-N3-N4 angle [122.1(3)°] and lies in the same plane as the O1, N1 and N2 atoms.

Table 2 Selected bond lengths (Å) and bond angles (°) for **2**.

Ni(1)-O(1)	1.836(3)	O(1)-Ni(1)-N(2)	94.55(16)
Ni(1)-N(2)	1.855(4)	O(1)-Ni(1)-N(3)	89.08(16)
Ni(1)-N(3)	1.900(4)	N(2)-Ni(1)-N(3)	175.39(17)
Ni(1)-N(1)	1.955(4)	O(1)-Ni(1)-N(1)	176.99(15)
Cl(1)-C(4)	1.751(5)	N(2)-Ni(1)-N(1)	87.28(17)
O(1)-C(1)	1.318(6)	N(3)-Ni(1)-N(1)	89.21(17)
N(1)-C(11)	1.485(6)	C(1)-O(1)-Ni(1)	126.2(3)
N(1)-C(9)	1.493(6)	C(11)-N(1)-C(9)	110.4(4)
N(1)-C(10)	1.495(6)	C(11)-N(1)-C(10)	108.8(4)
N(2)-C(7)	1.288(6)	C(9)-N(1)-C(10)	108.3(4)
N(2)-C(8)	1.479(6)	C(11)-N(1)-Ni(1)	108.9(3)
N(3)-N(4)	1.206(6)	C(9)-N(1)-Ni(1)	106.9(3)
N(4)-N(5)	1.154(6)	C(10)-N(1)-Ni(1)	113.5(3)
		C(7)-N(2)-C(8)	119.2(4)

		C(7)-N(2)-Ni(1)	127.6(3)
		C(8)-N(2)-Ni(1)	113.2(3)
		N(4)-N(3)-Ni(1)	122.1(3)
		N(5)-N(4)-N(3)	175.9(5)

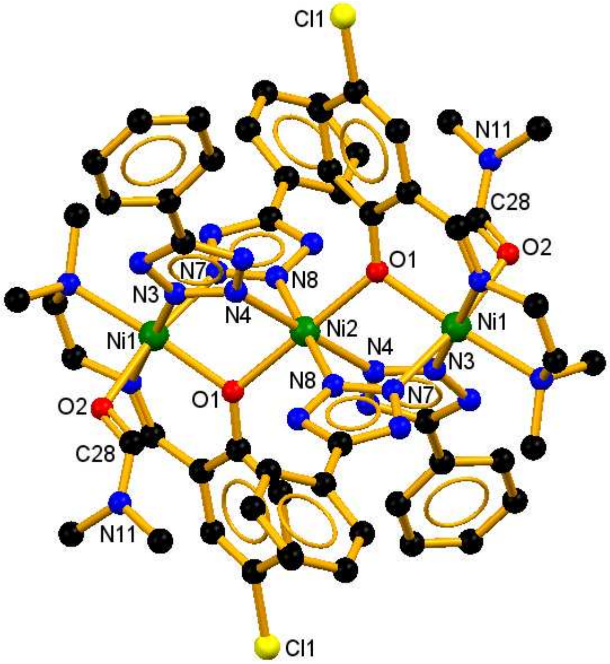


Figure 6 Molecular structure of [Ni_3L_2(5-Phenyltetrazolate)$_4$(DMF)$_2$] **4a** with atomic numbering scheme.

Complex **4a** crystallizes in space group P-1 (Table 1). It comprises of discrete centrosymmetric trinuclear units of the neutral compound [Ni_3L_2(5-Phenyltetrazolate)$_4$(DMF)$_2$] (Figure 6). The three nickel atoms are found to be in linear disposition. The central nickel atom Ni(2) has a coordination number of six, being bonded to the four nitrogen atoms of the bridging tetrazolato group (2,3-bridged) at distances ranging

2.067(3)-2.077(3) Å (Table 3) that form the square plane of the Ni(II) while the axial positions are occupied by bridging oxygen atoms O1 of phenoxo groups. The two terminal nickel atoms are bonded to three atoms of ligand L in the equatorial plane where as the fourth position of the plane has been taken up by bridging tetrazole nitrogen atom N3. The coordination environment surrounding the terminal nickel atoms are also distorted octahedral and the axial positions are taken up by another nitrogen N8 atom of bridging tetrazolate group and one DMF molecule, respectively. The Ni-N bond distances are found to be in the range 1.997(4)-2.151(3) Å, whereas the Ni-O distances remain in the range 2.056(2)-2.169(3) Å. The central nickel atom has been found to be bridged to the terminal nickels atoms through phenoxo-group of tridentate ligand and two bridging tetrazolate groups. The central nickel- terminal nickel distance was found to be 3.327(6) Å.

Table 3 Selected bond lengths (Å) and bond angles (°) for **4a**.

Ni(1)-N(1)	1.997(3)	N(1)-Ni(1)-N(3)	175.71(14)
Ni(1)-N(3)	2.035(3)	N(1)-Ni(1)-O(1)	90.55(13)
Ni(1)-O(1)	2.056(3)	N(3)-Ni(1)-O(1)	88.38(12)
Ni(1)-N(7)	2.141(3)	N(1)-Ni(1)-N(7)	94.06(13)
Ni(1)-N(2)	2.151(4)	O(1)-Ni(1)-N(7)	84.42(12)
Ni(1)-O(2)	2.170(3)	N(1)-Ni(1)-N(2)	82.63(14)
Ni(2)-N(8)#1	2.067(3)	N(3)-Ni(1)-N(2)	98.40(13)
Ni(2)-N(8)	2.067(3)	N(7)-Ni(1)-N(2)	96.31(13)
Ni(2)-N(4)	2.077(3)	N(1)-Ni(1)-O(2)	85.96(13)
Ni(2)-N(4)#1	2.077(3)	N(3)-Ni(1)-O(2)	89.84(12)
Ni(2)-O(1)#1	2.103(2)	O(1)-Ni(1)-O(2)	87.10(11)
Ni(2)-O(1)	2.103(2)	N(2)-Ni(1)-O(2)	92.11(13)

N(8)#1-Ni(2)-N(8)	180.0
N(8)#1-Ni(2)-N(4)	88.86(13)
N(8)#1-Ni(2)-N(4)#1	91.14(13)
N(4)-Ni(2)-N(4)#1	180.0(2)
N(8)#1-Ni(2)-O(1)#1	82.17(11)
N(8)-Ni(2)-O(1)#1	97.83(11)
N(4)-Ni(2)-O(1)#1	94.30(11)
O(1)#1-Ni(2)-O(1)	180.00(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z

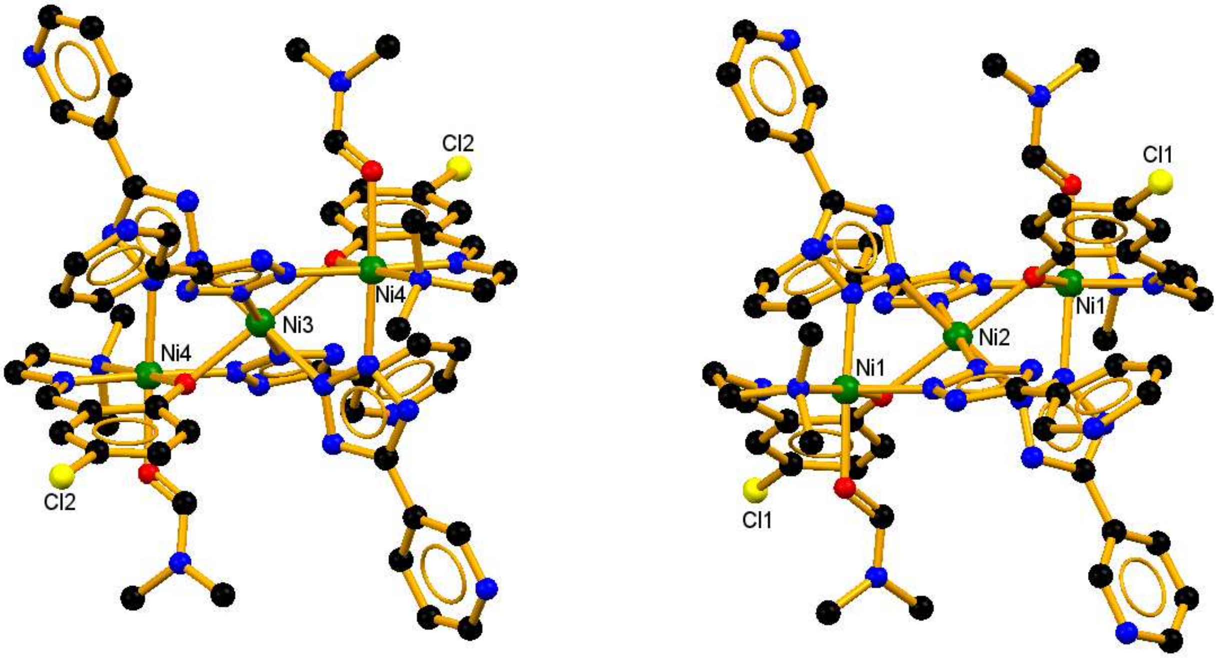


Figure 7 Molecular structure of [Ni_3L_2{5-(3-pyridyl)-tetrazolato}$_4$ (DMF)$_2$]· 2H_2O **4b** with atomic numbering scheme. Solvent of crystallization is omitted for clarity.

Compound **4b,** [Ni_3L_2{5-(3-pyridyl)-tetrazolato}$_4$ (DMF)$_2$]·2H_2O has a similar structure like compound **4a**. However, there are two crystallographically independent molecules in the unit cell (Figure 7). For both the molecules the three nickel centers are linearly arranged. For the central nickel atom the Ni-N bond distances are found to be in the range of 2.071(7)-2.107(7) Å, whereas the Ni-O$_{phenoxo}$ bonds are found in the range of 2.106(4)-2.117(5) Å (Table 4). Regarding the terminal nickel centers the Ni-N bond distances were found to be in the range of 1.970(6)-2.161(9) Å and Ni-O$_{phenoxo}$ and Ni-O$_{DMF}$ are 2.057(5) Å and in the range of 2.136(6)-2.143(7) Å, respectively. The central nickel- terminal nickel distances were found to be in the range of 3.333(1)-3.336 (1) Å.

Table 4 Selected bond lengths (Å) and bond angles (°) for **4b**[a].

Ni(1)-N(1)	1.970(7)	N(1)-Ni(1)-N(3)	178.6(3)
Ni(1)-N(3)	2.037(7)	N(1)-Ni(1)-O(1)	90.4(2)
Ni(1)-O(1)	2.057(5)	N(3)-Ni(1)-O(1)	88.7(2)
Ni(1)-N(8)	2.118(6)	N(1)-Ni(1)-N(8)	89.8(3)
Ni(1)-O(2)	2.135(6)	N(3)-Ni(1)-N(8)	89.0(3)
Ni(1)-N(2)	2.161(6)	O(1)-Ni(1)-N(8)	84.4(2)
Ni(2)-N(4)	2.072(6)	N(1)-Ni(1)-O(2)	89.9(3)
Ni(2)-O(1)#1	2.107(5)	N(3)-Ni(1)-O(2)	91.1(3)
Ni(2)-O(1)	2.107(5)	O(1)-Ni(1)-O(2)	87.0(2)
Ni(2)-N(9)#1	2.107(6)	N(8)-Ni(1)-O(2)	171.3(2)
Ni(2)-N(9)	2.107(6)	N(1)-Ni(1)-N(2)	83.0(3)
Ni(3)-N(21)#2	2.071(6)	N(3)-Ni(1)-N(2)	97.9(3)
Ni(3)-N(16)	2.081(6)	O(1)-Ni(1)-N(2)	172.8(3)
Ni(3)-N(16)#2	2.081(6)	N(8)-Ni(1)-N(2)	98.6(3)
Ni(3)-O(3)	2.117(5)	O(2)-Ni(1)-N(2)	90.0(3)
Ni(3)-O(3)#2	2.117(5)	N(4)# -Ni(2)-N(4)	180.00(14)
Ni(4)-N(14)	1.994(7)	N(4)#1-Ni(2)-O(1)#1	85.7(2)
Ni(4)-N(22)#2	2.037(6)	N(4)-Ni(2)-O(1)#1	94.3(2)
Ni(4)-O(3)	2.057(5)	N(4)#1-Ni(2)-O(1)	94.3(2)
Ni(4)-N(17)#2	2.115(7)	N(4)-Ni(2)-O(1)	85.7(2)
Ni(4)-O(4)	2.143(6)	O(1)#1-Ni(2)-O(1)	180.0(3)
Ni(4)-N(15)	2.151(6)	N(4)#1-Ni(2)-N(9)#1	90.4(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z #2 -x+1,-y,-z+1

[a] Refinement was carried out after solvent electron density was removed by the SQUEEZE routine in PLATON.

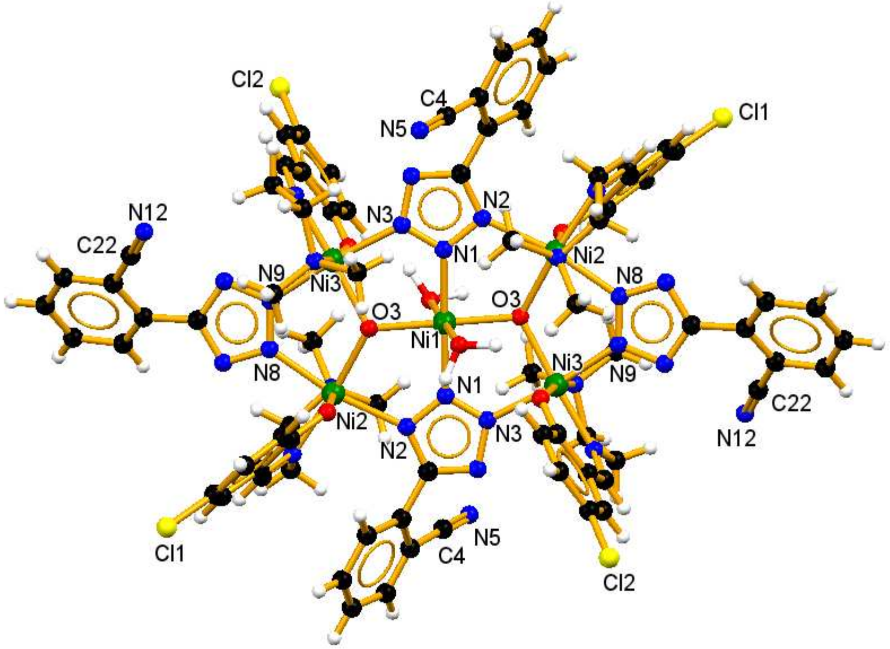


Figure 8 Molecular structure of $[Ni_5L_4\{5\text{-}(2\text{-cyanophenyl})\text{-tetrazolato}\}_4(OH)_2(H_2O)_2]\cdot 3H_2O\cdot DMF$ **4c** with atomic numbering scheme. Solvent of crystallization is omitted for clarity.

Discrete homopentanuclear nickel(II) clusters are relatively rare[10]. However there are many nickel (II) complexes which have been reported bearing a μ_3-OH ligand[11]. The pentanuclear structure of complex **4c** comprises of two dinuclear $[Ni_2L_2\{5\text{-}(2\text{-cyanophenyl})\text{-tetrazolato}\}]$ units which are each linked to the central nickel atom by bridging μ_3-hydroxo groups and also through another tetrazolate moiety which also connects two dimeric units through 1,2,3-tetrazolate bridge (Figure 8). The central nickel atom is six coordinated with $\{N_2O_4\}$ donor set. Two nitrogen atoms come from two bridging tetrazolate group and two oxygen donor is comprised of two μ_3-OH ligand to complete the equatorial positions. The apical positions have been taken up by water molecules. The Ni-N bond distance are found to be 2.044(5) Å, whereas the Ni-O$_{hydroxo}$ bond distance is 2.050(4) Å and Ni-O$_{water}$ bond distance is found to 2.117(4) Å (Table 5). The Ni-O$_{hydroxo}$ bond length is quite indicative that the μ$_3$-bridging ligand is hydroxo- but not oxo- where the expected bond length is in the range of 1.8-1.9 Å.[12] The terminal nickel atoms are also having octahedral geometry with {N$_4$O$_2$} environment. The ligand L provides the {N$_2$O} donor set where the other positions are taken up by two bridging tetrazolate group (2,3-bridged and 1,2,3-bridged) and another μ$_3$-hydroxo group. The Ni-N bond distances are found to be in the range 2.023(7) to 2.230(5) Å whereas the Ni-O bond distances remains within the expected range of 2.023(4) to 2.146 (4) Å. The central nickel atom and terminal nickel atoms are found to be separated to each other by 3.460 to 3.589 Å, where as the distance between two nickel centers of terminal dimer is 3.687 Å.

Moreover, the crystal structure of complex **4b** (two water molecules) and **4c** contains disordered solvent molecules (probably water and DMF), which could not be modeled by discrete atoms. Its contribution was subtracted from the diffraction pattern by the "SQUEEZE" method.

Table 5 Selected bond lengths (Å) and bond angles (°) for **4c**[a].

Ni(1)-N(1)	2.044(5)	N(1)-Ni(1)-N(1)#1	180.0(3)
Ni(1)-N(1)#1	2.044(5)	N(1)-Ni(1)-O(3)#1	91.87(19)
Ni(1)-O(3)#1	2.051(4)	N(1)#1-Ni(1)-O(3)#1	88.13(19)
Ni(1)-O(3)	2.051(4)	N(1)-Ni(1)-O(3)	88.13(19)
Ni(1)-O(4)	2.116(5)	N(1)#1-Ni(1)-O(3)	91.87(19)
Ni(1)-O(4)#1	2.116(5)	O(3)#1-Ni(1)-O(3)	180.0(2)
Ni(2)-N(7)	2.030(6)	N(1)-Ni(1)-O(4)	88.4(2)

Ni(2)-N(2)	2.170(6)	N(1)#1-Ni(1)-O(4)	91.6(2)
Ni(2)-N(6)	2.280(6)	O(3)#1-Ni(1)-O(4)	86.6(2)
Ni(2)-O(1)	2.044(5)	O(3)-Ni(1)-O(4)	93.4(2)
Ni(2)-N(8)	2.092(6)	N(1)-Ni(1)-O(4)#1	91.6(2)
Ni(2)-O(3)	2.146(4)	N(1)#1-Ni(1)-O(4)#1	88.4(2)
Ni(3)-O(2)	2.023(5)	O(3)#1-Ni(1)-O(4)#1	93.4(2)
Ni(3)-N(14)	2.024(6)	O(3)-Ni(1)-O(4)#1	86.6(2)
Ni(3)-N(9)	2.069(6)	O(4)-Ni(1)-O(4)#1	180.0(2)
Ni(3)-O(3)	2.083(5)	N(7)-Ni(2)-O(1)	88.6(2)
Ni(3)-N(3)#1	2.128(6)	N(7)-Ni(2)-N(8)	91.4(2)
Ni(3)-N(13)	2.230(6)	O(1)-Ni(2)-N(8)	92.4(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

[a] Refinement was carried out after solvent electron density was removed by the SQUEEZE routine in PLATON.

The magnetic properties of compound **4a**, **4b** and **4c** were studied on powdered samples by variable temperature susceptibility measurements. The susceptibility data were collected in a temperature range of 2 -300 K in an applied field of 0.1 Tesla and are shown as χ_MT vs. T (Figure 9 and Figure 10 respectively). The red lines correspond to the best simulation for **4b** and **4c**.

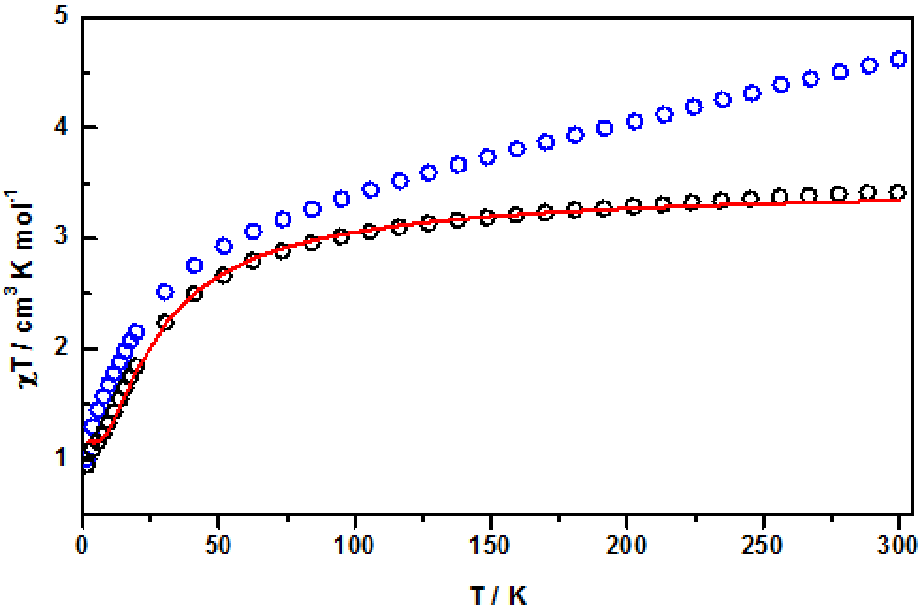


Figure 9 The resulting molar susceptibility data were plotted in □$_M$T *vs*. T in blue line for complex **4a** and in black line for complex **4b**. The red line corresponds to the best simulation for **4b**.

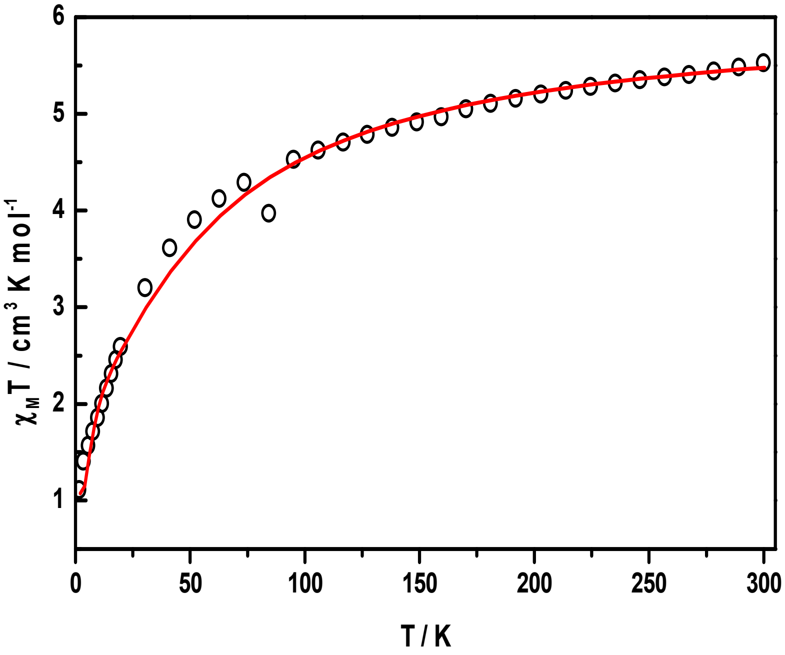


Figure 10 The resulting molar susceptibility data were plotted in □$_M$T *vs*. T for complex **4c**. The red line corresponds to the best simulation for **4c**.

For compound **4a** at room temperature no meaningful simulation could be obtained due to underlying impurities. The χ_MT-value for **4b** at room temperature is with 3.41 cm^3 K mol^{-1}

slightly higher than the expected one of 3.00 cm^3 K mol^{-1} for three uncoupled spins with $S_1 = S_2 = S_3 = 1$ but perfectly in agreement with the expected value considering g-values of 2.15 for the three nickel ions. Only a small decrease of the $\chi_M T$-value can be observed by lowering the temperature up to 70 K. Further cooling leads to a sharper decrease reaching a $\chi_M T$-value of 0.94 cm^3 K mol^{-1} at 2 K, indicating dominant antiferromagnetic interactions between the nickel centers.

For **4b** the magnetic data can be simulated satisfactorily by applying the isotropic exchange Hamilton operator: $\hat{H} = -2J\ (\hat{S}_1\hat{S}_2 \cdot \hat{S}_2\hat{S}_3)$. The best simulation is obtained with $J = -4.93$ cm^{-1} and $g_1 = g_2 = g_3 = 2.156$. A temperature independent paramagnetism, TIP, of $300X10^{-6}$ was included to obtain a good simulation.

DFT calculations are carried out to understand the anti-ferromagnetic interactions between the three Ni centers on complex **4b**. The magnetic behavior of polynuclear transition metal complexes have been studied by evaluating their magnetic exchange coupling constants. Several standard theoretical approaches are reported in literatures[13] but among all these, Broken Symmetry (BS) is the most popular one.[14] The BS approach uses unrestricted Hartree-Fock (UHF) or density functional theory (DFT) calculations for low spin molecular systems in which α and β spin densities are allowed to localize on their respective atomic centers. Generally, the calculated exchange coupling (J) constant differs very much from the experimental value due to the complexity of such problems and the limitation of DFT theory. Moreover, in the weakly coupled magnetic system, the J values even differ in both sign and magnitude from the experimental one.[15] In spite of all these, BS approach is very useful for understanding the mechanism of spin exchange in polynuclear complexes.[16] In the present study, we have performed DFT calculation with BS approach to evaluate the magnetic exchange coupling constant using the Hamiltonian $H= -2JS_1S_2$ on Yamaguchi formalism,[17]

$$J = -\frac{E_{HS} - E_{BS}}{<S^2>_{HS} - <S^2>_{BS}}$$

Where, E_{HS} and E_{BS} are the energies of the high spin state and broken symmetry state (low spin state) respectively, and $S^2 = S(S+1)$. The positive and negative value of J indicates ferromagnetic and antiferromagnetic interaction respectively.

The complexity of the magnetic systems increases if it has more than two magnetic centers. Therefore, such problems can be simplified if one of the magnetic centers can be substituted by a non-magnetic one.[18] As Fe(II) has two electrons less than Ni(II) therefore one of Ni (II) is substituted by Fe(II) and then the three center magnetic problem can be simplified into a two center magnetic problem. Similarly in our present study, we have substituted one of the Ni (II) atom by a Fe(II) atom.

DFT calculations were performed using Gaussian 09 program.[19] The X-ray coordinates of the complex were used for all the calculation. The unrestricted B3LYP functional and 6-31G*[20] basis set were used for all the atoms.

The calculated exchange coupling value of complex **4b** is found to be -5.78 cm^{-1}. Therefore the calculated value is in very good agreement with the experimental value of J= -4.93 cm^{-1}. To understand the magnetic exchange behaviour of complex **4b** it is important to note that Ni(1) and Ni(2) are bridged by one μ-phenoxo and two tetrazolate group in N(2)N(3) mode. There are few trinuclear nickel(II) complexes reported so far with μ-phenoxo bridge and it is also reported that the magnetic properties of such complexes are mostly governed by bridging Ni-O-Ni angles. For trinuclear Ni(II) complexes, ferromagnetic interaction is observed for Ni-O-Ni angles that are less than 93.5° while the magnetic coupling is antiferromagnetic for greater values.[21] In the present case the bond angles of Ni(1)-O(1)-Ni(2) is 106.50° and Ni(3)-O(3)-Ni(4) is 105.97°, respectively indicative of possible antiferromagnetic coupling as reported earlier.[21] Moreover from the Ni-O-Ni angle observed in this complex, the J value was expected in more lower range than the observed value. However, it should be also noted that there are reports where second bridging ligand can play countercomplementary effect leading to the decrease of antiferromagnetic coupling by formation of ferromagnetic exchange.[22] So far there are only few reports available where nickel centers are bridged by tetrazolate group in N(2)N(3) mode in presence of other bridging centers and most of the compounds reported are showing weak ferromagnetic interaction.[23] Considering the above facts it may be proposed that though there is weak ferromagnetic coupling between the nickel centers through tetrazole bridge however antiferromagnetic nature of the compound dominates because of the presence of more stronger exchange through phenoxo bridged ligand.For compound **4c** (Figure 10) at room temperature a χ_MT-value of 5.51 cm^3 K mol^{-1} is observed, which is slightly higher than the theoretical value of 5.00 cm^3 K mol^{-1} for five uncoupled spins with $S_1 = S_2 = S_3 = S_4 = S_5 = 1$, as expected for nickel(II) ions with g-values larger than 2.0. With lowering temperature a decrease of the χ_MT-value is observed reaching a χ_MT-value of 1.01 cm^3 K mol^{-1} at 2 K indicative for dominant antiferromagnetic interactions between the nickel centers.

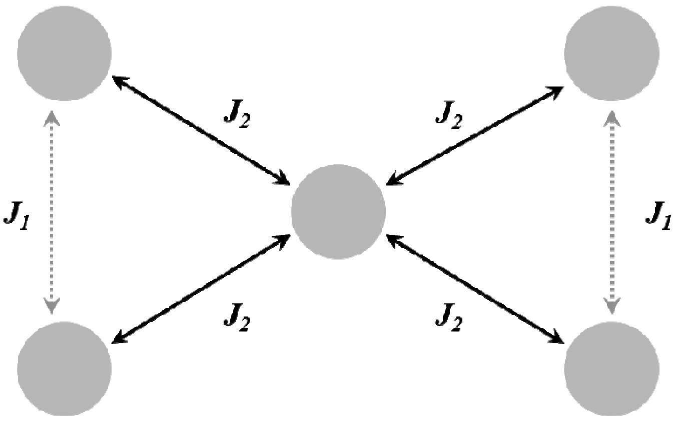


Figure 11 The magnetic data of **4c** can be simulated satisfactorily by applying the isotropic exchange Hamilton operator: $\hat{H} = -2J$ □ $\hat{S}_i\hat{S}_j$ and the exchange model.

The magnetic data of **4c** can be simulated satisfactorily applying the isotropic exchange Hamilton operator: $\hat{H} = -2J_{ij}\ \Sigma\hat{S}_i\hat{S}_j$ and the exchange model, shown in figure 11. The best simulation is obtained with J_1= -5.84 cm^{-1}, J_2 = -6.94 cm^{-1} and g_{all} = 2.20. A temperature independent paramagnetism, TIP, of $600X10^{-6}$ was included to obtain a good simulation.

It has been reported earlier the magnetic exchange properties for μ_3- or μ_2-hydroxo bridge depends upon the Ni-O-Ni angle and it has shown that generally angles with more than 97º inducts antiferromagnetic nature in the compounds where as angle less than that usually leads to the formation of ferromagnetic exchange.[24] For complex **4c** the average Ni-O-Ni angles are found to be in the range of 117º which predicts the magnetic exchange between nickel centers should be highly antiferromagnetic. Relatively higher value of *J* obtained for complex **4c** may be because of the countercomplementary effect from bridging tetrazolate groups in N(1)N(2)N(3) mode and N(2)N(3) mode. However, because of lack of more magnetic data regarding tetrazolate bridged nickel complexes it is difficult to elucidate the *J* value obtained for complex **4b** and **4c** in conclusive manner.

Conclusion

A tridentate ligand *p*-chloro-2-{(2-(dimethylamino)ethylimino)methyl}phenol (HL) and [2 + 3] cycloaddition between metal coordinated azide and different organonitriles have been used to limit the nuclearity of the isolated compound as tri- and pentanuclear nickel (II) complex. The nuclearity of the product depends on the nature of organonitrile used for cycloaddition. Thus when the organonitrile used is benzonitrile or 3-cyanopyridine trinuclear species **4a** and **4b** were obtained, respectively, formed by tetrazolate bridge (*via* N(2)N(3) mode) and a phenoxo bridge between central and terminal nickel centers. The nickel centers are found to be linearly disposed. The separation between metal centers are found to be in the range of

3.327-3.336 Å. Upon reaction with 1,2-dicyanobenzene complex **2** furnished a pentanuclear complex **4c**. The structure can be described as a central nickel center is connected to two nickel dimers by means of μ_3-hydroxo bridge apart from bridging tetrazole ligand which operates through 1,2,3-bridging mode. The distance between the central nickel atom and terminal nickel atoms are found to be in the range of 3.460-3.589 Å, where as the distances between two nickel centers of terminal dimer are 3.687 Å. The number of metal bound solvent molecules and solvent of crystallization in **4b** and **4c** were also confirmed by thermo-gravimetric analysis. The magnetic susceptibility data for compound **4a**-**4c** in the temperature range of 2 – 300 K shows dominant antiferromagnetic interactions between the nickel centres for all the complexes. The magnetic exchange parameters of one of the compound **4b** has been investigated by DFT in broken-symmetry approach.

Experimental

Materials and physical measurements

All the chemical reagents required were purchased from sigma and used without further purification. Ligand *p*-chloro-2-{(2-(dimethylamino)ethylimino)methyl}phenol (HL) was prepared according to reported method.[25] Infrared spectra (4000–500 cm^{-1}) were recorded with a BRUKER TENSOR 27 instrument in KBr pellets. Mass spectrometric analyses had been done on Bruker-Daltonics, microTOF-Q II mass spectrometer and microwave irradiation experiments had done in focused microwave CEM discover reactor 300W and the reaction tube used was with 10ml capacity and 13mm internal diameter. Elemental analyses were carried out with a ThermoFlash 2000 elemental analyzer. TGA measurements were performed by heating the crystalline samples from 20 to 300 °C at a rate of 5°C min^{-1} in air on a Metler Toledo TGA/DSC 1 STAR^{e} System thermal analyzer. The magnetic susceptibility data of compound **4a-4c** were collected in a temperature range of 2 – 300 K under an applied field of 0.1 Tesla on powdered samples with a SQUID magnetometer

(MPMS-7, Quantum Design). Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants. The temperature dependent magnetic contribution of the holder was experimentally determined and substracted from the measured susceptibility data. The resulting molar susceptibility data were plotted in $\chi_M T$ *vs*. T. The program julX[26] was used for spin Hamiltonian simulations of the data for compound **4a** and **4b**. Whereas the program clumag[27] was used for spin Hamiltonian simulations of the data for compound **4c**.

X-ray crystallography

Single crystal X-ray structural studies of compound **2, 4a to 4c** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data for all the complexes were collected at 150(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2. [28].

The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms. It should be noted that solvent molecules in the structure of **4b** and **4c** were randomly dispersed and thus difficult to refine using conventional discrete-atom models. To resolve this issue, the contribution of solvent electron density was removed by the SQUEEZE routine in PLATON.[29]

Caution! *Azide and tetrazolate compounds are potentially explosive. Only a small amount of material should be prepared and handled with care.*

Preparations

[Ni(L)Cl(H_2O)$_2$] (1). A methanolic solution (10 mL) of $NiCl_2·6H_2O$ (0.25 g, 1.04 mmol) was added dropwise to a solution of HL (0.23 g, 1.04 mmol) also in methanol (10mL). The resultant green solution was stirred for *ca.* 3 h and filtered. The filtrate was concentrated up to 10 mL under reduced pressure and filtered again. The resultant solution was kept at room temperature for slow evaporation to obtain a green crystalline precipitate of compound **1**. The solid was isolated by filtration and washed with ether and dried *in vacuo* (70% yield based on Ni). Anal. Calc. for $C_{11} H_{18} Cl_2 N_2 Ni O_3$ (355.87) : C 37.09; H 5.05; N 7.86%. Found: C 37.82; H 5.25; N 7.33%. IR (cm^{-1}, KBr): 3384 , 1650 , 1466 ; MS(ESI): m/z = 284.37 [M-Cl-2H_2O]$^+$.

[Ni(L)(N_3)] (2). To a solution (10 mL) of complex **1** (0.355 g, 1.0 mmol) in methanol, a methanolic solution (10 mL) of NaN_3 (0.078 g, 1.2 mmol) was added dropwise. The solution colour turned from green to red, and the solution was stirred for further 2 h, where after it was filtered. The red crystalline compound **2**, with some suitable crystals for X-ray diffraction, was obtained by concentration of the filtrate and keeping it at room temperature for several days. Compound **2** was isolated by filtration and dried *in vacuo* (67% yield based on Ni). Anal. Calc. for $C_{11} H_{14} Cl N_5 Ni O$ (326.43) : C 40.43; H 4.28; N 21.44%. Found: C 40.35; H 4.26; N 21.32%. IR (cm^{-1}, KBr): 2051 , 1647 , 1464, 1461 , 1385.

[Ni_3L_2(5-Phenyltetrazolato)$_4$(DMF)$_2$] (4a). A mixture of [Ni(L)(N_3)] (**2**) (120 mg, 0.367 mmol), 2 mL of benzonitrile and 3 mL of DMF were added to a cylindrical pyrex tube. The system was placed in the focused microwave reactor. The reaction mixture was left under irradiation for 2 hrs at 130°C. The solvent was then removed *in vacuo* and the resulting residue was treated with diethyl ether to obtain a reddish-brown powder which was then recrystallized from methanol/ether mixture. Anal. Calc. for $C_{28}H_{31}ClN_{11}Ni_{1.50}O_2$ (677.15) : C 49.61; H 4.57; N 22.74%. Found: C 49.16; H 4.45; N 22.45%. IR (cm^{-1}, KBr): 1650 , 1529 , 1464, 1387 , 1171.

[Ni_3L_2{5-(3-pyridyl)-tetrazolato}$_4$(DMF)$_2$].2H_2O (4b). Monoazide nickel complex [Ni(L)(N_3)] (**2**) (0.12 g, 0.367 mmol) and 0.153 g (1.5 mmol) of 3-cyanopyridine in 5 mL of DMF was taken in a cylindrical pyrex tube and it was irradiated for 2 hrs at 130° C. After removing the solvent *in vacuo* the resulting reddish-brown residue was washed several times with diethyl ether. The brown powder yielded was recrystallized from DMF/ether mixture. Anal. Calc. for $C_{52}H_{62}Cl_2N_{26}Ni_3O_6$ (1394.27) : C 44.75; H 4.44; N 26.10%. Found: C 44.11; H 4.43; N, 26.05%. IR (cm^{-1}, KBr): 3416 , 1646 , 1463 , 1421 , 1172.

[Ni_5L_4{5-(2-cyanophenyl)-tetrazolato}$_4$(OH)$_2$(H_2O)$_2$].3H_2O.DMF (4c). A solution of 0.12 g (0.367 mmol) of [Ni(L)(N_3)] complex **(2)** and 0.256 g (2 mmol) of 1,2-dicyanobenzene in 5 mL of DMF was taken in a cylindrical pyrex tube and it was irradiated for 2 hrs at 130° C. The solvent was then removed *in vacuo* and the resulting reddish-brown residue was washed several times with diethyl ether to obtain a brown powder which was then recrystallized from chloroform/hexane mixture. Anal. Calc. for $C_{79}H_{85}Cl_4N_{29}Ni_5O_{12}$ (2067.98) :. C 45.84; H 4.11; N 19.63 %. Found : C 44.60; H 3.83; N 18.89 % IR (cm^{-1}, KBr): 3422 , 2229 , 1649 , 1463 , 1296.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Cif file for the complex and other necessary supplementary figures are provided. CCDC number: 961048, 961049 (for the normal structures) and 961050, 984713 (for the "squeezed" refined structures) respectively.

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